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December, 1945

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INDUSTRIAL AND ENGINEERING CHEMISTRY

ANALYTICAL EDITION

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Editorial	747 Macropore-Size Distributions in Some Typical Porous SubstancesL. C. Drake and H. L. Ritter 787
Evaluation of Spectrographic Analytical Data H. V. Churchill and J. R. Churchill	Frederick B. Clardy, John C. Edwards, and John L. Leavitt 791
Determination of Ascorbic Acid	754 Determination of Water Content in Oils M. M. Acker and H. A. Frediani 793
Determination of Calcium Content and Total Hard- ness of Water	Determination of Ether Vapor in Gaseous Mixtures 757 C. C. Meloche and W. G. Fredrick 795
Determination of Helium Group Gases in Natural Gases and in Atmosphere	Determination of Dissolved Gases in Volatile Liquids C. C. Meloche and W. G. Fredrick 796
Lamp Method for Determination of Hydrogen in	Observations on Rare Earths
S. G. Hindin and A. V. Grosse	767 Glass Perforated Plate Distillation Column W. M. Langdon and D. J. Tobin 801
Determination of 4-Vinyl-1-cyclohexene (Butadiene Dimer) in Recycle Styrene	New Mercury Manometer Jesse Werner 805
Spectrochemical Determination of Small Amounts	MICROCHEMISTRY
of Aluminum in Steel	Qualitative Spot Tests for Rubber Polymers 772 H. P. Burchfield 806
Spectrophotometric Determination of Titanium in Steels	Sintered-Glass Valves . R. C. Taylor and W. S. Young 811 775
Use of Enzyme in Riboflavin Determination Lawrence Rosner, Evelyn Lerner, and Howard J. Cannon	778 NOTE ON ANALYTICAL PROCEDURES
Lead in Smelter Products	780 Improved Distilling Head for Laboratory Frac- tionating Columns B. G. Zimmerman 815
Pore-Size Distribution in Porous Materials	CORRESPONDENCE
Pressure Porosimeter and Determination of Com- plete Macropore-Size Distributions H. L. Ritter and L. C. Drake	Thermal Decomposition of Perchlorates and Determination of Sodium and Potassium in Silicates. William T. Hall and George G. Marvin 816

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December, 1945

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December, 1945



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Insoluble	10	%
Moisture		%
Chloride (Cl)	03	%
Ammonium compounds (as N)0.0	01	%
Phosphate (PO ₄)0.0	01	%
NH4OH precipitate	10	%
Silica (SiO ₂)0.0	05	%
Sulfur compounds (as SO ₄)0.0	03	%
Aluminum (Al),0.0	02	%
Arsenic (As)0.0	001	%
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Sulfur compounds (as SO ₄)	.0.004	%
NH4OH precipitate and Silica.	. 0.01	%
Silica (SiO ₂)	.0.005	%
Arsenic (As)	. 0.0000	1%
Calcium & Magnesium precip.	. 0.01	%
Heavy metals (as Pb)	0.0005	%
Iron (Fe)	.0.0005	%
Sodium (Na) (flame test) abt.	0.02	%

ACID HYDROFLUORIC Merck Reagent

Conforms to A. C. S. Specifications Assay: Minimum 47% HF

MAXIMUM IMPURITIES

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Sulfate (SO ₄)0.005	%
Sulfite (SO ₂)0.005	%
Heavy metals (as Pb) 0.0005	5%
Iron (Fe)	5%

ACID PERCHLORIC 70% Merck Reagent

Conforms to A. C. S. Specifications

MAXIMUM IMPURITIES

Non-volatile	0.005 %
Chloride (Cl)	0.001 %
Fluorine (F)	0 0001 %
Nitrogen compounds (as N)	0.003 %
Sulfate (SO ₄)	0.005 %
Ammonia (NHa)	0.003 70
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Lead (Pb) by Dithizone not d	letectable



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25000

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13

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INDUSTRIAL AND ENGINEERING CHEMISTRY

THE AMERICAN CHEMICAL SOCIETY

WALTER J. MURPHY, EDITOR

Academic Training for Analytical Chemistry

THE tremendous impetus given to applied science by war research has made colleges and universities look anew to what the aims of education are and by what curriculum they can be achieved. War research has often been conducted successfully by staffs who could not be called specialists in the fields in which they were assigned, but they were nonetheless eminently successful. For some years analytical chemists who have become successful in the newer physical approaches of the subject and in microtechniques have often not been trained as analysts. Men from graduate schools usually emerge as organic or physical chemists. Because of this, the question is often raised, especially in industry, "Where can properly qualified analytical chemists be found?"

Unalutical Edition

Attention and thought should be given to this problem while our educational structure is undergoing changes brought about by the war. Because opportunities in industrial analytical research are available, it would seem that the type of training at the undergraduate and graduate levels for these positions should be considered. This editorial is written to raise fundamental questions which should be the concern of all those interested in analytical chemistry.

It has been the good fortune of the writer to discuss with the heads of many of our larger industrial analytical laboratories the aims and problems of their several departments and the type of men and training which, in their experience, seems best. They agree that an analytical chemist should have fundamental undergraduate training in chemistry, followed by graduate work where specialization should come.

Analytical chemistry in industry is usually a means toward an end. Although attempts at precise definition are futile, the men most directly concerned with analytical chemistry in industry can be classified as follows: An analytical chemist is one familiar with the means but primarily concerned with the end in view. An analyst appreciates the end in view but is concerned primarily with the means—i.e., with analytical methods—in cases of unusual difficulty. A determinator is primarily concerned with the means in run-of-the-mill cases. The analytical chemist has been described (under other names) by Clarke [J. Chem. Education, 14, 562 (1937)] and by Ashley [*Ibid.*, 19, 589 (1942)]; as to the other two classifications, see Lundell [IND. ENG. CHEM., ANAL. ED., 5, 222 (1933)]. The analytical chemist and the analyst, although differing in outlook and in experience, must each have abilities of a high order; it is with their training that we are chiefly concerned.

While emphasis on classical analytical chemistry in industry has declined, the expansion and growth of analytical chemistry have been tremendous, especially along physical and microchemical lines. This growth has been dictated by the needs of industry. However, much of the credit for this expansion must go to persons who have specialized in fields other than analysis. Part of the answer to this has been that, until recently, industry has not set up analytical departments so that research in all branches of analysis could be carried on. It preferred to consider analysis as a routine function.

Research on analytical methods is often carried on by departments which are predominantly organic or physical. The weakness of this approach is the lack of appreciation of the factors of precision and accuracy, and failure to coordinate their study of methods, physical and chemical, in the solution of an analytical problem. This divorcing of research from the routine has discouraged people from specializing in analysis in colleges, and consequently they do not seek analytical positions when they complete their studies.

It has become increasingly apparent in undergraduate schools that analytical chemistry, in common with other branches of chemistry, has become too broad for an undergraduate to master. Consequently, it is the feeling of many in industry that the student should be discouraged from specializing in analytical and encouraged to master fundamentals of chemistry, physics, and elementary mathematics. Undergraduate courses in chemistry should be designed to provide not analytical chemists, nor inorganic chemists, nor physical chemists. They should rather provide the fundamental training needed to become a chemist.

Training in Fundamentals

Fundamental training in chemistry ought to give to the gifted undergraduate a mastery of the principles of chemistry as well as of allied subjects. Such training should be planned in harmony with the advice that has been given by one university to its undergraduates:

A student, when making his choice of courses, must realize that he presumably has before him a lifetime of necessary specialization, but only three or four years of freedom in which to study the interrelation of ideas and knowledge, to broaden his intellectual interests and human sympathies, to fit himself to take his part as an intelligent man in whatever social and economic order may lie ahead.

Detailed recommendations for such fundamental training cannot be given. Even broad recommendations will not apply with equal force to all colleges or universities; for such institutions differ too much among themselves, and the high-school training their students have received is far from uniform.

Perhaps not over two thirds of a four-year undergraduate course of study will be devoted to technical subjects. This time is all too short for the thorough, fundamental training of even the gifted students. It is suggested, however, that the following measures ought to further this objective:

1. Decrease memory work and place less emphasis on descriptive chemistry. Select the facts taught for their value in illustrating chemical principles.

2. Begin the emphasis on these principles in the freshman course. Make this one of the most important chemistry courses offered.

3. Use experiments to illustrate principles as well as to develop manipulative skill.

4. In close cooperation with the English department, use the writing of reports on the laboratory exercises as a continuing means of improving the student's command of English. In the last two years, encourage the student to use the literature in his laboratory work, so as to familiarize him with technical writing in one or two foreign languages, and with the mechanism of gathering chemical information.

5. Give specialization after principles have been laid down, upon which later specialization in organic, physical, and analytical chemistry may take place. Place emphasis upon orderliness and neatness.

Graduate Work in Analytical Chemistry

It is advisable for analytical chemists and analysts to have graduate training. The analytical chemist's graduate training should be broader than that of the analyst; successful analytical chemists have often done graduate work in physical chemistry.

Specialization should come in the graduate courses. The undergraduate should know the principles upon which a spectrograph operates; the analyst who specializes in spectroscopy should know the characteristics of the various instruments, of the different light sources, plates, densitometers, and so on. Similar considerations apply to the other physical methods, to microchemistry, and to "classical" analytical chemistry (the analysis of silicate rocks, the separation of substances by precipitation, etc.).

To be a successful analytical chemist requires, above all, judgment in the selection of approach and the method, or methods, which will give the answer with required precision and accuracy. This rare judgment does not develop successfully in the minds of men who specialize only in organic or physical chemistry or physics, even though these specialties are a very necessary part of analysis.

With the expanding emphasis on all phases of analysis, it is important that universities meet this need by encouraging men to train for such positions by offering suitable courses and graduate research.

The broad training in chemistry favored by many for undergraduates is possible in most first-class schools. The training of graduate analytical chemists, however, appears to be difficult because of a lack of equipment, necessarily expensive, for teaching newer instrumental techniques and professors who are outstanding in analytical chemistry for direction of research. These are serious difficulties, and some industrial organizations have tried to solve this by training programs based on the up-to-date methods which they themselves have developed. This solution of the problem is not one which will give strength or encouragement to analytical chemistry in our colleges and universities.

L. T. HALLETT, Associate Editor



Semiautomatic Spectrographic Analysis

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Figure 1. Plate-Racking Mechanism and Exposure Control Shutter

WITHIN recent years the marked trend has been to take the spectrograph out of the research laboratory and put it into the industrial plant. One of the prime advantages of the spectrograph over other analytical methods is the speed with which results can be obtained. In large industrial plants, every second

saved in analyzing material needed for production saves many dollars. The spectrograph has helped reduce to a minimum the time required for analysis, but there is still room for improvement. With this in mind, an attempt has been made to simplify spectrographic operation by reducing to a minimum the time required for such operations as changing the plate after each exposure, focusing the electrodes, controlling the exposure, and changing the electrodes.

All these labor-saving devices have been used successfully for many months in the Lancaster RCA Laboratories. No spectroscopist should waste his time doing these things that simple mechanical devices can do for him.

A study of the operations involved in making a plate shows that 12 seconds are required for the operator to turn the plate down after each exposure, 20 seconds to change a pair of electrodes, and 3 seconds to focus the new pair of electrodes on the slit. Thus, a plate consisting of 12 samples and an iron reference requires a total time of the desired length of the photographed spectrum. When an exposure is finished, the operator merely presses a button (Figure 3, 4) and the plate is changed mechanically. At the same time another advantage is gained by the use of this mechanism. An exposure with a moving plate can now be made by running the motor continuously during the exposure. This tech-



Figure 2. Inside View of Safety Cage

Semiautomatic devices are described which simplify spectrographic operation by reducing considerably the time required for changing the plate after each exposure, focusing the electrodes, controlling the exposure, and changing the electrodes.

20 minutes if a 1-minute exposure is allowed for each sample and 0.5 minute for the iron reference. Of those 20 minutes, 7.5 are spent in doing operations that can be done faster and more efficiently by mechanical means.

The hand-racking method was eliminated by removing the crank handle on the plate-racking mechanism and substituting a 20-cm. (8-inch) wheel (Figure 1). A belt connects this wheel (Figure 1, 1) with the shaft of a small motor (Figure 1, 2), and the outlet on the motor is plugged into an electrical control timer mounted under the spectrograph table in such a manner that the operator can reach it without moving from his normal operating position. Pulley sizes are chosen so that 7 seconds are required to move the plate 3.5 mm., which corresponds to the length of the slit opening and

INDUSTRIAL AND ENGINEERING CHEMISTRY



Figure 3. Rear View of Safety Cage

- A.c. arc source Spark source Timer for shutter control Button to operate plate-racking mechanism
- Control for bottom electrode holder Control for upper electrode holder Controls for vertical motion of electrodes Control for horizontal motion of electrodes

nique (1-4) is very useful in determining correct exposure times and the length of time required to burn substances completely.

Three seconds are required to move the two electrodes into the correct position, using a swinging arm to judge the correct height. This operation is simplified by mounting a projection bulb (Figure 2, 4) behind the electrodes, so that it will throw an image of the electrodes on the slit.

It is often desirable to preburn samples before making the exposure, by means of a magnetically operated shutter (Figure 1, 3) in front of the slit. This shutter is plugged into another timer which after the preburning is complete opens the shutter and then after the set time elapses closes the shutter to provide a carefully controlled exposure. Painting the shutter black and white makes it a good screen to receive the image of the electrodes and to aid in focusing them.

The largest portion of the time required is that used to change the elec-trodes. To eliminate this, two semiautomatic rotary electrode holders were built (Figure 2, 1, 2). The upper one is held in a vertical position and the lower in a horizontal position, so that only one pair of electrodes can touch at any one time. Both halders account at any one time. Both holders accommodate 13 electrodes, since 13 samples are run on a small plate.

The upper copper electrode holder is 1.25 cm. (0.5 inch) thick and 10 cm. (4 inches) in diameter with 13 holes equally spaced on the edge. The upper electrodes and iron reference are placed in these holes and held in place by wing A gear fastened on the end of screws. the holder shaft is engaged by a plunger to ensure proper positioning of the test electrodes. Two bevel gears on the other side of the holder connect to a Bakelite rod extending outside of the safety cage. In this way the operator can change the electrodes from his normal operating position. The back view of the safety cage is shown in Figure 3 with the No. 6 knob connect-ing to the upper electrode holder.

The lower aluminum electrode holder 15 cm. (6 inches) in diameter. Thirteen holes 0.47 cm. (3/16 inch) in

diameter equally spaced hold the small ³/₁₆-inch electrodes; another set of 0.78cm. (5/16-inch) holes are spaced between the smaller holes to hold the large electrodes. An escapement mechanism (Figure 2, 3) can be seen under the (Figure 2, holder. Pulling the Bakelite rod extending out of the safety cage (Figure 3, 5) moves the electrodes to the next position. A wing screw holds the aluminum support to the center shaft. Loosening the screw permits moving the holder to take either the small or the large electrodes.

It is now possible to change and focus the electrodes in the 7 seconds it takes for the plate to move to the next position. Thus, the time required to run a complete plate is only 15 minutes, including the time necessary to load all the samples. Five minutes out of 20 minutes have been saved and operator fatigue is reduced.

When this equipment was first put into use, contamination of the other electrodes from the pair burning was expected; however, no difficulty was experienced. Every type of metal, powder, and liquid used normally was tested by making every other electrode a blank. In no case did the blank show even spectroscopic traces of the material in the preceding electrode. For that reason, no shields were provided to take care of electrode sputtering. However, such shields could be made if the need ever

should arise. All the devices described here are used with the Bausch & Lomb large Littrow spectrograph but can easily be adapted to other instruments according to individual needs.

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Figure 4. Side View of Spectrograph Plate-racking mechanism Safety cage

Evaluation of Spectrographic Analytical Data

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The authors have two objects in presenting this paper: (1) to furnish accuracy and precision data to those interested in the spectrographic analysis of metals, and (2) to illustrate the value of a simple statistical approach to the handling of a large number of separate data.

SPEED and accuracy are cardinal criteria in the evaluation of analytical methods. In industrial chemical laboratories, these criteria must be applied with proper regard to the process being controlled and available laboratory personnel. Speed is often essential, even though it may mean some sacrifice of accuracy. Precision or reproducibility of results is of paramount importance in such cases. However, with the development of instrumental methods, which are inherently more nearly objective than traditional methods, speed may be gained with no essential sacrifice of either accuracy or precision. Typical of such a case is the use of emission spectrography in metallurgical analytical laboratories.

In most metallurgical uses of the spectrograph, the method replaces chemical methods which produce results adequate in approach to accuracy and precision. Using analytical data derived in the routine operation of plant laboratories of Aluminum Company of America, it has been possible to compare the results obtained by spectrographic methods with those which would have been reported if the work had been done chemically.

It is the practice in Aluminum Company of America plant laboratories to analyze chemically on a routine basis a small number of the aluminum alloy samples that are analyzed and reported spectrographically. Data thus derived are of great value in indicating weaknesses in procedures and their application. Proper use of the data leads to re-evaluation of the standards used, improvements in apparatus, changes in laboratory operation, and better training of personnel. The analytical data of plant laboratories clear through the Analytical Division of Aluminum Research Laboratories where they are studied.

The continuous flow of data provides valuable information about the performance of spectrographic standards and also enables the Analytical Division to ascertain what determinations and what alloys present specific difficulties. A statistical summary of a portion of the data for 1944 is given in Table I. All the spectrographic and chemical analyses were made by standard routine procedures (1, 2). The material is arranged as follows:

Data for particular elements are arranged in order of increasing average concentration of the element in the group being covered. Each average level of concentration may cover either determinations made on a particular alloy or determinations made using a particular standard. Since the plant laboratories naturally tend to analyze chemically any sample which shows any peculiarities when analyzed spectrographically, the average composition shown is not necessarily representative of the level of composition sought by plant operators, but should be construed as the fortuitous average of the concentrations selected for chemical checking. It would be misleading to designate specifically the various alloys being tested and thus possibly indicate that the average concentrations shown were metallurgical optimums. They are averages of concentrations in samples selected for checking for other reasons than uniformity or specificity of composition. Data have been included regardless of whether they appeared to be normal or abnormal. The authors have not included material when less than ten data were available for a particular determination. Such data will be included in future studies when the amount of data is sufficiently great to be significant.

The terminology used in the tables is largely self-explanatory. The treatment of data, the specific calculations illustrated, and the interpretation of the results follow the general pattern set by standard texts and reference books on statistics (3, 5, 8) and by recent papers (6, 7) dealing with the application of statistical methods to similar analytical problems.

ERRORS IN SPECTROGRAPHIC ANALYSIS

Errors in spectrographic analysis may be divided into two categories, random and systematic. Random errors originate largely in faulty technique, fluctuations in line voltage, variations in humidity, irregularities in photographic emulsions, variations in composition or structure from point to point on the sample, and errors in calculation. Systematic errors in spectrographic analysis arise largely from standardization. They may be caused by errors in the values assigned to standard samples, differences in metallurgical history of samples and standards, and differences in the technique used on standards and samples.

The random differences between spectrographic and chemical analyses are measured by the standard deviation, s, which is defined mathematically as

$$s = \sqrt{\frac{\Sigma d^2 - \frac{(\Sigma d)^2}{n}}{n-1}}$$
(I)

d = deviation of individual spectrographic results from chemical results

n = number of comparisons

This equation is more convenient for handling large masses of data than the possibly more familiar equation

$$s = \sqrt{\frac{\Sigma (d - \vec{d})^2}{n - 1}}$$

in which \overline{d} is the average bias of spectrographic results with respect to chemical results. The two equations are mathematically equivalent.

This term provides a more useful measure of precision than almost any other conventional expression. In a normally distributed group of statistics including a sufficient amount of data, 67% of the data will differ from the mean by no more than one standard deviation and 95% of the data is included within two standard deviations. The standard deviation is always larger than the average error and, while to the casual reader it may present the data in a less favorable light, it is more useful than the average error since it enables a much more complete and rigorous interpretation, especially when used in conjunction with the bias.

Since each group of data represents a finite group of spectrographic and chemical comparisons, the accuracy with which the standard deviation of the population represented by the statistical sample is determined will vary with the number of determinations sampled and the magnitude of standard deviation. A measure of the validity of the standard deviation as the authors have calculated it is provided by its own standard deviation, s_* , which is calculated from

$$s_s = \frac{s}{\sqrt{2n}}$$
 (II)

This quantity will be found virtually negligible for most of the data presented. A second type of error is introduced by any departures from normal statistical distribution among the original data. Such departures will affect the validity of the distributional

				Table I. Stati	istical Summary	10 00			
No. of Determinations Compared	Average % by Chemical Method	Spectrogr Chemical Standard deviation	aphic vs. Results Average bias	Probability of Significance of Bias	No. of Determinations Compared	Average % by Chemical Method	Spectrogra Chemical Standard deviation	phic vs. Results Average bias	Probability of Significance of Bias
		Silicon				Сор	per (contd.)		
$\begin{array}{r} 45\\1761\\106\\46\\54\\3282\\508\end{array}$	$\begin{array}{c} 0.08 \\ 0.09 \\ 0.12 \\ 0.14 \\ 0.16 \\ 0.17 \\ 0.19 \end{array}$	$\begin{array}{c} 0.012 \\ 0.009 \\ 0.021 \\ 0.019 \\ 0.010 \\ 0.019 \\ 0.019 \\ 0.023 \end{array}$	$\begin{array}{r} +0.0004 \\ +0.003 \\ +0.007 \\ +0.016 \\ -0.013 \\ -0.0005 \\ -0.009 \end{array}$	$\begin{array}{c} 0.17 \\ 0.9999 + \\ 0.9993 \\ 0.9999 + \\ 0.9999 + \\ 0.87 \\ 0.9000 + \end{array}$	49 52 403 168 204 31	$\begin{array}{c} 0.42 \\ 1.73 \\ 3.94 \\ 4.05 \\ 4.07 \\ 4.08 \end{array}$	$\begin{array}{c} 0.041 \\ 0.146 \\ 0.081 \\ 0.145 \\ 0.155 \\ 0.186 \end{array}$	$\begin{array}{c} -0.008\\ -0.013\\ +0.091\\ +0.036\\ -0.027\\ +0.067\end{array}$	$\begin{array}{c} 0.82 \\ 0.48 \\ 0.9999 + \\ 0.998 \\ 0.99 \\ 0.99 \\ 0.95 \end{array}$
128	0.23	0.018	-0.006	0.9998		М	anganese		
$107 \\ 136 \\ 420 \\ 594 \\ 207 \\ 14 \\ 255 \\ 59 \\ 613 \\ 230$	$\begin{array}{c} 0.31\\ 0.42\\ 0.43\\ 0.62\\ 0.66\\ 0.68\\ 0.92\\ 0.99\\ 5.05\\ 11.70\\ \end{array}$	0.019 0.025 0.028 0.046 0.036 0.059 0.059 0.059 0.052 0.047 0.258 0.389	$\begin{array}{c} -0.001 \\ -0.008 \\ +0.004 \\ +0.011 \\ +0.008 \\ -0.01 \\ +0.011 \\ -0.018 \\ +0.072 \\ +0.11 \end{array}$	$\begin{array}{c} 0.42\\ 0.9997\\ 0.996\\ 0.9999+\\ 0.999\\ 0.47\\ 0.9992\\ 0.995\\ 0.995\\ 0.9999+\\ 0.9999+\\ 0.9999+\\ \end{array}$	18 30 69 145 60 41 3207 86 624 145 443 443	$\begin{array}{c} 0.03\\ 0.05\\ 0.06\\ 0.16\\ 0.35\\ 0.60\\ 0.61\\ 0.63\\ 0.79\\ 1.13\\ \end{array}$	$\begin{array}{c} 0.024\\ 0.008\\ 0.024\\ 0.018\\ 0.017\\ 0.027\\ 0.031\\ 0.033\\ 0.031\\ 0.036\\ 0.040\\ \end{array}$	$\begin{array}{c} +0.004\\ +0.001\\ -0.009\\ +0.009\\ -0.008\\ -0.017\\ -0.010\\ -0.015\\ -0.009\\ -0.015\\ -0.011\end{array}$	$\begin{array}{c} 0.51 \\ 0.50 \\ 0.997 \\ 0.9999 + \\ 0.9995 \\ 0.9997 \\ 0.9999 + \\ 0.9999 + \\ 0.9999 + \\ 0.9999 + \\ 0.9999 + \\ 0.9999 + \\ \end{array}$
763	0.13	0.013	-0.0003	0.47		М	agnesium		
51 82 821 56 1403 1893 3288 57 112 326 53 130 000	$\begin{array}{c} 0.17\\ 0.22\\ 0.29\\ 0.30\\ 0.34\\ 0.37\\ 0.40\\ 0.44\\ 0.46\\ 0.49\\ 0.50\\$	$\begin{array}{c} 0.013\\ 0.024\\ 0.030\\ 0.029\\ 0.033\\ 0.017\\ 0.031\\ 0.024\\ 0.030\\ 0.025\\ 0.033\\ 0.033\\ 0.025\\ 0.033\\ 0.033\\ 0.035\\ 0.033\\ 0.035\\ 0.033\\ 0.033\\ 0.035\\ 0.033\\ 0.035\\ 0.033\\ 0.033\\ 0.035\\ 0.033\\ 0.$	$\begin{array}{c} -0.020\\ -0.009\\ +0.007\\ +0.004\\ +0.010\\ +0.009\\ -0.023\\ -0.004\\ -0.004\\ -0.004\\ -0.006\\ +0.020\\ -0.008\\ +0.020\\ -0.008\\ -0.008\\ +0.020\\ -0.008\\ -0.008\\ +0.020\\ -0.008\\ +0.004\\ -0.008\\ +0.004\\ -0.008\\ +0.004\\ -0.008\\ +0.004\\ -0.008\\ +0.004\\ -0.008\\ +0.004\\ -0.008\\ +0.004\\ -0.008\\ +0.004\\ -0.008\\ -0.008\\ +0.004\\ -0.008\\$	$\begin{array}{c} 0.9999 + \\ 0.9999 + \\ 0.9999 + \\ 0.9999 + \\ 0.9999 + \\ 0.9999 + \\ 0.9999 + \\ 0.78 \\ 0.84 \\ 0.9999 + \\ 0.9999 + \\ 0.9999 + \\ 0.9909 + \\ 0.9909 + \\ 0.9909 + \\ 0.9900 \\ 0.9909 + \\ 0.9900 \\$	$\begin{array}{c} 27\\ 103\\ 98\\ 57\\ 547\\ 202\\ 3170\\ 1110\\ 402\\ 94\\ 425\end{array}$	$\begin{array}{c} 0.04\\ 0.36\\ 0.54\\ 0.59\\ 0.91\\ 1.19\\ 1.47\\ 1.48\\ 1.56\\ 1.56\\ 2.37\\ \end{array}$	$\begin{array}{c} 0.010\\ 0.025\\ 0.028\\ 0.032\\ 0.042\\ 0.058\\ 0.072\\ 0.021\\ 0.054\\ 0.055\\ 0.087\\ \end{array}$	$\begin{array}{c} -0.002\\ +0.014\\ -0.011\\ -0.009\\ -0.007\\ -0.031\\ -0.011\\ +0.011\\ -0.048\\ -0.007\\ -0.062\end{array}$	$\begin{array}{c} 0.69\\ 0.9999+\\ 0.9998\\ 0.96\\ 0.9999+\\ 0.9999+\\ 0.9999+\\ 0.9999+\\ 0.9999+\\ 0.9999+\\ 0.78\\ 0.9999+\\ \end{array}$
179	0.56	0.042	+0.004 +0.030	0.9998		Cl	nromium		
$ \begin{array}{r} 1327 \\ 259 \\ 244 \\ 163 \end{array} $	0.67 1.33 1.44 1.46	0.023 0.055 0.101 0.131 Copper	+0.004 +0.010 +0.056 +0.076	$\begin{array}{c} 0.9999 + \\ 0.996 \\ 0.9999 + \\ 0.9999 + \end{array}$	607 29 110 23 49 81	0.01 0.02 0.20 0.22 0.23 0.24	0.013 0.009 0.016 0.021 0.015 0.055	$\begin{array}{r} +0.010 \\ +0.004 \\ +0.0015 \\ +0.010 \\ +0.014 \\ +0.010 \end{array}$	$\begin{array}{c} 0.9999 + \\ 0.98 \\ 0.67 \\ 0.97 \\ 0.9999 + \\ 0.89 \end{array}$
311 49 52	0.02 0.06 0.07	0.002 0.015 0.013	+0.002 +0.003 +0.003	0.9999+ 0.83 0.89	30 33	0.24 0.25	0.019 0.013 Nickel	+0.012 - 0.004	0.998 0.91
140 55 49 1541	0.16 0.16 0.30	0.018 0.019 0.026 0.027	+0.009 -0.014 +0.012 -0.009	0.9999+0.9999+0.9999+0.9999+	432 205	$\begin{array}{c} 2.03\\ 2.06\end{array}$	0.073 0.098	$+0.0006 \\ -0.018$	0.13 0.991

inferences drawn from the standard deviations. Tests for "skewness", "flatness", and other departures from normality are described in standard statistical texts and allowances can be made for such departures by using special mathematical devices. Analytical data of the type here presented generally approach normal distribution to such a degree that the assumption of normality does not seriously impair the interpretation. A third source of error lies in the fact that the standard deviation properly applies only to a continuous distribution of data. A discontinuity is introduced by the fact that all of the authors' analytical results have been rounded off to the nearest hundredth of a per cent. When this grouping unit and the standard deviation are of similar magnitude, as they are in any of the data presented, a correction may be desirable. MacColl (6), in an excellent statistical treatment of analytical data, recommends the use of Sheppard's correction in such cases. This correction was not applied, since it would not contribute materially to the usefulness of the data under consideration.

Systematic errors are measured by the "average bias". "Average bias" is the algebraic mean difference between chemical and spectrographic results, assigning a positive sign when the spectrographic result is higher and a negative sign when it is lower than the chemical result. "Average bias" thus measures the tendency of the spectrographic result to run higher or lower than the chemical result. It does not represent the systematic error of the spectrographic result, but rather the algebraic difference of the systematic errors of the spectrographic results. For example, if the mean absolute error of the spectrographic results happened to be -0.02 and that of the chemical results +0.05, the bias figure as considered here would be -0.07%.

In considering a particular bias figure, it is important to know whether the calculated bias represents a real difference between the average chemical and spectrographic analyses or is simply a fortuitous result of the random errors of the two methods. A means of judging the precision with which the bias is estimated is provided by the standard error. The standard error of the bias, s_a , is given by the formula

$$s_{\bar{d}} = \frac{s}{\sqrt{n}} \tag{III}$$

For example, a bias of -0.012 obtained for a group of 512 samples yielding a standard deviation of 0.021 could be expressed as $-0.012 \pm \frac{0.021}{\sqrt{512}}$ or -0.012 ± 0.001 if we wished to include in the bias figure itself a measure of the precision with which it was determined. The probability of the bias being real and not merely a fortuitous result of statistical sampling errors is indicated by the term, "probability of significance of bias", given in the last column of the table. Strictly speaking, this is the probability that the observed bias is larger than the bias which might have resulted from random errors alone. The probabilities were obtained by applying "Students' t Test" (3) in which

$$t = \frac{d}{s_d} \tag{IV}$$

 \overline{d} = average bias $s_{\overline{d}}$ = standard error of \overline{d}

The probability figures were obtained by referring the calculated t values to standard statistical tables (4). Interpolations

between tabulated figures were made graphically by the use of Keuffel and Esser No. 359-23 Probability paper. Special graph papers of this type greatly facilitate the representation of statistical functions of the type here involved. The probability figures were rounded off to 0.01 below 0.99, to 0.001 from 0.990 to 0.999, and to 0.0001 from 0.9990 to 0.9999. Reporting the figures to a greater number of digits would not be justified because of the errors involved in the estimation of the standard deviation. Probabilities higher than 0.9999 have been reported as 0.9999+ to avoid the inferences which might be drawn from rounding such figures off to 1.0000. The magnitude of the probability assists in judging whether the bias is real or fortuitous, but has little direct bearing on whether its magnitude is of practical significance. For example, in one of the groups of iron analyses, the bias is +0.004 at an average iron content of 0.55%. The probability of significance is 0.9998, but a bias of +0.004 is too small to merit much consideration.

INTERPRETATION OF DATA

It must be remembered in interpreting the data that both the bias and the standard deviation are net resultants of both spectrographic and chemical errors. If some means were available for determining the absolute bias and the standard deviation of the chemical analyses, estimates of the true bias and standard deviation of the spectrographic results could be obtained by the application of the formulas

$$\bar{d}_s = \bar{d} + \bar{d}_c \tag{V}$$

$$s_s = \sqrt{s^2 - s_s^{\dagger}} \tag{V1}$$

in which

$$d_{\bullet}$$
 = the average absolute bias of spectrographic results

 \overline{d} = the net average bias as given in the tables

 \vec{d}_e = the average absolute bias of chemical results

 s_{i} = standard deviation of the spectrographic results

s = net standard deviation as given in the table

 $s_c = \text{standard deviation of chemical results}$

As an example of the interpretation of the data on the basis of the foregoing principles, let us take as an example one of the groups of data on Magnesium in Table I. The following statistics are given for the group selected:

Number of determinations compared	1110
Average % Mg by chemical method	1.48
Standard deviation	0.021
Spectrographic saib	+0.011
Probability of significance of bias	0.9999 +

Making the assumption of normal distribution, a standard deviation of 0.021 means that the random discrepancies between spectrographic and chemical analyses are 0.021 or less in 67% of cases and 0.042 or less in 95% of cases. The precision with which the standard deviation has been determined is measured by its own standard deviation, s_{s} , calculated from Formula II.

$$u_{e} = \frac{0.021}{\sqrt{2 \times 1110}} = 0.00045$$

On the average, 67% of the observed standard deviations will fall within s, and 95% within 2s, of the true standard deviation. In this isolated case, we may say, therefore, that there is a 67% chance that the observed standard deviation lies within 0.00045 of 0.021 and a 95% chance that it lies within 0.0009 of 0.021. The bias of ± 0.011 indicates that so the set of th

The bias of +0.011 indicates that, on the average, the spectrographic results tend to be 0.011 higher than the chemical results. The accuracy of this conclusion is measured by the standard error, s_{a} , obtained by applying Formula III.

$$s_{d} = \frac{0.021}{\sqrt{1110}} = 0.00063$$

The odds are 2 to 1 that the true bias (the bias for an infinite number of samples) is within ± 0.0006 of the observed value of ± 0.011 , and 19 to 1 that it is within ± 0.0013 of ± 0.011 . To test the significance of this bias further, "Students' t Test" is applied. From Formula IV we obtain

$$=\frac{4}{s_d}=17.5$$

Referring to standard t tables, we find that the chances of obtaining an apparent bias of ± 0.011 or more when no true bias exists is less than 1 in a 1,000,000,000 in this particular case. The probability of significance of the bias is, therefore, far in excess of 0.9999 and is simply reported as 0.9999 + in the table. The authors, therefore, regard it as a virtual certainty that there is a real difference between spectrographic and chemical results. Had the probability been less than 0.9999, a graphical interpolation would have been required to determine its value.

The example selected happens to represent the magnesium analyses obtained on a particular type of alloy, using a particular spectrographic standard. Using this standard to analyze a sample of this same alloy having a chemically determined magnesium content of 1.48%, and taking both the standard deviation and average bias into consideration, we may say that the odds are 2 to 1 that the spectrographic result will lie between 1.470 and 1.512%, and 19 to 1 that it will lie between 1.449 and 1.533%. Moreover, we have determined the accuracy with which the standard deviation and average bias have been determined, and have evaluated the probability of the average bias representing a real difference between the two methods. If data were available for estimating the standard deviation of the chemical results and their average bias with respect to true content, we could go even further with the interpretation by the application of Formulas V and VI. In the absence of such data, our spectrographic data can only be compared with chemical data, and our direct interpretation tends to give a conservative picture of the precision of spectrographic analysis.

In the analysis of many alloys, statistical data have been especially valuable in checking the performance of standards. In the analysis of many fabrication alloys, a special type of standard, known as an "SS" standard, is used. "SS" standards are prepared in large quantities and are the daily check standards used in a large number of laboratories. When a new standard of the "SS" type is first put into service, all the laboratories using the standard submit comparative spectrographic and chemical data. These data are carefully analyzed and any apparent bias is carefully investigated to determine whether the systematic error lies in the chemical or in the spectrographic analysis. In most cases the effect is found to be attributable to the spectrographic behavior of the standard, and a compensating change is made in the composition assigned to the standard. The application of such corrections has usually resulted in the reduction of the bias to insignificance in the case of the alloys for which "SS" standards are available. Similar corrective measures are taken whenever the statistical studies warrant, but the effectiveness of such bias corrections diminishes as the total quantity of the standard. and hence of the statistical data, is reduced. In all cases, however, the statistical studies provide an excellent check on the performance of the standards and the proper execution of the spectrographic techniques.

It is interesting to note that copper analyses on some alloys show rather high biases and standard deviations. A portion of this effect is ascribable to the fact that the concentration to be determined is rather high, but a large part of the excessive error is caused by the fact that some plant laboratories do not regularly make this determination spectrographically. Up to the present, copper in the neighborhood of 4% has not been determined spectrographically on certain alloys because the results obtained in preliminary tests were not completely satisfactory. Since the determination has not been run on a routine basis, the laboratories have little significant experience to produce data to improve the quality of results. However, there are included in the table data on a complicated alloy in which copper is regularly determined spectrographically. On this alloy the standard deviation was only 0.081 as compared to 0.145, 0.155, and 0.186 for the three other groups representing similar copper contents in other alloys. The divergence of these standard deviations is caused not

by any inherent difference in the copper determination among the four alloys, but rather by the simple fact that the alloy for which the very satisfactory standard deviation of 0.081 was obtained is one which is regularly analyzed spectrographically on a largescale routine basis, while the other three alloys are normally analyzed chemically with only an occasional spectrographic analysis as a high-speed service to the metallurgical staff.

The results on some alloys are indicative of specific difficulties. For example, in some cases being analyzed, the complexity of the alloy, its tendency to show serious segregation, and the apparently large effects of variations in structure and composition tend to make the spectrographic analyses more variable than one would expect for the contents involved. In actual plant laboratory practice, these variations are ironed out to a large extent by making multiple determinations and averaging the results. For example, the spectrographic determination of silicon of 11.70% average concentration does not show the precision required in many laboratories. The low bias suggests that the average of quadruplicates might provide acceptable accuracy.

In general, the statistics indicate that analyses regularly made spectrographically are of consistently high quality. The magnitude of the standard deviations and biases is in general no higher than would be expected had the comparisons been made among chemical analyses made by different routine analysts.

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Determination of Ascorbic Acid

Application of the Indophenol-Xylene Extraction Method to Determination in Large Numbers of Tomato and Tomato Juice Samples

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The xylene method, as modified for rapid determination of ascorbic acid in tomatoes and tomato juice, is particularly adaptable to the determination of large numbers of samples and can be handled with accuracy by comparatively inexperienced technicians. The difficulties involved in the choice of extractant, clarification of extracts, choice of buffer, ascorbic acid losses following addition of buffer, and oxidizing substances in xylene are described, and methods of avoiding these difficulties are given.

N PREVIOUS investigations of the ascorbic acid content of plant materials a titrimetric method (6, 7) was used in these laboratories. In the hands of an experienced operator this method was satisfactory and gave values which were in agreement with the photometric method of Bessey (1, 15). Critical evaluations of the titrimetric method have been presented by various workers (8, 9, 11). Since it requires experienced technicians, the authors have recently replaced it with the xylene method (3, 4, 17, 18) which is more objective, gives good results in the hands of comparatively inexperienced technicians, and hence is more suitable for large-scale routine analyses.

This paper gives a brief description of the xylene method as adapted for analysis of large numbers of tomato and tomato juice samples, the various difficulties encountered, and the precautions which are necessary to avoid them.

REAGENTS

Dissolve 500 grams of C.P. sodium acetate ACETATE BUFFER. trihydrate in enough distilled water to make 1 liter of solution; then mix with 1 liter of C.P. glacial acetic acid.

ASCORBIC ACID STANDARD. Prepare daily by dissolving a weighed amount of the vitamin in some of the acid which is used for extracting the samples. A solution which contains 20 micrograms per ml. is convenient, and 1- to 7-ml. aliquots of such a solution can be used. The ascorbic acid can be titrated iodo-

metrically (2) to test its purity. XYLENE. Use C.P. or reagent grade, providing it meets the test for oxidizing substances (see below). Redistill from glass if oxidizing substances are present.

2,6-DICHLOROPHENOLINDOPHENOL SOLUTION. Prepare by dissolving 40 mg. of the crystals in hot water, filter, cool, and dilute to 100 ml. Store this concentrated solution in the cold room at 3° to 5° C., and dilute about 15 ml. to 100 ml. before use. Use enough of the concentrated dye so that when a 5-ml. aliquot of the diluted dye is mixed with 2 ml. of the buffer and 5 ml. of the extracting acid and then is transferred to 15 ml. of xylene, the xylene solution gives 30% transmission in the Evelyn colorimeter with filter 520.

METHOD AND APPARATUS

The extract is prepared and filtered essentially as described by Morell (16). The first portion of the filtrate is poured back through the filter if it is not perfectly clear. An aliquot of from to 10 ml. of the filtrate, depending on the ascorbic acid concen-tration, is pipetted into a large test tube, and about 2 ml. of the acetate buffer, followed immediately by 5 ml. of the dye, are added from automatic pipets. The solution is mixed thoroughly, but briefly, after each addition. After about 15 seconds, 15 ml. of xylene are added from another automatic pipet, and the tube is stoppered with a rubber stopper and shaken vigorously for 10 to The xylene layer is drawn through a cotton 15 seconds. plug into a colorimeter tube by means of the apparatus illus-trated in Figure 1. This solution is read in an Evelyn colorim-eter with filter 520 or 515.

The use of a rubber stopper has no harmful effect on the xylene solution. However, it is necessary to avoid rubber connections on the automatic pipets by using glass siphons for filling them. It is essential to allow about 15 seconds for the reaction with the dye, because even with moderate amounts of ascorbic acid the reaction is not completed in less time (10).

The xylene layer can be clarified by any one of three methods. It can be allowed to stand until it is clear, centrifuged, or drawn through a small wad of absorbent cotton (cf. Kirkpatrick, 12). The authors prefer the latter. A fresh cotton plug, which need not be moistened, is inserted for each aliquot. The clarified xylene solutions are read in a photoelectric colorimeter, usually within an hour. Comparisons show that the methods of clarifying the xylene all give the same results. The intensity of the color of the dye after extraction with xylene is stable for at least 3 hours (3), but changes appreciably on standing overnight. The xylene can be used again after distillation in an all-glass still. It is preferable to dry the xylene with calcium chloride before redistilling.



Xylene is drawn through absorbent cotton plug into colorimeter tube.

The ascorbic acid concentration of the aliquot is ascertained from a standard curve, which is constructed by plotting on semilogarithmic graph paper the per cent transmission of a dyexylene solution against ascorbic acid concentration. The values obtained between 35 and 90% transmission show excellent agreement with Beer's law.

When this method is used in routine analyses of tomato samples duplicate determinations seldom give transmission values which differ by more than one scale division on the Evelyn colorimeter galvanometer—i.e., 1% transmission. Such a difference corresponds to from 2 to 4 micrograms of ascorbic acid.

This method gives results which agree satisfactorily with the Bessey photometric method (Table I).

DIFFICULTIES AND NECESSARY PRECAUTIONS

CHOICE OF EXTRACTANT. The authors have compared 3%metaphosphoric acid with the 5% sulfuric-2% metaphosphoric acid mixture recommended by Mack and Tressler (14); with fresh acid solutions, identical results were obtained. The authors prefer to use 3% metaphosphoric acid for the following reasons (see also Fujita and Ebihara, δ): It is more stable at room temperature, as is illustrated in Figure 2. The data in this figure were obtained by measuring the amount of metaphosphate and orthophosphate phosphorus (19) present at various

Table I. Comparison of Xylene and Bessey Photometric Methods for Determination of Ascorbic Acid in Ripe Tomatoes

		in mipe remateer
	Mg. of Ascorbic Acid per 100	Grams of Fresh Fruit
Sample	Bessey photometric	Xylene
No.	method	method
1	24.0	22.6
23	25.2	25.0 18.9
4	20.3	21.3
5	19.9	19.2
6 7	19.9	19.4
8	17.0	17.0
	1 00 10	00.00
	AV. 20.16	20.09

times. Initially only 86% of the phosphorus was in the form of metaphosphate phosphorus. There is about the same percentage hydrolysis of the metaphosphoric acid in the sulfuric-metaphosphoric acid mixture in 6 hours as in the 3% metaphosphoric acid in a week. This necessitates more frequent preparation of the extracting acid if a mixture of the two acids is used.

Pure ascorbic acid is more stable in 3% metaphosphoric acid than in the metaphosphoric acid-sulfuric acid mixture. The 3% metaphosphoric acid is preferable, at least in the case of fresh tomatoes and canned tomato juices, because it is much easier to obtain perfectly clear filtrates using metaphosphoric acid alone than the acid mixture. With the former acid, the filtrates are nearly always perfectly clear from the start using Whatman No. 1 filter paper. With the mixture, it is usually necessary to pour the first portion of the filtrate back through the paper.

Other workers have used mixtures of several types of acids with metaphosphoric acid for extracting plant materials (13, 14, 20) because they considered a low pH essential to ensure stability of the ascorbic acid in the extracts. The authors have found that the ascorbic acid in 3% metaphosphoric acid extracts of tomatoes is stable on standing overnight at room temperature. Hence, they do not consider the use of a strong acid essential in ascorbic acid analyses of tomatoes.

Other stabilizing agents, such as oxalic acid, would presumably be satisfactory, provided they meet the tests required of a stabilizing agent; the authors have not tried this acid.

It is essential that approximately clear filtrates be obtained in the case of tomatoes and tomato juice because the suspended particles carry carotenoids which are extracted by the xylene and give an appreciable blank value. Centrifugation is not nearly so efficient in removing these carotenoid-carrying particles as is filtration. With dehydrated cabbage and sweet and Irish potatoes clear filtrates are not necessary, as no appreciable xyleneextractable pigments have been found in the filtrates. When



Figure 2. Relative Stability of a 3% Metaphosphoric Acid Solution and a Mixture of 5% Sulfuric and 2% Metaphosphoric Acids at Room Temperature

applying the method to other products it is advisable to extract the filtrate directly with xylene and compare the resulting extract with a sample of pure xylene. This would indicate the necessity of obtaining clear filtrates by refiltration.

CHOICE OF BUFFER. With 3% metaphosphoric acid as an extractant it makes very little difference whether an acetate buffer, such as that described above, or the citrate buffer of Bessev (1) is used. The final pH of the solution is not critical; values anywhere between pH 3 and 4 are satisfactory. However, if large amounts of a strong acid extractant, such as the 2% metaphosphoric-5%

sulfuric acid mixture are used, the acetate buffer is preferable because of its stronger buffer capacity.

ASCORBIC ACID LOSSES FOLLOWING ADDITION OF BUFFER. It is essential that the dye and xylene be added immediately after the buffer has been added to the extract. Only enough time should elapse to permit a completion of reaction of the dye with the ascorbic acid. In some tomatoes the ascorbic acid is very rapidly destroyed after the buffer is added. This is illustrated in Figure 3, which shows the behavior of similar extracts from two tomatoes; in one case a considerable portion of the ascorbic acid is lost in a very short time after addition of the buffer. Similar results are obtained by the xylene and Bessey photometric methods (1). The rate of loss in extract A is about as rapid as the authors have ever observed. The rate in extract B is intermediate. In all extracts studied there was some loss if the aliquots were allowed to stand after the buffer was added. However, the amount of ascorbic acid lost during a determination is apparently not significant when determinations are made rapidly, as described above. The loss occurs as rapidly in extracts that have been boiled as it does in unboiled extracts, and hence is probably not enzymatic, even if any enzyme is extracted from the tomatoes by the acid. It is not accelerated by the addition of small quantities of copper and iron salts. The type of knife used to cut the fruits likewise makes no difference, as shown by comparing a new chromium-plated knife and an old chromiumplated knife, on which the brass plate was exposed, with grinding the tomatoes directly in the blender without slicing.





The disappearance of ascorbic acid always seems to be more rapid in 2-ml. aliquots of the extracts than in 1-ml. aliquots. In some cases the reduced ascorbic acid content of a 2-ml. aliquot 1 hour after adding the buffer was less than that of a 1-ml. aliquot which had been similarly treated. As a consequence the authors had difficulty getting different sized aliquots to check in routine analyses in which several minutes elapsed between adding

Table	e II.	Effect	of Xy	lene	on Ox indo	idatio pheno	n of Lo	euco-	2,6-dic	hlorop	henoi	
Ascorbic	7 X	ylene 1 15	(Reag	ent) 60	7 X3	vlene 2 15	(Reage 30	nt) 60	Xylene 7	3 (Tech 15	nical C 30	rade) 60
Acid Micro- grams	min.	min.	min.	min.	min. Per d	min. cent tra	min. nsmissi	min. on ^a	min.	min.	min.	min.
0 20 100 160	$29.8 \\ 33.5 \\ 53.3 \\ 99.5$	30 33.8 53.8 99.5	30 34 53.8 99.5	$30.5 \\ 34.3 \\ 54 \\ 99$	$29.8 \\ 32.5 \\ 52 \\ 92.5$	30 32 51 81	30 31.8 47 60	$30.3 \\ 30.5 \\ 42.3 \\ 39.3$	$30 \\ 33 \\ 51 \\ 94.5$	$30 \\ 33 \\ 50 \\ 91.5$	$30.3 \\ 32.8 \\ 46 \\ 86.5$	30.5 31.8 33 79
^a Per ce easured	ent tra from p	ansmiss point of	ion as additi	measu on of c	red in dye to	an Ev acid so	elyn co lution.	olorim	eter wit	h filter	520.	Time

the buffer and the dye. This difficulty disappeared when the dye was added as rapidly as possible after the buffer. This loss in ascorbic acid occurs when either 3% metaphosphoric acid or 5% sulfuric-2% metaphosphoric acid is used for extracting the sample.

OXIDIZING SUBSTANCES IN XYLENE. Most C.P. grades of xylene are suitable to use in the determination. However, the presence of oxidizing substances has been observed in technical grades of xylene and occasionally even in reagent grades. The effect of these substances on the leuco form of the dye is shown in Table II. These values were obtained by taking 5 ml. of 3% metaphosphoric acid containing an appropriate amount of ascorbic acid, and adding 2 ml. of citrate buffer, 5 ml. of dye solution (standardized for 30% transmission), and 15 ml. of xylene. The xylene was removed, and the per cent transmission was measured. It can be seen that at an ascorbic acid concentration of 160 micrograms the xylene-dye mixture should show approximately 100% transmission, and at 0 ascorbic acid concentration the transmission is approximately 30%. Only in the case of xylene 1 was the color relatively stable in the xylene solution; in the other xylene samples a fairly rapid development of color was indicated by the progressively lower transmission readings obtained when the mixture was allowed to stand for various lengths of time. For this reason it is always advisable to test the xylene for oxidizing substances before use. A simple test consists of completely decolorizing a small amount of dye solution with ascorbic acid and then shaking vigorously with the xylene to be tested. If no color develops in the xylene layer within 10 minutes it is considered suitable for use. If oxidizing substances are found the xylene should be distilled in an all-glass still.

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Determination of Calcium Content and Total Hardness of Water

Nephelometric-Photometric Procedure

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A rapid photometric-nephelometric procedure for the determination of calcium in water is described. A solution of potassium oleate in Duponol reacts with ammoniacal solutions of calcium to form a colloidal suspension of calcium oleate whose turbidity is proportional to the concentration of the calcium present. The degree of turbidity is measured in a photoelectric colorimeter with a suitable filter.

THE Third Army Medical Laboratory was faced with the problem of doing chemical analyses on water samples from Engineer Water Points whose locations and sources of supply varied almost daily with military necessity. In addition, chemical analyses for calcium, magnesium, and total hardness were performed on water samples from a new type of ion-exchange unit which was being tested for field operation. Since this entailed running large numbers of these determinations, it was thought desirable to attempt to develop a rapid photometric procedure for calcium which could compare favorably in accuracy with the more complicated and time-consuming gravimetric and volumetric procedures. This method could then be used in conjunction with an already published procedure for the photometric determination of magnesium in water, and the standard formula used for the calculation of total hardness.

Although other investigators such as Gregoire and co-workers (1, 2) have used potassium oleate as a reagent for the nephelometric determination of calcium, it was recognized that magnesium was an interfering substance. Gregoire and Sola (3) made use of this fact to determine magnesium with the potassium oleate reagent. Romeo and Gambordella (6) also used this reagent for the simultaneous determination of calcium and magnesium in water. In the attempt to modify the reagent recommended by the latter authors, it was found experimentally that the emulsifying agent known as Duponol stabilized the colloidal suspension over long periods of time and that its presence prevented the formation of magnesium oleate and thus made the reaction specific for calcium.

The reaction between calcium ion and the potassium oleate-Duponol reagent was then investigated to determine such factors as the optimum spectral region for measurement, optimum concentration of reagents, effect of time of standing, pH, and temperature on the colloidal suspension, and effect of various concentrations of other ions on the reaction.

The optimum concentration of Duponol and the ratio of potassium oleate to Duponol were determined experimentally for a fixed amount of calcium standard (0.40 mg. of calcium) in a 10ml. volume. The variation of temperature from 15° to 25° C. did not affect the transmission values and these transmission values remained constant at room temperature after a 30-minute time interval. The optimum spectral region for making the photometric measurements was found to be about 420 m μ . The colloidal suspension was most stable in slightly ammoniacal solution and the addition of ammonia to a sample and the filtration of any precipitate formed, previous to the addition of the potassium oleate-Duponol reagent, served to remove many of the interfering ions. These experimental criteria were then applied to the solution of the problem of the photometric determination of calcium ¹ Home address, 3082 Brighton 13th St., Brooklyn, N. Y. The method has an average error of $\pm 4\%$ over the range of 0.004 to 0.28 mg. of calcium in 10 ml. of solution. Only a few ions commonly present in water interfere; their maximum permissible concentrations are given. The method can be used in conjunction with a previously published method for the determination of magnesium in water to determine total hardness.

and total hardness in known and unknown water samples and are presented in this paper.

PRINCIPLE OF THE METHOD

Potassium oleate reagent in Duponol solution reacts with calcium salts in ammoniacal solution to give a white colloidal suspension of calcium oleate. The degree of turbidity is proportional to the amount of calcium present over the range from 0.01 to 0.70 mg. of calcium carbonate (0.004 to 0.28 mg. of calcium) in 10 ml. of solution and is measured in a photoelectric colorimeter with a suitable filter. Most of the common ions, when present in quantities usually found in treated or untreated waters, have little or no effect on the reaction.

REAGENTS AND APPARATUS

POTASSIUM OLEATE REAGENT. This reagent is prepared according to the procedure of Romeo and Gambordella (β): Shake 7.05 grams of oleic acid (Eastman Kodak) with a solution of 1.60 grams of potassium hydroxide in 5 ml. of distilled water. Transfer the emulsion by means of 50 ml. of 70% alcohol to a flask. Reflux the mixture for 1 hour and dilute with distilled water to 250 ml. in a volumetric flask.

DUPONOL SOLUTION. Prepare a 3% solution in distilled water. Duponol P.C. is an emulsifying reagent sold by the Dyestuffs Department of E. I. du Pont de Nemours and Co., Inc., Wilmington, Del.

POTASSIUM OLEATE-DUPONOL REAGENT. To each 100 ml. of Duponol solution add 20 ml. of potassium oleate reagent. Allow to stand 12 hours or longer and filter off, or remove by centrifugation, any sediment formed. This reagent is stable at room temperature but will come out of solution at lower temperatures. It can be brought back into solution by warming in an incubator at 37° C.

CALCUM STANDARD SOLUTION. Dissolve 0.5 gram of pure calcite (calcium carbonate) in a 500-ml. Erlenmeyer flask with a little dilute hydrochloric acid, being careful to avoid spattering. Add about 200 ml. of distilled water and boil for a few minutes to drive off the carbon dioxide. Cool to room temperature and transfer to a 500-ml. volumetric flask. Neutralize with ammonium hydroxide. Make up to volume with carbon dioxide-free distilled water. Store in a glass-stoppered bottle. This standard should be checked for exact calcium content using a gravimetric or permanganate titration procedure. 1.00 ml. = 1.00 mg. of calcium carbonate = 0.40 mg. of calcium.

DILUTE CALCIUM STANDARD SOLUTION. Dilute the above standard solution 1 to 10 in a volumetric flask with distilled water. 1.00 ml. = 0.10 mg. of calcium carbonate = 0.04 mg. of calcium.

An Evelyn photoelectric colorimeter with selected test tubes graduated at 5 and 10 ml. was used in this investigation. A spectral transmittance curve was prepared with a Coleman spectrophotometer, and a wave length of 420 m μ corresponding to Corning filter No. 511–3 mm. was found to be most suitable for this determination.

EXPERIMENTAL

STUDIES OF REAGENT CONCENTRATIONS. The following studies were undertaken to determine the effect of varying the concentration of Duponol and proportion of potassium oleate reagent to Duponol solution on the turbidity of a solution having a constant calcium content.

Effect of Variation of Duponol Concentration. The effect of varying the Duponol concentration was determined using 1, 3, 5, 7, and 10% solutions of Duponol. The 3% Duponol concentration was chosen as the most suitable as it gave stable readings after a 20-minute time interval, did not inhibit the formation of the calcium oleate as did the higher concentrations of Duponol, and the turbidity appeared more in the nature of a true colloidal suspension than that given by other concentrations of Duponol. Effect of Variation of Potassium Oleate Reagent. To 10.0-ml.

Effect of Variation of Polassium Oleate Reagent. To 10.0-ml. aliquots of 3% Duponol solution were added, respectively, 0.2, 0.6, 1.0, 1.4, and 2.0 ml. of the potassium oleate reagent and the contents mixed by inversion.



Figure 1. Effect of Variation of Potassium Oleate Reagent

Readings taken after 30-minute waiting period

One milliliter of dilute calcium standard (0.04 mg. of calcium) and 0.05 ml. of concentrated ammonium hydroxide were added to each of five colorimeter tubes, graduated at 5 and 10 ml., and distilled water was added to the 5-ml. mark. The contents of the tube were mixed by shaking and 5 ml. of the various potassium oleate-Duponol reagents were added to each tube with a 5-ml. volumetric pipet. The contents of each tube were immediately mixed by inverting the tube several times. The blank tube containing 5 ml. of distilled water and 5 ml. of the 3% Duponol-2.0 ml. of potassium oleate reagent was set at 100% transmission. The other tubes were then read at various time intervals and the results are given in Figure 1 for the 30-minute interval.

Since relatively stable values were obtained after 20 minutes' standing with mixtures containing 1.4 ml. or more of potassium oleate reagent per 10 ml. of the 3% Duponol solution and since there is but little change in transmission values between the 1.4-ml. value and the 2.0-ml. value, the latter was chosen for the preparation of the combined reagent.

Éffect of Variation of Temperature. For each of the five temperatures shown in Figure 2, 0.20 and 0.50 ml. of the dilute calcium standard (0.08 and 0.20 mg. of calcium) were pipetted in duplicate into the graduated colorimeter tubes, 0.05 ml. of concentrated ammonium hydroxide was added to each tube, and the contents were diluted to the 5-ml. mark and mixed. The tubes were then placed in a water bath maintained at the proper temperature, and after a 30-minute time interval 5 ml. of the potassium oleate-Duponol reagent adjusted to the same temperature were added to each tube with a 5-ml. volumetric pipet. The contents were immediately mixed by inverting several times and the tubes replaced in the bath. The transmission values were read at various time intervals in the photoelectric colorimeter against a reagent blank set at 100% transmission and the results obtained are shown in Figure 2 for the 30-minute time interval.

These results indicate that the temperature has little or no effect between 15° and 25° C. but beyond this range a marked increase in transmission values occurs, these values increasing with the temperature. While control of the temperature is not essential for routine analysis, more consistent values have been obtained by maintaining the temperature at about 20° C.

obtained by maintaining the temperature at about 20 ° C. Effect of Variation of Alkalinity. It has been found experimentally that concentrations of ammonium hydroxide greater than 0.5%, after the final dilution to 10 ml. in the colorimeter tube, have an inhibitory effect on the formation of the colloidal suspension. If the concentration of the ammonium hydroxide is kept below this critical level, variation in the concentration of the ammonium hydroxide has no effect on the transmission values obtained. PREPARATION OF STANDARD CURVE. Quantities of calcium standard solution ranging from 0.1 to 0.7 mg. of calcium carbonate, or 0.04 to 0.28 mg. of calcium, were pipetted in duplicate into the graduated colorimeter tubes, 0.05 ml. of concentrated ammonium hydroxide was added to each tube, and distilled water added to the 5-ml. mark. The contents were mixed by shaking and 5 ml. of the potassium oleate-Duponol reagent were added with a 5-ml. volumetric pipet. The contents were immediately mixed by inverting each tube several times and the tubes placed in a water bath at 20 ° C. Transmission values were read in the photoelectric colorimeter at a 30-minute time interval against a reagent blank set at 100%. The curve obtained is shown in Figure 1.

PROCEDURE FOR UNKNOWN SAMPLES. Into a 50-ml. volumetric flask 45 ml. of the unknown water sample were measured. The sample was neutralized with concentrated ammonium hydroxide until just alkaline to litmus and 1 ml. of the ammonium hydroxide added in excess. The solution was mixed, diluted to the 50-ml. mark with distilled water, and mixed again. It was allowed to stand for 15 minutes or longer. If a precipitate forms, the sample was filtered through a good grade of filter paper. A 2.00-ml. and a 5.00-ml. aliquot were pipetted into graduated colorimeter tubes and the first tube was diluted to the 5.0-ml. mark. For the blank tube 0.05 ml. of concentrated ammonium hydroxide and distilled water were added to the 5-ml. mark. Five milliliters of the potassium oleate-Duponol reagent were added to each tube from a volumetric pipet, and the solution was mixed several times by inversion and read in the photoelectric colorimeter after a 30-minute waiting period, the blank tube being set at 100% transmission. The calcium content is read from the standard curve and the value obtained multiplied by 1.11 to give the actual calcium content of the sample. Where more accurate results are desired the tubes may be placed in a 20 ° C. water bath during the waiting period.



This procedure will determine the calcium content of water samples in the range of 8 to 350 p.p.m. of calcium carbonate. A 1.00-ml. aliquot extends the range of the method to 700 p.p.m. of calcium carbonate, and samples below 8 p.p.m. of calcium carbonate can be determined after the concentration of a suitable aliquot.

DETERMINATION OF CALCIUM CONTENT OF KNOWN SOLUTIONS. The calcium content of known solutions was determined in duplicate as given above under the Procedure for Unknowns and the results obtained are given in Table I.

	and him south		I have have held
Ta	ble I. Determinat	tion of Known Sa	mples
Sample	Calcium Carbonate Present	Calcium Carbonate Found	Deviation
1 2 2	P.p.m. 500 400	P.p.m. 520 392	+4.0 -2.0 +2.2
3 4 5 6	200 100 20	210 108 22	+ 3.3 + 3.0 + 3.0 + 8.0 + 10.0



Figure 3. Spectrophotometric Curve for Calcium

DETERMINATION OF THE CALCIUM CONTENT OF UNKNOWN TATER SAMPLES. The calcium content of the unknown water WATER SAMPLES. samples was determined in duplicate with potassium oleate-Duponol reagent following the procedure given above. A volume of the water sample was then taken so that its total calcium content was about 50 mg. and its calcium content was run in duplicate by both gravimetric and permanganate titration procedures as given by Kolthoff and Sandell (4). The results obtained are given in Table II.

DETERMINATION OF CALCIUM, MAGNESIUM, AND TOTAL HARD-NESS IN KNOWN WATER SAMPLES. The magnesium content of the water sample was determined photometrically by the method of Ludwig and Johnson (5) which uses Titan yellow as the colorimetric reagent (Table III). The only modification in their procedure was that a solution of 0.05% of the Titan yellow in 2% Duponol was used in the determination, thus eliminating the unstable starch solution. The total hardness was then calculated from the formula: Total hardness (as calcium carbonate), p.p.m. = 2.495 Ca + 4.1115 Mg.

	lable II. D	etermination of	Unknown Sampl	es
Sample	Potassium Oleate- Duponol Procedure	Gravimetric Procedure as CaC_2O_4 . H_2O	Potassium Permanganate Procedure	Deviation from Average
1	<i>F</i> . <i>p</i> . <i>m</i> .	<i>F</i> . <i>p</i> . <i>m</i> .	<i>F</i> . <i>p</i> . <i>m</i> .	% -0.59
23	409 286	412 290	409 289	-0.49 -1.38
4	192 65.5	195 67 9	192 64 0	-1.04 -0.76
ő	38.0	41.4	39.8	-6.40

Table III. Determination of Known Samples for Calcium, Magnesium, and Total Hardness

Calcium Content		tent	Magnesium Content		Total Hardness		
Sample	Known	Found	Known	Found	Calculated	Found	method
	P.p.m.	P.p.m.	P.p.m.	P.p.m.	P.p.m. $CaCO_2$	P.p.m. $CaCO_3$	P.p.m. CaCO ₁
1	104.5	102 101	60.0	$\begin{array}{c} 58.3 \\ 59.0 \end{array}$	507	494	504 493
2	43.6	$\begin{array}{c} 42.9\\ 41.9\end{array}$	15.0	17.6 17.0	170	177	$\begin{array}{c} 175\\164 \end{array}$
3	20.9	$\begin{array}{c} 20.4\\ 20.4 \end{array}$	10.0	$\begin{array}{c} 12.4\\ 12.6\end{array}$	93.4	102	90 90

EFFECT OF IONS COMMONLY PRESENT IN WATER. An investigation was made of the effect of various ions which may be found in treated or untreated water with the purpose of determining their maximum allowable concentration (Table IV).

DISCUSSION

In the preparation of the standard curve, transmission values were read at various time intervals for 24 hours; little or no change in these values took place after a 30-minute waiting period. The spectrophotometric curve obtained by this procedure gives a straight line with amounts of calcium from 0.004 to 0.12 mg. Beyond this value the curve deviates rather sharply but the results obtained by this procedure have been found to be highly reproducible for values up to 0.28 mg. of calcium even with new batches of the potassium oleate-Duponol reagent.

	Table IV. I	nterference of Various	lons
Ion	Added as	Other Ion, P.p.m. Calcium, P.p.m.	Maximum Permissible Concentration, P.p.m.
Cu ++ Fe + + Mn ++ Mg ++ Zn ++ Al +++ Sr ++ Pb ++ As +++ Ba ++	$\begin{array}{c} Cu(NO_3)_2\\ FeCl_3\\ MnCl_2\\ Mg(NO_3)_2\\ AlCl_4\\ Sr(NO_3)_2\\ Pb(NO_3)_2\\ Pb(NO_3)_2\\ Ag_3O_3\\ BaCl_2\\ \end{array}$	$\begin{array}{c} 0.13\\ 0.13\\ 0.5\\ 2.0\\ 1.0\\ 0.5\\ 0.25\\ 0.5\\ 0.03\\ 1.0\\ \end{array}$	$50 \\ 50 \\ 200^{a} \\ 1000^{a} \\ 500^{a} \\ 200 \\ 100 \\ 200^{a} \\ 10 \\ 500^{a} \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 \\ 1$

^a Interference due to this ion not investigated beyond concentration given.

The results given in Tables I and II indicate that the method is subject to maximum errors up to about 10% in the lower range of values but that this error decreases sharply for the higher calcium values. The average error for these determinations is approximately $\pm 4\%$ and the results obtained compare favorably with the gravimetric or titration procedures. The method is particularly useful for carrying out large numbers of determinations, as in routine or control analysis of water samples, and where great accuracy is not the prime consideration.

The interference of ions other than those given in Table IV was also studied: Ag⁺, Hg⁺⁺, Bi⁺⁺⁺, Cd⁺⁺, Sb⁺⁺⁺, Sn⁺⁺, Ni⁺⁺⁺, Co⁺⁺, Na⁺, K⁺, NH₄⁺, CO₃⁻⁻, SO₄⁻⁻, SO₃⁻⁻, S₂O₄⁻⁻, CrO₄⁻, B₄O₇⁻⁻, C₄H₄O₆⁻⁻, HPO₄⁻⁻, F⁻, C₂O₄⁻⁻, AsO₂⁻, HAs-04--, Cl-, Br-, I-, CN-, Fe(CN)6-4, Fe(CN)6---, CNS-, S⁻⁻, NO₂⁻, NO₃⁻, C₂H₃O₂⁻, ClO₃⁻, SiO₃⁻⁻. No anions below concentrations of 500 p.p.m. and few cations in concentrations less than 100 p.p.m. interfere with the procedure. Large amounts of magnesium, which are a source of difficulty in the oxalate procedure, have no effect in this procedure. Even when these ions are present in relatively large amounts and the amount of turbidity formed by a given concentration of calcium is either increased or decreased by the presence of these ions the method may still be used if the standard curve is made up in the presence of these ions. Such a procedure is now in progress for the photometric determination of calcium in biological fluids.

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Determination of Helium Group Gases in Natural Gases and in the Atmosphere

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Methods for determining helium plus neon, argon, and krypton plus xenon by procedures involving fractional distillation, fractional desorption from activated charcoal, and absorption of reactive gases by hot calcium are described. The analysis of the atmosphere by these techniques agrees well with data of earlier investigators and indicates that 100 ml. of dry air, free from carbon dioxide, contain 0.00232

THIS paper describes a continuation of a study extending from 1905 to the present. The first major publication appeared in 1907 when one of the authors in collaboration with Mc-Farland (3) presented analyses of natural gases from Kansas, Oklahoma, Indiana, West Virginia, Missouri, Louisiana, and California, and found high values for the helium content of some samples. It was reasonable to expect other elements of the same family also in certain natural gases. Accordingly a qualitative study was conducted, and both neon and argon were detected in some samples (4). Several years later, the senior author and Seibel (37) obtained qualitative evidence for the existence of krypton and xenon in a few natural gases of Kansas.

During 1927 and 1928 Cady and Cady collaborated in a quantitative study of several mid-continent natural gases, using desorption from activated charcoal to separate the noble gases. The results were not published because only the values for helium and argon were accurate. It was found, however, that krypton could be more easily detected in some gases than in air. Because these samples were believed to contain a much higher percentage of krypton than the atmosphere, the junior author resumed the study in 1939 at the University of Washington and did the work reported in this paper. However, none of the natural gases analyzed contained even as high a percentage of krypton and xenon as does air. It is possible that other gases may be very rich in these rare noble gases, by comparison with air, but the chance that this is true seems poor. Although the study has failed to discover a good commercial source for krypton or xenon, the work contributes to the art of determining the different noble gases and has increased the precision with which the percentage of neon plus helium in the atmosphere is known.

Within the period of the authors' interest, numerous papers have reported the content of helium and of argon in gases issuing

from the earth and of krypton and xenon in gases from hot springs, mines, and fumaroles, but there are no quantitative data regarding the occurrence of the latter elements in natural gases associated with petroleum.

Very little definite information about the occurrence of neon other than in the atmosphere has been published. Many determinations of helium in the natural gases of North America have been made, but little is known about the abundance of the other noble gases. Most of the analyses which are complete, except for the determination of neon, have been made upon gases from European springs and mines by Moureu and Lepape (19, 20) and from fumaroles by Sborgi (35).

¹ Senior author, deceased May 26, 1943.

ml. of helium plus neon, 0.00012₀ ml. of krypton plus xenon, and 0.93₅ ml. of argon. Two of these data are at least equal in accuracy to older values, but the figure for argon is probably inferior to the commonly accepted volume, 0.932 ml. Several natural gases, rich in nitrogen, were analyzed; none was found to contain a higher proportion of any rare gas, except helium, than is present in air.

Extensive reviews (12, 18, 19, 20, 23, 34) dealing with the occurrence of the helium group gases are available. More recent publications in the field include (7, 15, 25, 26, 32, 35, 38).

The analytical procedures described below involve the isolation of very small amounts of the rare gases, measured at such low pressures that rapid diffusion of the gas within the system makes unnecessary forced circulation of the gases. Methods involving this type of technique have been developed by Paneth and co-workers (23).

APPARATUS

Figure 1 shows only the essential features of the apparatus. A buret, A, is used to add measured small samples of gas to the part of the system between stopcocks C_1 , C_3 , and C_7 . The buret is carefully calibrated and is designed to permit samples ranging in volume from 0.25 to 55.0 cc. to be measured with a limit of error decreasing from about 2% to less than 0.1% of the total amount. This error is smaller than that made in measuring the volumes of the different rare gases obtained from the sample.

A McLeod gage, B, measures the gas within the system, the capillary tube above the bulb being used for pressures up to 3.27×10^{-2} mm. of mercury and the larger tube just below the capillary for pressures up to 3.0 mm.

Mercury is forced into the gage until its height in the large tube at the side is about the same as that of the top of the capillary. When a reading is to be made, mercury is forced up into the instrument and the levels of the liquid in the capillary and in the large tube are measured on a millimeter scale without allowing either column to fall and without tapping the tubing. This operation is repeated several times, using different positions of the mercury, and using each set of readings to calculate the pressure. The average of these individual values is considered to be the pressure of the gas. By using the large tube instead of the adjacent capillary for establishing one of the mercury levels, a source of error due to sticking of mercury is eliminated. It is



in the tube at the top of the gage. The amount of this correction is easily measured when the system is highly evacuated by observing the levels of the mercury menisci at different positions.

The authors have found this correction substantially constant over several months. It should be confirmed occasionally to detect changes which may occur.

A piece of graph paper placed behind the tubing of the gage is used as the millimeter scale and one of the heavy marks is placed on the same level as the top of the bore in the capillary measuring tube. This procedure results in determinations of the pressure which are reproducible to within 0.5% at 2×10^{-3} mm. and to a slightly greater accuracy at higher pressures. The absolute error is probably somewhat larger than this.

Traps D and E are filled with activated charcoal of a type suitable for the adsorption of gases. Coconut charcoal and a granular grade of wood charcoal made from compressed sawdust have been used with equally good results.

rap D contains 20 grams of charcoal, while E holds only 4 grams packed in 5-mm. layers between sheets of copper gauze which press against the inner wall of the glass bulb. The metal is used to allow the temperature of the charcoal to be changed rapidly. Both traps may be cooled by immersion in liquid oxygen or some other cold liquid.

Vessels F, G, and H are sections of iron pipe 21 mm. in internal diameter, and 42, 29, and 18 cm. long, respectively. They contain calcium turnings and are closed at the ends by steel disks attached by silver solder. Each piece of pipe is placed within a section of a three-unit split

electric furnace of the type commonly used for the analysis of organic compounds. Ends of the pipe project far enough from the heating units to prevent melting of the solder. A 35-cm. length of 6.35-mm. outside diameter Monel metal tubing leads from the iron pipe to the glass portion of the system. The metal to glass seal is made with Picein cement.

Of the two mercury vapor diffusion pumps, I is used to evacuate the system and J to transfer the gas during the analytical operations.

The measuring bulb, M, which has a volume of 517.3 cc., is used to measure a gas sample as it is introduced into the fractionating column, L. A capillary tube of small volume connects Mto L. The rubber tubing connecting bulbs N and M has a heavy wall and is long enough to permit a pressure of 2 atmospheres to be established within M. Heavy rubber bands hold the plugs of stopcocks C_8 and C_{19} in place.

wall and is long enough to permit a pressure of 2 autospheres to be established within M. Heavy rubber bands hold the plugs of stopcocks C_9 and C_{10} in place. Mercury is used as the liquid in buret A, manometer K, and bulbs M and N. All glass is Pyrex brand. Most of the tubing has an internal diameter of 7 mm, and the stopcocks other than C_1 , C_9 , and C_{10} are the 6-mm. bore vacuum type manufactured by the Eck and Krebs Company, New York.

Auxiliary equipment includes a Leeds & Northrup Type K potentiometer for use with the thermocouple used to determine the temperature of the bath surrounding trap E and a small Bausch & Lomb spectrometer with a constant deviation prism to observe the spectrum of the gas compressed into the capillary of the McLeod gage.

A detailed diagram of L is shown in Figure 2. This column is similar to those of Podbielniak (30) and others, but is designed to distill a liquefied gas of high nitrogen content. The whole column is shielded by a tall slender Dewar vessel which is stripsilvered to permit visibility. A tube of 4-mm. internal diameter, packed with a closely fitting spiral of No. 20 B. & S. gage Nichrome wire, comprises the actual fractionating column. At the bottom of the tube is a cylindrical bulb of 1.6-cm. internal

PICEIN PUMP N VACUL CM ~ COLUMN VESSEL OXYGEN JACKET PDEWAR LIQUID SO VACUUM BULB DISTILLING WIRE CM NICHROME

Figure 2. Fractionating Column

diameter and 18-ml. capacity which contains a drip indicator at the end of the column. The whole of the distilling bulb and the lower 79 cm. of the column tube are thermally insulated by a vacuum jacket whose outer wall is a glass tube of 2.3-cm. internal diameter. The walls of the jacket above the bulb are silvered. At the top of the column is a 60-ml. reservoir for liquid oxygen. A single tube leading to the reservoir is used to introduce the liquid refrigerant and to remove the gaseous oxygen set free by evaporation. Vaporized oxygen may escape into the atmosphere either directly and at atmospheric pressure or indirectly through two Hyvac oil pumps, connected in parallel. It is necessary to use the pumps when nitrogen is being distilled under a pressure in the range of 1 to 1.5 atmospheres.

A small electrical heater made from a spiral of Nichrome wire, located at the bottom of the boiler bulb, is connected to leads of No. 24 enameted copper wire which enter the column through Picein seals near the top and pass down through the center of the tube. A rheostat regulates the current through the heater to a value which gives the desired reflux rate.

The volume of the system enclosed by stopcocks C_1 , C_2 , C_s , C_5 , C_6 , C_7 , and C_8 is close to 1030 cc.—the average of the values 1031, 1029, 1029, and 1031 obtained by adding measured quantities of dry air to the system from the gas buret, A. After adding the air, the pressure in the system was measured using the manometer of the gas buret. When calculating the volume of the system from this pressure, corrections were made for the air remaining in the buret and in the tube of the McLeod gage below the bulb. As an independent check on the volume, all parts of the system were measured while the apparatus was being assembled. The total volume so obtained was 1024 cc. An additional 6 cc. of volume could easily be present as a result of the glass blowing where tubing was sealed together.

PRELIMINARY OPERATIONS

The apparatus is prepared for use by pumping gas from the system while heating the charcoal traps and the pipes containing calcium. The former are heated to about 200° C. and the latter to about 710° to 850° C. This pumping is continued until most of the gases and vapors have been removed.

The following are used as tests of sufficient pumping: (a) After closing stopcocks C_1 , C_3 , C_4 , C_5 , C_6 , and C_8 and pumping until the pressure within the system remains constant, C_7 is closed and the heating of the charcoal trap, E, is stopped. As the trap cools to room temperature, the pressure within the system should fall to 10^{-4} mm. of mercury or less. (b) The system is pumped while C_1 , C_2 , C_3 , C_4 , and C_8 are closed and C_6 and C_6 are open. During the pumping operation the calcium ovens remain at a bright red heat and the pressure within the system gradually falls to about 10^{-1} to 10^{-2} mm. of mercury. When the electric heater units are turned off and C_7 is closed, the pressure falls rapidly. If it drops to 10^{-3} mm., the removal of gases from F and G is considered satisfactory. (c) In the case of the calcium in pipe H, heating and pumping are continued many hours. The behavior of the calcium in H is tested by evacuating the system to a McLeod gage pressure of about 10^{-6} mm. with C_1 , C_2 , C_5 , C_6 , and C_8 closed. After C_7 is also closed and pumping is stopped, H is heated to about 710° C. This causes a little gas to be set free from the calcium. The heater unit on H is then turned off, and the calcium cools slowly to room temperature. Unless the pressure indicated by the McLeod gage falls to 8×10^{-6} mm. or below, the heating and pumping process is continued.

Trap D is ready for use after pumping while heating for only about 0.5 hour. Only the helium and neon need to be completely removed.

After vessels E and H have been conditioned for use, care is taken to avoid contamination of the reagents by air and other crude mixtures of gases.

ANALYTICAL DETERMINATIONS

1. TOTAL CONTENT OF HELIUM GROUP GASES. The gas to be tested is dried, and a sample is measured in gas buret A, the volume chosen being such that the noble gas, when occupying 1030 ml., will have a pressure between 10^{-3} and 3×10^{-2} mm. Usually a 2.5-ml. sample is satisfactory.

After the system is evacuated and all stopcocks except C_5 and C_6 are closed, gas is admitted from the buret. The active gases are absorbed by the calcium at about 800° C. in F and G until the pressure becomes nearly constant. Usually 2 or 3 hours are allowed for this step, but a shorter time is sometimes sufficient. F and G are allowed to cool to room temperature. If the pressure does not fall below 3×10^{-2} mm., the heating is continued.

When it becomes apparent that the calcium in F and G will absorb very little more gas, the heating is discontinued, and the diffusion pump, J, is used to pump all the gas into the upper part of J. C_{6} and C_{6} are then closed and C_{4} is opened. The operation of J is stopped, and the gas is allowed to diffuse throughout the system. The remaining trace of active gas reacts with hot calcium at about 700° C. in H. As the cleanup progresses, the temperature of H is decreased slowly over about 30 minutes by changing the setting of the rheostat in series with the heater unit. Finally the electricity is turned off and H cools in about 1 hour nearly to room temperature. As soon as the tube becomes cool, the pressure of the gas within the system is carefully measured, using the McLeod gage. From this pressure is subtracted a small correction term which is the pressure of the reactive gas (probably hydrogen) remaining unabsorbed by the calcium. The difference is considered to be the pressure of the rare gas. The size of the correction term depends upon the length of time spent pumping gas from the hot calcium and varies from 3×10^{-6} to 8×10^{-6} mm. This term is determined before starting each run by measuring the gas pressure of about 10^{-6} mm. and the calcium in H has been heated to 700° C. and subsequently allowed to cool nearly to room temperature. This same procedure is used to establish the correction term used in connection with the other determinations described below. Duplicate determinations of the term agree within 1×10^{-6} mm.

From the pressure of the mixture of noble gases, the volume and temperature of the system, and the original volume of the sample, the per cent by volume of noble gas in the sample being analyzed is calculated.

2. HELIUM PLUS NEON IN A GAS OF HIGH HELIUM CONTENT. Gas remaining from the above determination is used in this procedure.

Trap E is cooled by immersion in a bath of liquid oxygen or nitrogen and stopcock C_2 is opened to allow the gases other than helium and neon to become adsorbed. Adsorption occurs rapidly and appears to be complete within about 15 minutes. After waiting about 30 minutes, diffusion pump J is operated for 5 to 10 minutes to pump all the helium and neon from E. C_2 is then closed, J is turned off, and H is heated to 700° C. H is then allowed to cool nearly to room temperature and the pressure of the gas remaining in the system is measured and used to calculate the per cent by volume of helium plus neon.

the per cent by volume of helium plus neon. In most natural gases of high helium content, this element is very much more abundant than neon. One may easily find out whether much neon is present by compressing the gas with the McLeod gage to a pressure of about 1 mm. When a spark is caused to pass through the gas by holding the metal end of an ordinary electric leak tester near the upper end of the capillary of the McLeod gage, the light produced by helium is yellow. This color is changed toward the red when neon is present; only a small proportion of neon is required to cause the light from the spark to be orange. If the spectrum is observed with a directvision spectroscope, some red lines may be readily observed when the gas mixture contains only 1% neon by volume. If the red lines are not detected, this determination of helium plus neon is for all practical purposes a determination of helium only.

3. HELIUM PLUS NEON IN A GAS OF LOW HELIUM CONTENT. If a gas—for example, air—has a much smaller content of helium and neon than of argon, procedure 2 is not satisfactory, for the pressure of helium plus neon is too low to be measured accurately. It is preferable that the pressure of the rare gas be over 10^{-3} mm.

If the content of helium plus neon is low, a second determination is made using a larger sample of the gas being tested. This sample is measured in the gas buret and its volume is chosen to give a final pressure of helium plus neon in the system of about 10^{-3} to 2×10^{-2} mm. In the case of air, a sample having a volume between 50 and 1000 ml. is satisfactory. After thoroughly evacuating the system and closing all stopcocks except C_3 , the sample is introduced, and C_1 is closed. Trap D is then cooled by liquid oxygen or nitrogen and the decrease in pressure within the system is followed by using the McLeod gage. When the pressure becomes constant, diffusion pump J is used to pump all the gas into the upper part of J. C_3 is then closed, J is turned off, and C_2 is opened. The charcoal in trap E is cooled by liquid oxygen or nitrogen, and the gas is allowed to stand for 15 to 30 minutes, or until there is no further decrease in pressure. J is used to transfer all the free gas into the upper part of J. After closing C_2 , J is turned off, C_4 is opened, and H, which has been previously heated to 700° C., is allowed to cool nearly to room temperature. The pressure of the gas is now measured, and from it is subtracted the correction term representing the pressure of the reactive gas remaining unabsorbed by calcium. From this corrected pressure, the room temperature, and the volume of the system, one calculates the volume of helium plus neon and uses this quantity to calculate the per cent by volume of the mixture of these two elements in the original sample of gas.

4. NEON. No satisfactory procedure for determining this element has been developed during this research. The difficulty arises from the fact that activated charcoal must be cooled to -225° C. or below to bring about the quantitative adsorption of neon (11, 27). The authors have been unsuccessful in their efforts to reach a temperature this low by pumping from a bath of evaporating nitrogen. A temperature low enough to cause the adsorption of about 80% of the neon was reached, however, and two very crude determinations of the element were made in natural gases of small helium content. The method for separating neon from helium failed completely for gases of a He/Ne ratio above 100.

5. ARGON PLUS KRYPTON PLUS XENON. This determination is made immediately following the determination of total helium group gas and of helium plus neon by procedures 1 and 2.

At the conclusion of procedure 2, the helium and neon are pumped from the system. C_7 and C_4 are then closed and C_2 is opened. With E at room temperature, the gas in the system is pumped into the top of J, the period of pumping being about 30 minutes. After closing C_2 , J is turned off. C_4 is opened, allowing the gas to diffuse into H, which has been previously heated to redness. After a few minutes, the heating of H is discontinued and the tube is allowed to cool nearly to room temperature. The pressure, temperature, and volume of the gas remaining in the system are now used to calculate the volume, at standard conditions, and the per cent by volume of argon plus krypton plus xenon. In all samples which have been tested, this quantity is essentially the same as the argon content only.

If the volumes have been measured correctly, the percentage of total rare gas (procedure 1) should be equal to the percentage of helium plus neon (procedure 2 or 3) plus the percentage of argon plus krypton plus xenon (procedure 5).

6. KRYPTON PLUS XENON. Before starting this determination, the supply of calcium turnings in tubes F and G is renewed, if necessary, and gas is pumped from the new turnings in the manner previously described.

Gases are also pumped from E until it is certain that the helium group gases have been thoroughly removed. C_2 is then closed. The fractionating column, L, is evacuated to a pressure of about 1 mm. and C_8 is closed.

L is prepared for operation by adding enough liquid oxygen to fill the Dewar vessel about halfway to the top. Liquid oxygen is poured through a funnel into the reservoir at the top of the column and gaseous oxygen is then pumped from the inlet-outlet tube to lower the temperature in the head of the column. While the gas is being condensed, as well as during distillation, it is occasionally necessary to replenish the supply of liquid oxygen in the reservoir. The gas to be analyzed is dried, freed from carbon dioxide, and collected in measuring bulb M. From here it is forced into the

The gas to be analyzed is dried, freed from carbon dioxide, and collected in measuring bulb M. From here it is forced into the fractionating column, where it condenses and flows into the distilling bulb. Under a pressure of about 2 atmospheres, air may be easily condensed and collected as a liquid in the bulb. The first liter of gas requires about 0.5 hour to become condensed, for the liquid flowing down the tube continually evaporates until the interior of the column grows cold. After the first liter has been condensed, further gas may usually be added, as rapidly as the gas-measuring bulb can be filled and emptied. The size of the sample suitable for an analysis depends upon the krypton plus xenon content of the gas. If the sample contains over 10^{-3} cc. but less than 3×10^{-2} cc. of these gases, the procedure gives satisfactory results. In practice, samples ranging from 1.5 to 18 liters have been used. Most of the samples of natural gas had a volume of 2.5 or 3 liters.

A gas of high helium content is difficult to condense because the column becomes filled with gaseous helium. The difficulty may be overcome by alternately raising and lowering the leveling bulb attached to M, thereby causing gas alternately to flow into and out from the fractionating column. It is sometimes necessary, however, to discard some helium from the column before the whole sample can be introduced. Before discarding helium by opening stopcock C_8 for a short time, the leveling bulb is raised and lowered several times until no further condensation seems to occur. This procedure permits substantially all the krypton and xenon to condense in the column.

If the gas which has been condensed does not contain as much as 2.5 liters of gaseous methane, this substance is now added until at least 2.5 liters, free from krypton and xenon, are present. The gas for this research has been prepared from methyl iodide using the Grignard reaction.

 C_9 is now closed, and a current of about 1 ampere is passed through the Nichrome heating coil in the condensed liquid in the column. This current is somewhat less than that which causes flooding in the fractionating column. The boiling of the liquefied sample and the return of the condensate to the boiler can be observed through the slit in the strip-silvered Dewar flask.

After refluxing has been in progress for several minutes, C_8 is opened just enough to allow the gas to escape slowly into the apparatus and through C_7 and C_{11} into the atmosphere. As introgen distills, manometer K indicates a pressure of 1.2 to 1.7 atmospheres. During this stage, a constant reflux of about 3 drops per second of liquid nitrogen is maintained and the gaseous nitrogen distillate is withdrawn at a rate of 8 to 10 liters per hour. As the last of the nitrogen distills, the pressure indicated by K falls rapidly, and when it reaches about one atmosphere, C_{11} is closed and the Hyvac forepump is started. Oxygen, if present, now distills, and as the last of it passes away the pressure again falls. The temperature at the head of the column is allowed to rise to the boiling point of oxygen at atmospheric pressure, and the distillation is continued at a reduced rate of take-off of gas. As the methane distills, K indicates a pressure of about 100 mm. No special flowmeter is needed to measure the rate of take-off from the column. With C_7 completely opened, the flow rate can be measured simply by means of the McLeod gage. The greater the rate of flow, the higher the pressure indicated by the gage. Distillation of methane is continued until 1 to 1.5 liters of the gas have been discarded. C_8 is then closed and C_5 , C_6 , and C_8 are opened.

As the distillation has been in progress tubes F and G have been heated to about 800° C. As the gas enters these tubes it is absorbed by the hot calcium. After most of the gas has become absorbed, the temperature of F and G is lowered to about 700° C. to reduce the rate of oxidation of the iron by air, and the apparatus is allowed to stand overnight. By the next morning all liquid has evaporated from the distilling bulb of the fractionating column, and the pressure in the system has fallen to about 0.1 to 1 mm. When the heating of F and G is discontinued, the pressure normally falls to about 3×10^{-2} mm. and it is possible to operate pump J to collect the gas in J. C_8 is now closed and the pump is turned off.

The pressure of the gas in the apparatus is measured, and F and G are again heated to about 800° C. and allowed to cool. If the pressure is lowered appreciably by the action of the hot calcium heating and cooling are repeated until the pressure remains unchanged. The gas is now pumped into J, and C_5 and C_6 are closed. As the gas diffuses back into the system from J, C_4 is opened to allow red hot calcium in H to absorb active gases which remain. As H cools the pressure falls nearly to that of the noble gas in the system. This noble gas is a mixture of krypton and xenon with a small amount of argon and/or helium. Traces of the latter gases remain even when a very high reflux ratio is maintained as methane is removed from the fractionating column. Normally there is much more argon than helium, but when a natural gas of high helium content is distilled, an appreciable amount of this element is found in the krypton plus xenon fraction.

To complete the determination, use is made of a technique similar to that of Peters and Weil (29) to remove the remaining argon and helium from the krypton. The charcoal in E is cooled with liquid oxygen and the gas allowed to become adsorbed during about 1 hour or until there is no further drop in pressure in the system. The trap is then placed in a bath of alcohol or ether held at a temperature of -101° to -99° C. and after waiting for 20 minutes pump J is set in operation. After pumping has continued for 10 minutes, C_2 is closed and J is turned off. The gas in the system is cleaned up by hot calcium in H, and the pressure of the noble gas pumped off in the 10-minute period is measured.

There now follows a repetition of three or four pumping cycles conducted according to a regular plan, each cycle requiring 1 hour. Trap E is first warmed with warm water for 10 minutes to allow the gases to become desorbed from the charcoal. As this goes on, C_4 is closed and the heater on H is turned on. E is dried and then cooled with liquid oxygen for 10 minutes. The trap is then immersed in alcohol held at -101° to -99° and while this temperature is maintained, J is turned on. After the trap has been kept in the bath for 20 minutes, C_2 is opened and is kept open for 10 minutes. The stopcock is again closed and J is turned off. C_4 is now opened to allow the gas to come into contact with hot calcium and after a few minutes the electric heater for tube H is turned off. When H has cooled for 10 minutes, the pressure within the system is measured.

This cycle is repeated until a graph of the pressure of the pumped-off gas plotted against the number of periods of pumping shows a linear relationship. A straight line is then drawn through the points showing this behavior and the line is extended to the axis corresponding to no pumping. The pressure at which the line intersects the axis is taken as the pressure of the argon and helium removed by pumping. It has been the authors' experience that two periods of pumping result in the removal of nearly all the argon from the charcoal. Two or three more cycles establish the rate of removal of krypton.

all the argon from the charcoal. Two of three more cycles establish the rate of removal of krypton. Trap E is now held at about 50° C. for at least 2 hours while gas is pumped into the upper part of J. C_2 is then closed, J is turned off. Tube H is heated to redness and is then allowed to cool nearly to room temperature. The pressure of gas in the system is measured carefully and the temperature is observed. The difference between this pressure and the pressure of the argon and helium pumped off at -100° is considered to be the pressure of krypton plus xenon. This value is used to calculate the volume and the per cent by volume of krypton plus xenon.

ORIGIN OF SOME OF THE ABOVE METHODS

Rayleigh and Ramsay (33) were the first to isolate and measure crude argon by chemically absorbing the other gases of the atmosphere. The first to use hot metallic calcium as the absorbing agent was Moissan (17). Soddy (39) contributed greatly to the understanding of the process.

Chlopin and Lukasuk (5) used a modified McLeod gage to measure helium, and a few years later Paneth and Peters (23, 24)introduced their micromethod which uses the usual form of this instrument. The methods of the latter authors and of Peters and Weil (29) have been extensively copied in developing the procedures described in the present paper.

The quantitative adsorption of gases other than helium, neon, and hydrogen upon activated charcoal was discovered by Dewar (\mathcal{S}) in 1904 and was first used by Cady and McFarland (\mathcal{S}) as a means for determining helium in natural gases. This method has been used successfully and extensively by a large number of investigators.

Although helium was separated from neon by selective adsorption upon activated charcoal many years ago (31), the conditions for making a quantitative separation of this type were first learned by Peters (27).

When both "helium" and "argon" have been determined in gases it has been common practice to determine the total rare gas and then to determine the "helium" by adsorbing the other gas on cold activated charcoal. Such a procedure was first used by Moureu and Biguard (21).

The separation of argon from krypton and xenon by fractional desorption from activated charcoal at -120° C. was first described by Valentiner and Schmidt (40). Several years later Peters and Weil (29) found that the temperature of charcoal could be as high as -93° C. without a great loss of krypton.

Although fractional distillation is commonly used industrially for the separation of the rare gases (16), its use for the determination of these elements in moderate sized samples of gas is novel.

ANALYSIS OF AIR

As the procedures which have been described were being developed, numerous samples of air were analyzed. At first this was done to establish the validity of the methods, but as the work approached completion careful determinations of helium plus neon and of krypton plus xenon were made, the purpose being to increase the certainty with which these quantities are known.

Vol. 17, No. 12

Table I contains data which were taken after the procedures had been worked out.

The best literature values for these three quantities are:

Total rare gas 0.935%, the average of eight determinations by Schloesing (36), individual values ranging from 0.9325 to 0.9369%; 0.9335%, the average of nine determinations by Moissan (17), individual values ranging from 0.9323 to 0.9366% Hadiwa always are 0.09266\% by Wotcore (11): 0.092100% by

Moissan (17), individual values ranging from 0.9323 to 0.9366%. Helium plus neon 0.00236% by Watson (41); 0.00219% by Paneth, Peterson, and Chloupek (25); 0.00222% by Gerling (9, 10); 0.0020% by Claude (6). Krypton plus xenon 0.00011 \pm 0.00001% by Moureu and Lenane (22): 0.000116 \pm 0.00001% by Domically of the second

Krypton plus xenon 0.00011 \pm 0.00001% by Moureu and Lepape (22); 0.000116 \pm 0.00001% by Damkohler (7); and 0.000152 \pm 0.000016% by Brody and Korosy (2). (The latter value is obtained by adding the probable percentage of xenon to the value 1.44 \times 10⁴% krypton reported by these authors.)

Table I indicates that the methods of the present research can be used in these three determinations with fairly good reproducibility. It is probable that the average values for the second and fourth columns are correct to within 1% of the percentage as given. The error in the determination of krypton plus xenon may be somewhat greater. In the determination of the total rare gas, the value of 0.937% should be considered inferior to the average, 0.934%, of the data of Schloesing (36) and Moissan (17). Determinations of helium plus neon and of krypton plus xenon as given in the fourth and sixth columns are at least as precise as any others which have been published and help to recognize the better of the conflicting old values.

The determinations of helium plus neon by Paneth, Peterson, and Chloupek (25) and by Gerling (10) are probably somewhat on the low side because of adsorption of neon by activated charcoal at the temperature of liquid air. The older value of Watson (41) appears to be superior. He gives the helium content of the atmosphere as 1 part in 185,000 and the neon content as 1 part in 55,000, corresponding to 0.00054 and 0.00182% by volume, respectively. Another old value, that of Claude (θ), is low. He subjected a large amount of air to fractional distillation and found 0.0005 and 0.0015% by volume, respectively, for helium and neon.

Table I. Content of Helium Group Gases in Dry Air					
Total Ra	ire Gas	Helium -	+ Neon	Krypton +	Xenon
Volume of sample used, ml. at S.T.P.	% by volume	Volume of sample used, ml. at S.T.P.	% by volume	Volume of sample used, ml. at S.T.P.	% by volume
1.002 2.640 0.278 2.615 2.581	0.941 0.933 0.942 0.929 0.935	$50.43 \\ 256.2 \\ 461.5 \\ 666.0 \\ \dots$	$\begin{array}{c} 0.00233\\ 0.00232\\ 0.00230\\ 0.00230\\ 0.00234 \end{array}$	$\begin{array}{c} 1.024 \times 10^{4} \\ 1.83 \times 10^{4} \\ 1.68 \times 10^{4} \end{array}$	0.000119 0.000122 0.000119
2.599 Av.	0.946		0.00232		0.000120

The krypton plus xenon content of the atmosphere determined in the present research agrees well with that reported by Damkohler (7) and fairly well with that of Moureu and Lepape (22). Since the three independent investigations are in agreement, the higher value of Brody and Korosy (2) is probably incorrect.

Combining the data of the present research with those of other investigators leads to the conclusion that the content of the rare gases other than emanation in dry air is as indicated in Table II.

The list of references given has been critically selected, choosing only those determinations which appear to be the most accurate. Without doubt, all these gases will eventually be determined with greater precision, but the one most in need of further study at present is helium. Most of the uncertainty in the neon content of the atmosphere is due to the indefinite knowledge of the percentage of helium.

ANALYSES OF NATURAL GASES

Samples of several natural gases have been analyzed using the procedures described. Gases of high nitrogen content were chosen, because they seemed most likely to be rich in the helium group elements. All determinations were made with care, and each result as given in Table III is probably correct to one less significant figure than is written. A possible exception pertains to the percentages of krypton plus xenon; these analyses were made before the procedure for separating the last traces of argon from krypton plus xenon had been fully developed, and the values in the table may be somewhat too high. When air was analyzed by the same technique, percentages of krypton plus xenon ranging from 0.00014 to 0.00015 by volume were found.

Determinations of oxygen, carbon dioxide, combustible gases, and residual "nitrogen" were made using ordinary Orsat type equipment and procedures (Table III).

Table II. Helium Group Gases in Dry Air				
Element	% by Volume	Percentage Probably Correct to Within:	Literature References	
Helium Neon Argon Krypton Xenon	0.0005 0.0018 0.932 0.000110 0.000008	0.0001 0.0001 0.001 0.001 0.000006 0.000003	(1, 6, 41) (6, 10, 25, 41), this research (14, 17, 30) (2, 7, 32), this research (7, 22)	

I. Gas from Rattlesnake No. 1G well of the Rattlesnake Field in San Juan County, N. M. Sample taken March 20, 1944; gas comes from the Ouray of Mississippiom sand at a depth of 7004 feet.

II. Gas from Bitlabito No. 1 well of the Bitlabito Field in San Juan County, N. M. Samples taken March 13 and November 5, 1944. This is a poor well, the gas accompanying water from a depth of 810 to 900 feet.

III. Gas from Bivins No. A2 well of the Cliffside Field near Amarillo, Tex. The gas comes from the Panhandle Big Lime of the Permian age at a depth of 3208 feet.

IV. Gas from Bivins No. A3 well of the Cliffside Field near Amarillo, Tex. The gas comes from the Blaine Formation of the Permian age at a depth of 740 feet.

V. Casinghead gas from the Bates No. 10 well in the Rock Crossing Field, Wilbarger County, Tex. The gas comes from the Ellenburger lime at a depth of 3805 feet. Collected October 10, 1941.

VI. Gas sample from the high-pressure residual gas line of the Mankins Plant of the Phillips Petroleum Company. The sample was taken June 18, 1941, while the plant was processing gas from the K.M.A. Field, Tex.

VII. Gas from the Olsen No. 1A well located a few miles south of Russell, Kan. The gas comes from the Kansas City Limestone at a depth of 3060 feet. Sample collected in August, 1940.

VIII. Gas from the Dobson No. 2 well at Dexter, Kan. Collected in April, 1940.

IX. Gas from the Harvey well in the Elkhorn Valley in the Northeastern part of Nebraska.

X. Casinghead gas from the Phillips No. 2 Deroin Well, East Watchorn Field, Pawnee County, Okla. Producing from the Wilcox sand at 3900 feet depth.

As a check, samples I and III have been analyzed in the laboratory of the Amarillo Helium Plant of the United States Bureau of Mines.

I. CO₂, 2.2%; O₂, 0.4%; CH₄, 12.0%; C₂H₅, 3.1%; He, 7.76%; residual nitrogen, 82.3%, which includes the helium and argon.

III. CO₂, 0.7%; O₂, 0.5%; CH₄, 60.9%; C₂H₅, 11.3%; He, 1.81%; residual nitrogen, including rare gases, 26.6%.

Except for the determination of CO_2 in sample I, there is good agreement of these data with those in Table III. The Bureau of Mines' value for helium in sample II is 5.86.

The gas reported as Kr + Xe in Table III was in each case mostly krypton, as judged by visual spectroscopic examination.
Table III. Composition of Gases in Per Cent by Volume										
Sample	CO_2	O2	Com- bustible	N_2	He	Ne	A	Kr + Xe		
I III ^b III IV V VI VII VIII ^c IX	$\begin{array}{c} 3.20 \\ 0.30 \\ 0.80 \\ 1.50 \\ 0.00 \\ 0.25 \\ 0.50 \\ 0.70 \end{array}$	0.40 0.40 0.50 1.40 0.70 1.20 0.70 1.10	15.10 40.20 72.10 0.00 68.40 88.50 70.10 0.20	72.9 52.6 24.7 96.8 30.6 10.0 28.0 97.0	$\begin{array}{c} 7.55 \\ 6.00 \\ 1.73 \\ 0.047 \\ 0.19 \\ 0.052 \\ 0.55 \\ 2.20 \\ 0.074 \end{array}$	a a 0.00080 < 0.001 a a a 0.0020	$\begin{array}{c} 0.890\\ 0.530\\ 0.196\\ 0.290\\ 0.124\\ 0.0356\\ 0.140\\ 0.078\\ 0.93\\ 0.$	0.000033 0.000054 0.000055 0.000082 0.000036 0.000017 0.000053		

^a So little Ne was present that its spectrum was not observed visually in the sample of He + Ne. ^b Data for CO₂, O₂, combustible gases, and N₂ furnished by Amarillo Helium Plant of U. S. Bureau of Mines. ^c Analyzed only for He and A. Judging from previous analyses of gas from the same field, composition is about 0.0% CO₂, 0.1% O₂, 15% combustible gases, and 820% N.

83% N2.

None of the gases tested contained more neon, argon, krypton, or xenon than air. One cannot conclude that North American natural gases rich in these elements are nonexistent, but the possibility seems sufficiently remote to make a continuation of the survey a poor gamble. The relative proportions of the different noble gases other than helium are approximately the same as in the atmosphere. In this respect the gases resemble the large number of samples from European wells, springs, and mines tested by Moureu and Lepape (19, 20).

The most interesting sample tested is I which, in addition to its surprisingly high helium content, is abnormally rich in argon. In proportion to the argon, the krypton content is low, the ratio $\frac{\mathbf{Kr} + \mathbf{Xe}}{\mathbf{Kr}}$ being only about 30% of the same ratio for air.

DISCUSSION

The procedures for determining total helium group gases and neon plus helium as described are reliable and moderately rapid. A total time of 5 hours is adequate for running the two determinations. One could probably reduce this to 2 or 3 hours as a routine method. The procedure for krypton plus xenon is also reliable and as accurate as any method previously described. It is, however, a time-consuming process which requires 8 to 10 manhours of work and a total elapsed time of 24 hours or more.

If one wishes to run complete rare gas analyses on a routine basis, he should investigate the possibility of using one or more physical methods of analysis-for example, some form of mass spectometer might be used rapidly and successfully to determine each noble gas in the mixture of these elements isolated from the initial sample. Hipple (13) reports that such an instrument has been used to analyze the gas taken from electron tubes.

Desorption from activated charcoal held at definite and controlled temperatures works very nicely for removing helium and neon from the heavier gases, but is more difficult to use for separating argon from krypton and xenon. The conditions for separating these elements have been described by Valentiner and Schmidt (40) and by Peters and Weil (28, 29). The work of Peters and Weil is the more thorough; as the result of a study of adsorption isotherms, they conclude that argon can be quantitatively separated from krypton and xenon by adsorbing a mixture of these gases upon cold activated charcoal. If the temperature of the carbon is then held at -93° to -100° C., argon may be quantitatively removed by pumping with a diffusion type pump, leaving all the krypton and xenon on the charcoal. The corresponding temperature at which one may pump away krypton, leaving all the xenon on the charcoal, is given as about -80° C. These procedures have been shown by the inventors to be satisfactory for the analysis of mixtures containing approximately equal amounts of the different gases. The authors were unsuccessful, however, in attempts to analyze crude argon from air by this method and found that the procedure needed further development.

Two factors make the quantitative separation of argon from krypton by desorption from charcoal at about -100° C. difficult: Some krypton is removed with the argon, and the rate of desorption of argon becomes extremely slow after most of this gas has been removed. As a consequence, a continued removal of gas by pumping fails to desorb all the argon and carries away an appreciable fraction of the krypton. A short pumping period is desirable in order to minimize loss of krypton.

The authors have modified the procedure of Peters and Weil by measuring the amount of krypton desorbed and greatly reducing the pumping time required for the quantitative removal of argon from cold activated charcoal. The cyclic technique described under procedure 6 accomplishes these changes. The amount of krypton pumped off in each cycle is measured and the total time of pumping is reduced by loosening the most

tightly adsorbed portion of the argon. After each period of pumping, the argon is desorbed by warming the charcoal. When the gas is again adsorbed argon may be rapidly pumped away for another 10-minute period. Three 10-minute cycles permit quantitative desorption of a small sample of gaseous argon. An equally complete removal of argon in a single step requires several hours of pumping.

The slow desorption of the last portion of a sample of argon is illustrated by an experiment in which 14.3 ml. of the gas were adsorbed upon 8.5 grams of activated charcoal at -183° C. After the gas had become completely adsorbed, the temperature of the charcoal was increased and held between -99.5° and -103.5° C, while argon was pumped away. The gas was removed rapidly at first, but the rate decreased to a very low value within 2 hours. A total pumping period of 7 hours was used. During the last 2.5 hours only 0.015 ml. of gas was removed, in spite of the fact that as much as 0.21 ml. remained adsorbed. This rate of desorption is many times smaller than that which is found when one starts to remove a recently adsorbed sample of argon.

Samples of argon were adsorbed on the 8.5-gram sample of charcoal at -183° C. The carbon was warmed to about -100° C. and held at this temperature while argon was pumped off for a 10-minute period.

Measurements similar to these have been made to determine the fraction of krypton removed from the charcoal held at about -100° C. during a 10-minute pumping period.

Fraction removed in 10 minutes, % 2.	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 2.7
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These data indicate that three cycles each containing a 10minute pumping period should remove 99% of the argon and leave about 92% of the original krypton still adsorbed on the charcoal.

One who is familiar with common methods for analyzing gases under atmospheric pressure is inclined to feel that the authors' procedures do not provide for a sufficient circulation of the gas over the active reagents, and may propose that a circulating pump be installed. The weak point in his reasoning is that he does not realize how rapidly gases circulate by diffusion while under low pressures. The low-pressure technique has been used by several others, who have found circulation by diffusion to be adequate.

As an added bit of experimental evidence the authors have measured the rate of adsorption of argon upon the activated charcoal in trap E, both when the gas is pure and when it is mixed with helium. The carbon was held at a temperature of -183° C. and the initial pressure of argon in the system was 9.6×10^{-3} mm. Runs were made with helium present in sufficient amount

to exert a pressure of: 0.019, 0.0079, and 0.0000 mm. Although the presence of helium appeared to retard the adsorption a little, the effect was not greater than the experimental error. Even in the absence of helium, adsorption of argon was a rather slow process and the presence of helium up to a pressure of 0.02 mm. did not interfere seriously. One half of the argon was adsorbed in 2.0 minutes and three fourths in 3.5 minutes. The time required for substantially complete adsorption was about 20 minutes.

While developing the procedure for determining krypton plus xenon, several unsuccessful attempts were made to separate these two gases from each other by fractional distillation.

A mixture of air or atmospheric nitrogen was distilled with about 3 liters of gaseous methane and 2 liters of carbon tetra-fluoride. Carbon tetrafluoride boils at -128° C., between the boiling points of krypton and xenon. Before testing the procedure it was believed that this substance would carry over the krypton in the distillate and leave the xenon behind in the liquid. As the distillation proceeded, the last part of the methane and the first part of the carbon tetrafluoride to distill were collected and allowed to react with hot calcium. This fraction was thought to contain the krypton but no xenon. The residual carbon tetrafluoride remaining in the still was thought to contain xenon but almost no krypton. In each run the krypton fraction contained an amount of noble gas corresponding to about 0.00014 to 0.00015% of the original sample of air and most of the gas was krypton. The rare gas in the supposed xenon fraction contained little krypton but also very little xenon; it was nearly pure argon. This argon was probably held on the walls of the glass and was, therefore, not removed by fractional distillation.

It was definitely established that xenon was carried over with the krypton in this procedure by working with the residue remaining after the evaporation of some commercial liquid oxygen. When this was distilled, the volume of rare gas in the krypton fraction was 7.8 ml. and the volume of rare gas (mostly argon) in the supposed xenon fraction was only 0.018 ml. The volume of xenon should have been about 0.5 ml.

The failure of this method may be easily explained. When a mixture of methane and carbon tetrafluoride is liquefied, two liquid phases are obtained. In the course of the distillation there must be a time when the refluxing liquid in the upper part of the column is methane and in the bottom portion is carbon tetrafluoride. The liquid methane is many degrees colder than the carbon tetrafluoride and seems to be the liquid in which both the xenon and the krypton are the more soluble. Both krypton and xenon are, therefore, concentrated in the top of the column. As the last of the liquid methane evaporates these rare gases are carried along in the gas stream.

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Determination of Sodium and Potassium in Silicates, Addendum

The following note was inadvertently omitted from the article "Determination of Sodium and Potassium in Silicates", by Marvin and Woolaver [IND. ENG. CHEM., ANAL. ED., 17, 554 (1945)].

The present paper and all results were obtained without knowledge of work performed by Lundell and Knowles reported in an article, "The Analysis of Soda-Lime Glass" [J. Am. Ceram. Soc., 10, 829 (1927)]. On page 849 of this paper the following sentences are significant: "The most promising rapid methods for determination of alkalies in soda-lime glass appear to be those based on attack with hydrofluoric and perchloric acids followed by evaporation to dryness and careful heating to convert the perchlorates to oxides and chlorides. Such an attack should leave the R2O: group as oxides, the alkaline earths as basic chlorides, and the alkalies as chlorides." Preliminary results based on this outlined procedure are given. Further work was proposed on this method of analysis, but there appear to be no other results in the literature by Lundell and Knowles up to the present time.

Lamp Method for Determination of Hydrogen in Liquid Organic Compounds

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This paper proposes a lamp method for the determination of hydrogen in liquid organic compounds, especially saturated hydrocarbons. The analysis of a series of pure compounds, ranging in volatility from diethyl ether to cetane and containing from 10 to 16% hydrogen, indicated an average accuracy of 0.03% hydrogen and an average precision of 0.02% hydrogen. Analysis of known mixtures gave results of similar reliability. The suggested technique does not give the same accuracy with compounds burning with a smoky flame. A special burner for such materials will be described.

THERE was need for a simple, reliable, and accurate method for the determination of hydrogen in saturated hydrocarbons, as a means of estimating the paraffin and naphthene content of gasolines. The usual procedure in analyzing organic materials for hydrogen is some modification of the Liebig combustion, wherein the sample is burned in air or oxygen and the vapors are passed over cupric oxide or lead chromate. However, the accuracy of the combustion procedure, as a routine method, is only of the order 0.1 to 0.2% hydrogen and very careful technique, especially in handling volatile liquids, is required.

Since gasolines are essentially hydrocarbon in nature, these analyses stress only the determination of hydrogen content-the procedure is sufficiently accurate so that the carbon content may be determined by difference.

The simple technique of the sulfur lamp method (1) was adapted to the determination of hydrogen in liquid organic materials. Briefly, the procedure consists in burning the sample with air at the end of a cotton wick and collecting the water formed in the combustion by a desiccant. This procedure offers several advantages over any of the usual combustion techniques.

The Liebig-type combustion calls for a high order of analytical technique when liquid samples are handled. Furthermore, with highly volatile materials, rather involved modifications of prorequire are needed. The present method is simple and does not require a highly skilled analyst. (In the petroleum industry, the lamp method is a routine, plant laboratory procedure.) The rate of combustion is easily controlled, even for low-boiling ma-terials. By merely varying the number of wicks in the burner, and cooling the sample in an ice bath, the entire range of vola-tilities from diethyl ether to cetane, a C_{10} paraffin, may be covered with no change in procedure.

The Liebig-type combustion consumes a large amount of nalyst time. The time for a single determination varies from analyst time.



some 1.5 to perhaps 6 hours, as in the case of the procedure (2) adopted in Army-Navy aviation gasoline specifications for determination of hydrogen content, with an average over-all time of 4 to 6 hours. Of this, about half is operator time. The lamp method requires an over-all time of some 2.5 to 3 hours for a method requires an over-all time of some 2.5 to 3 hours for a single determination; of this, however, less than 30 minutes is actual analyst time. Thus, an analyst can run some 3 or 4 determinations simultaneously. In the lamp method, tedious weighings of absorption vessels to constant weight are avoided. For a single analysis, only 4 weighings are made: the sample-containing vessel before and after the run and the absorption tube before out offer the run. These provides a control of the other before and after the run. These weighings are carried out only to the nearest milligram.

The accuracy of results obtained by the lamp method, as a routine procedure, is of the order of 0.03% hydrogen, absolute. The average deviation of repeated analyses from the mean is about 0.02% hydrogen.

The technique described below is not recommended for compounds burning with a smoky flame. A modification of the procedure for such compounds will be described later.

EXPERIMENTAL

The apparatus shown in Figure 1 is the standard lamp burner and chimney used in the A.S.T.M. D90-41T procedure, for sulfur determinations, except that the tube leading from the chimney is cut off about 2.5 cm. (1 inch) from the chimney and a 30-cm. (12-inch) length of glass tubing, about 7 mm. in inside diameter, is sealed on at a right angle to the chimney. This is then attached through a short length of rubber tubing to an absorption tube. The air inlet on the chimney is not used, and is closed off with a policeman. The compressed air used in the combustion is puripoliceman. The compressed air used in the combustion is puri-fied by passage through calcium chloride and phosphorus pent-oxide. The absorption tube is filled in this manner: 1.25-cm. (0.5-inch) layer of glass wool; 5-cm. (2-inch) layer of 12-mesh calcium chloride; 1.25-cm. (0.5-inch) layer of glass wool; 1.9-cm. (0.75-inch) layer of phosphorus pentoxide; glass wool to the top of the trap. One filling is sufficient for the absorption of some 10 grams of water. The absorption tube is cooled in an ice bath during the run.

To make a determination, the weighed absorption tube is con-nected to the chimney tube and immersed in an ice-water bath. A short length of glass tubing is connected to the exit tube of the absorber (to prevent any possible diffusion of water vapor back into the tube). The burner is then threaded with the cotton wicks, the number of strands used depending on the volatility of the sample-for example, with cyclohexane, six wicks were used; with cetane, four wicks; and with diethyl ether, nine wicks. The are then put in the flask, the burner is inserted, and the whole is quickly weighed (to = 1 mg.). The lamp is brought to the apparatus, the policemen removed, the air line connected, the burner lighted (using a microburner) as soon as the liquid reaches the top of the wick, and the air pressure adjusted so that the flame is maintained beneath the smoking point. The burner is then in-

serted in the chimney. From this point on, the combustion requires no further atten-From this point on, the combustion requires no further atten-tion on the part of the operator. After a period of 1 to 1.5 hours (or longer if desired), the lamp is quickly removed from the chimney, stoppered with the policemen as before, and weighed. The absorption bulb is removed, wiped with cheesecloth, and allowed to stand until it reaches room temperature, when it is weighed (to ± 1 mg.). The part opt hydrograp is calculated from the formula

The per cent hydrogen is calculated from the formula:

% hydrogen = $\frac{\text{weight of } H_2O \text{ absorbed}}{\text{weight of sample burned}} \times 11.191$

(using the value 1.0080 for the atomic weight of hydrogen).

A few specific points may be noted in this procedure:

For volatile samples, such as ether or cyclohexane, the flask containing the sample is maintained in an ice bath during the run. For more volatile materials, a dry ice-acetone bath may be used. When the flask has been cooled during the combustion, the cooling bath is removed some 10 minutes or so before the end of the run, and the flask is dried with a cloth while still in the chimney and allowed to come to room temperature before being removed.

With nonvolatile samples, there is a tendency for moisture to condense in the tube before reaching the absorber, because less sample is burned in a given time and the heat of combustion is insufficient to raise the entire chimney tube to a temperature of 100 ° C. To prevent this, a 30-cm. (12-inch) length of Nichrome wire, B. & S. No. 22, is loosely wrapped around the chimney tube and connected to a Variac; sufficient current is supplied to maintain the tube at slightly over 100 ° C.

The phosphorus pentoxide in the absorption tube serves a dual purpose. It is used primarily to trap any small amounts of water that may have escaped the calcium chloride, and it also indicates any incomplete combustion, with consequent formation of unsaturates, by a decided darkening. A faint coloration in the phosphorus pentoxide may be disregarded.

The sample being analyzed must, of course, be dry. With hydrocarbons, filtration through filter paper and use of calcium chloride or other drying agents are usually sufficient.

The above procedure involves a definite, though slight, error. The actual amount of the error may, however, be precisely determined and corrected for. It arises from the fact that a measurable time elapses between lighting the wick and inserting it in the chimney, and between removing the flask after the run and stoppering it. The total time involved is of the order of 10 to 20 seconds, and should be noted for each analysis. A correction to the results may then be applied in this manner:

Let: t = time for the complete analysis, in secondss = time lost, as noted above, in secondsw = grams of water absorbedy = grams of sample burned

$$- \times 11.191 = \%$$
 H (uncorrected)

The correction is:

 $w \times \frac{t}{t-s} = W =$ (grams of water, corrected)

Then,

 $\frac{W}{y} \times 11.191 = \%$ H (corrected)

To take an actual example, 2.111 grams of heptane gave 3.015 grams of water. The time of the run was 1 hour and 10 minutes, and the "lost" time was 20 seconds. Then,

 $\frac{3.015}{2.111} \times 11.191 = 15.98\% \text{ H (uncorrected)}$ $3.015 \times \frac{4200}{4200 - 20} = 3.029 \text{ grams of } \text{H}_2\text{O}$

4200 - 20 3.029 × 11 101 = 10.0007 H (compared)

 $\frac{3.029}{2.111}$ × 11.191 = 16.06% H (corrected)

For the average analysis, this correction is of the order of 0.05% hydrogen or less.

The results obtained in the analysis of pure compounds are indicated in Table I.

ANALYSIS OF MIXTURES

Inasmuch as this procedure was developed primarily for analysis of mixtures, there must be no fractionation during the combustion. With the paraffin-naphthene mixtures handled in this laboratory, measurement of refractive index (Na-D line, at 20° C.) is the simplest method of determining whether or not any change in composition has occurred. Table II indicates the results of such measurements and shows that fractionation does not take place, even with mixtures containing components of widely differing volatilities. As may be noted, the only change in refractive index occurs in the gasolines; however, the average change is only ± 0.0004 unit and, since these samples contained components boiling below room temperature, a variation of this amount is well within the actual handling error.

Actual results of analyses on known mixtures are given in Table III.

DISCUSSION

The method presented is simple and the technique may be quickly learned by a moderately skilled analyst. No elaborate apparatus is used and little operator time per analysis is required. There is no difficulty whatever in turning out six to eight (or even more) analyses in an 8-hour day.

Although all the authors' work, with few exceptions, has been with hydrocarbons, there is no reason why the procedure in its present form, or a slightly modified version, should not be equally applicable to a wide variety of organic materials. Thus, for highboiling liquids ($>300^{\circ}$ C.), the lamp and burner may be heated, to increase the rate of rise of sample in the wick. In the case of molecules containing, say, sulfur, the water formed may be trapped in a freezing bath, preferably liquid nitrogen, and the sulfur oxides determined by the usual chemical procedures.

As an interesting sidelight on the purity of the water formed in the combustion, samples of *n*-heptane and iso-octane were burned and the water was collected in a clean receiver cooled in dry ice. The densities of both the water samples were 0.9982 ± 0.0001 grams per ml., at 20° C., and the refractive indices, for the D line at 20° C., 1.3329 ±0.0001, in exact agreement with the values for pure water.

Table 1. Analysis of Pure Compounds for Per Cent Hydrogen

			Time				
Material	Amount	Water	of	"Lost" Time	H (Uncorrected)	H (Corrected)	H Theo-
material	Grams	Grams	Min.	Sec.	%	%	%
1-Heptane	2.111 3.977 7.890	$3.015 \\ 5.688 \\ 11.317$	70 105 180	20 25 20	15.98 16.00 16.05	16.06 16.06 16.08	16.10
						16.07 ± 0.01	
lso-octane	$2.970 \\ 2.428 \\ 1.941$	$\begin{array}{r} 4.203 \\ 3.406 \\ 2.742 \end{array}$	110 80 60	20 20 10	15.83 15.70 15.81	15.88 15.77 15.85	15.88
						15.83 ± 0.04	
Cyclohexane	$3.201 \\ 3.327$	4.091 4.240	95 90	25 20	$\begin{array}{c} 14.30\\ 14.26 \end{array}$	14.36 14.31	14.37
						14.34 ± 0.03	
Methylcyclo- hexane	$3.596 \\ 2.782$	$\begin{array}{r} 4.600\\ 3.548\end{array}$	110 90	$\begin{array}{c} 25\\ 20 \end{array}$	$\substack{14.31\\14.27}$	14.36 14.32	14.37
						14.34 ± 0.02	
Cetane	$2.327 \\ 1.649 \\ 2.208$	$3.141 \\ 2.226 \\ 2.973$	120 75 90	10 10 20	$15.11 \\ 15.11 \\ 15.06$	$15.13 \\ 15.14 \\ 15.12$	15.13
						$\frac{15.13}{15.13} \pm 0.01$	
Ethyl alcohol	$3.775 \\ 4.333$	4.418 5.074	75 75	10 20	13.09 13.10	13.12 13.16	13,13
						13.14 ± 0.02	
Acetone	$5.044 \\ 4.129$	4.687 3.847	90 80	30 20	$\begin{array}{c} 10.40\\ 10.43 \end{array}$	10.46 10.47	10.41
						10.47 ± 0.01	
Ether	$\begin{array}{c} 7.019 \\ 6.674 \end{array}$	8.491 8.108	70 70	20 20	$\begin{array}{c} 13.54\\ 13.59\end{array}$	13.60 13.65	13.60
						13.63 ± 0.03	

The purity of these reagents is indicated by their properties:

	Refractive Index, D Line at 20° C.	Density, 20° C.	Remarks
-Heptane so-octane Syclohexane Iethylcyclohexane	$\begin{array}{c} 1.3877 \pm 0.0001 \\ 1.3914 \pm 0.0001 \\ 1.4261 \pm 0.0001 \\ 1.4230 \pm 0.0001 \\ 1.4230 \pm 0.0001 \end{array}$	$\begin{array}{c} 0.6837 \ \pm 0.0001 \\ 0.6919 \ \pm 0.0001 \\ 0.7782 \ \pm 0.0001 \\ 0.7694 \ \pm 0.0001 \\ 0.7693 \ \pm 0.0001 \\ 0.720 \ \pm 0.0001 \end{array}$	Certified knock-rating standard Certified knock-rating standard Melting point, 5° C.
etane Sthyl alcohol ccetone Sther	1.4340 = 0.0001	0.7739 ± 0.0001	Publicker Alcohol Co. R.G.AGeneral Chemical Co. R.G.AGeneral Chemical Co.

Table II. Measurement of Refractive Indices of Mixtures

		active Inde	ve Index		
Mixture composition	Boiling Range, °C.	Most and least volatile components	Original sample	Sample after burning	
Cyclohexane-iso-octane	80-100	1.4262	1.4151	1.4151	
Methylcyclohexane-n-heptane	98–101	1.3915	1.4042	1.4042	
Gasoline cut	100-125	1.4231	1.4107	1.4107	
Aviation gasoline, A	22-166	1.37	1.4172	1.4166	
Aviation gasoline, B	22-166	1.37	1.4135	1.4139	
Motor gasoline, A	24-215	1.38	1.4329	1.4333	
Motor gasoline, B	24-215	1.38	1.4290	1.4286	
		(Accuracy =	0.0002)		

$\begin{tabular}{|c|c|c|c|} \hline Table III. Analysis of Mixtures \\ \hline n-Heptane-methylcyclohexane & Actual & Determined \\ $\%$ & $\%$ \\ \hline n-Heptane-methylcyclohexane & $14,90$ & 14.88 ± 0.04 \\ 2 & 15.18 & 15.188 ± 0.01 \\ 3 & 15.48 & 15.488 ± 0.04 \\ 15.48 & 15.48 & 0.01 \\ 15.48 & 15.47 ± 0.05 \\ n-Heptane-methylcyclohexane & 11.69 & 12.02 ± 0.02 \\ 16-octane-toluene & 11.67 & 11.63 \\ $Aviation gasoline & 13.6 ± 0.1^a & 13.07 ± 0.04 \\ $Motor gasoline & 12.9 ± 0.1^a & 13.07 ± 0.04 \\ \hline \end{tabular}$

^a Analyzed by usual carbon-hydrogen combustion procedure (2).

Aromatic materials, and other compounds that burn with a smoky flame, may also be handled by making a quantitative dilution with a pure saturate and burning the mixture, since mixtures containing as much as 50% by weight of aromatics may be satisfactorily analyzed. The composition of the aromatic may then be calculated at only a slight decrease in accuracy.

The apparatus described is crude and the authors have, knowingly, left it in that condition to make the analysis as simple as possible. For greater accuracy, the changes indicated herewith may be made. Connections should be through ground joints rather than rubber tubing. Similarly, ground-glass caps should be used to close off the burner and chimney.

The "lost" time correction could be eliminated by setting up an electrical ignition system in the chimney for lighting the wick, together with a mechanical arrangement for capping the burner before removing it from the chimney.

A wick of asbestos fiber, with a platinum tip, may be used to burn the samples.

A second absorption tube may be connected in the line when burning very volatile materials, since, at the high air velocity required for complete combustion, some 2 to 3 mg. of water may carry over from the one absorber.

As a final point, weighings may be carried to 0.1 mg. and correction made for reduction to vacuum.

As indicated above, determination of per cent hydrogen alone is sufficient for proving the composition of hydrocarbons. For this reason, the authors have not attempted to make the procedure quantitative for carbon. Some preliminary work indicates about 98% conversion to carbon dioxide; however, by minor changes of procedure (such as use of oxygen in the air stream, oxidation of carbon monoxide, etc.) the method should prove as accurate for carbon determination as for hydrogen.

A forthcoming paper will deal with the application of the procedure to the determination of paraffins and naphthenes in gasolines, and will indicate some of the types of problems that may be solved by this method.

ACKNOWLEDGMENT

The authors wish to express their appreciation to Jack Grider for his assistance with the analytical work.

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Determination of 4-Vinyl-1-cyclohexene (Butadiene Dimer) in Recycle Styrene

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Butadiene dimer is determined in recycle styrene by quantitatively polymerizing the styrene, using sodium as a catalyst. The vinyl-cyclohexene is determined by the iodine chloride method. The method is sensitive to 0.2% vinylcyclohexene and is accurate to about $\pm 0.2\%$ (absolute) over a range of 1 to 20% vinylcyclohexene.

THE determination of butadiene dimer in recycle styrene is of interest not only in determining the purity of the recycle material but also in allowing more accurate material balances in the polymerization process. The vinylcyclohexene is steamdistilled together with the recycle styrene in the latex stripping operation, and therefore the butadiene recovery is decreased and the styrene recovery is increased by the dimer formation.

Chemical methods tried in the past have been unsuccessful because of the similar reactivities of the two compounds towards

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² Present address, Department of Chemistry, State University of Iowa, Iowa City, Iowa. addition agents. Since styrene shows much greater reactivity in polymerization and vinyl group reduction reactions, the possibility of removing the interference of styrene by reduction to ethylbenzene or by polymerization was considered. Preliminary experiments showed that sodium-amalgam reduction of the styrene was too slow and incomplete to be practical, while polymerization proceeded rapidly using sodium as a catalyst.

PURIFICATION OF 4-VINYL-1-CYCLOHEXENE

A Dow Chemical Company product, $n_{D}^{so} = 1.4650$, was purified by conversion to the tetrabromide, recrystallization, and debromination.

BROMINATION. The commercial product was brominated under conditions similar to those described for cyclohexene (4).

The vinylcyclohexene was purified by shaking with potassium iodide solution, drying, and distilling. The fraction at 126– 128 °C. was collected. In a 2-liter, three-neeked, round-bottomed flask fitted with a 500-ml. separatory funnel, a mechanical stirrer, and a thermometer, was placed a solution of 162 grams of vinylcyclohexene in a mixture of 300 ml. of carbon tetrachloride and 15 ml. of absolute alcohol. The flask was surrounded by an icesalt bath. The stirrer was started, and when the temperature reached -5° , a solution of 420 grams (134 ml.) of bromine in

Table 1. Effect of Time of Standing and Excess of Reagent on Iodine Chloride Addition by Dow Vinylcyclohexene

		-			
Weight of Sample Mg.	ICl Added Ml.	Excess ICl %	Time Min.	ICl Used <i>Ml</i> .	Theoretical Unsatu- ration %
32.88 32.88 32.88 40.65 40.65 40.65	10 10 20 20 20	76 76 185 185 185	10 20 80 21 45 60	$\begin{array}{r} 4.41\\ 4.75\\ 5.10\\ 6.53\\ 6.56\\ 6.52\end{array}$	77.8 83.8 90.0 93.0 93.5 92.9

290 ml. of carbon tetrachloride was added from the separatory funnel at such a rate that the temperature of the reaction mixture did not exceed $+5^{\circ}$. After the addition of the bromine (period of 7 hours) the carbon tetrachloride was removed under vacuum and the residual oil obtained was taken up in petroleum ether (90° to 110° C.) and cooled. The white crystals which formed melted at 73° to 80° C. Yield, 313.2 grams. Recrystallization from petroleum ether (90° to 110° C.) did not change the melting point.

DEBROMINATION OF TETRABROMIDE. The vinylcyclohexene tetrabromide was not separated into the cis and trans isomers reported by Lebedev and Sergienko (3) but was used as such in the debromination.

In a 2-liter, three-necked, round-bottomed flask fitted with a 500-ml. separatory funnel, a mechanical stirrer, and a reflux condenser, were placed 32 grams of magnesium turnings in 400 ml. of absolute ether. To this well-stirred solution was added a solution of 282 grams of vinyleyclohexene tetrabromide in 400 ml. of dry benzene at such a rate that the ether refluxed gently. The reaction could be started, if slow, by heating the mixture slightly. After completion of the addition of the tetrabromide solution, the resulting mixture was refluxed for 4 hours and then poured onto a mixture of ice and ammonium chloride. The organic layer was separated, washed once with an ammonium chloride solution and twice with water, and then dried over sodium sulfate. The ether and benzene were removed by distillation through a 25-cm. (10-inch) Fenske column and the vinyl-cyclohexene thus obtained was distilled. The fraction boiling from 126-127° C. was collected. Yield, 25 grams. The vinyl-cyclohexene was refractionated and a sample boiling at 126-127° C. taken, $n_D^{*0} = 1.46385$, 1.46395.

DETERMINATION OF VINYLCYCLOHEXENE

Several halogen addition methods were tried, to find one which could be used with dioxane as a solvent and at the same time would give essentially stoichiometric results.

BROMINE TITRATION. The method of Uhrig and Levin (7) using bromine in glacial acetic acid as the reagent, but using dioxane as the sample solvent, was tried in a direct titration to an end point. The method gave excellent results for styrene but did not yield satisfactory results for vinylcyclohexene because the reaction was very slow near the end point.

The slowness was undoubtedly caused by the low reactivity of the ring unsaturation. To illustrate, the addition of a 200%excess of 0.3 *M* bromine solution to a solution of cyclohexene in cyclohexane followed by back-titration after 2 minutes of standing resulted in the use of only 93% of the theoretical amount of bromine. The addition of excess bromine was unsatisfactory owing to appreciable blanks with dioxane.

IODINE BROMIDE ADDITION. The Woburn iodine absorption method of von Mikusch and Frazier (8), using a 0.16 M iodine bromide solution in glacial acetic acid, was tried on pure cyclohexene and on Dow vinylcyclohexene (unpurified).

A large excess of halogen and a long time were required to approach theoretical unsaturation. For example, using a 500% excess of reagent for 1 hour, a value of 93% of the theoretical unsaturation was obtained for cyclohexene.

IODINE CHLORIDE ADDITION. Iodine chloride in carbon tetrachloride has been used as a reagent for determining unsaturation of natural rubber by Pummerer and Mann (5) and Pummerer and Stark (6) and for butadiene copolymers by Kemp and Peters (2). A 0.1 M solution was found to give a rapid addition of halogen using a reasonable excess of reagent, and a negligible blank when dioxane was used as the sample solvent.

From the results of Table I it is concluded that an excess of around 200% of iodine chloride should be present to obtain reproducible results. The time of standing beyond 20 minutes is unimportant. These experiments were done on Dow vinyl-cyclohexene, dissolved in 5-ml. portions of dioxane and allowed to stand at room temperature with 0.1072 M iodine chloride, and back-titrated with 0.1 N thiosulfate after the addition of potassium iodide solution.

The results given in Table II were obtained on pure vinylcyclohexene. In this series, a known weight of sample in 5 ml. of dioxane with 5 ml. of glacial acetic acid was allowed to stand 20 minutes at 0° C. in the dark with 20 ml. of 0.1026 M iodine chloride solution, and back-titrated in the usual way.

Table II.	lodine	Chloride	Addition	Using Pu	re Viny	lcyclohexene
			-			

Weight of	Excess		Theoretical
Sample	ICI	ICl Used	Unsaturation
Mg.	%	Ml.	%
47.43	134	8.33 8.35	97.3 97.5
28.46	290	5.01 4.99	97.5 97.2
9.49	1070	1.65 1.65	96.4 96.4
4.74	2220	0.825 0.835	96.5 97.5

The excess of reagent is unimportant over a wide range beyond 150%. With pure cyclohexene a halogen consumption of 97% was reached compared with 93% with the unpurified material. Under similar conditions, cyclohexene and styrene showed 95.0 and 97.2% of theoretical halogen addition, respectively.

Using a more concentrated (0.3 M) iodine chloride in large excess (300%) overnight in the dark at room temperature, an apparent unsaturation of 101 to 104% was found for pure vinylcyclohexene. Under these conditions a relatively large and poorly reproducible blank was obtained for dioxane (0.1 to 0.3 m]. of iodine chloride). Less than 0.01 ml. of 0.1 M iodine chloride was used in 20 minutes by 5 ml. of dioxane.

Changing the temperature from room temperature to 0° C. made a difference of less than 0.5%. The lower temperature, however, gave a smaller and more reproducible polystyrene blank; hence a temperature of 0° is recommended for the procedure.

POLYMERIZATION OF STYRENE BY SODIUM

POLYSTYRENE BLANK. A series of experiments was carried out to determine proper conditions for quantitative polymerization of styrene. In each of the experiments listed in Table III, a mixture of 5 ml. of styrene and 45 ml. of solvent was refluxed with 6 grams of sodium. The blanks reported represent the consumption of 0.1 M iodine chloride by a 5-ml. aliquot of the resulting mixture.

Dioxane which had been purified by prolonged refluxing with sodium followed by distillation proved to be the most satisfactory solvent. Toluene also appeared promising, but gave a higher blank than dioxane. Benzene was unsatisfactory because its boiling point is below the melting point of sodium, and a fresh surface is necessary for quantitative reaction.

On the assumption that the reason for the blank was the presence of monomeric styrene, experiments designed to allow reduction to follow polymerization were carried out. After 30 minutes of refluxing with dioxane, an equal volume of alcohol was added, and the refluxing was continued until the sodium was dissolved. Considering the dilution by the alcohol, the combined treatment had no advantage over polymerization alone. Moreover, the dioxane-alcohol mixture is a poor solvent for polystyrene and for sodium ethoxide. The blank appears to be caused mainly by polystyrene rather than by residual monomer, since no treatment lowered it below a certain minimum (about 0.7% of the iodine chloride consumption of the original styrene).

Another indication that polystyrene is largely responsible for the blank is that centrifuging to form clear solutions was found to give a smaller and more reproducible blank. However, polystyrene prepared by peroxide-catalyzed polymerization did not use detectable amounts of iodine chloride. Structural differences in the sodium-polymerized material may be responsible for a different behavior with respect to halogen.

The blank was found to be smaller and more reproducible if the sample was cooled to 0° in an ice bath before adding the iodine chloride and allowed to stand for the reaction at 0°.

The blank did not change when the time of standing with iodine chloride at 0° was varied between 20 minutes and 1 hour. When alcohol reduction followed the polymerization, however, a rapidly changing blank was observed (Table III). For this reason also, the use of alcohol was abandoned.

Metallic sodium and 40% sodium amalgam were both found to be efficient catalysts. Using equivalent amounts of sodium, the blanks obtained with the two catalysts were the same. Since amalgamation appeared to possess no advantage, metallic sodium is recommended in the final procedure.

Using 5 ml. of styrene with 45 ml. of dioxane, the amount of sodium was unimportant if it exceeded 3 grams. The best procedure found was to use 6 grams of sodium, with vigorous shaking during refluxing to break up the sodium into small drops. The use of a drying tube at the top of the reflux condenser was unnecessary if no condensation of moisture had occurred inside the reflux condenser. Drying of the condenser tubes before each experiment is recommended.

The polymerization reaction is essentially complete in 20 to 30 minutes. However, owing to uncontrollable variations in conditions, the time required for quantitative polymerization varied from one experiment to another. In the procedure, a 1-hour time is specified, followed by the titration of another aliquot after a second hour. Blanks with pure styrene run in parallel with the unknowns help to control variations in conditions.

Increasing the amount of styrene from 5 to 10 ml. in a total volume of 50 ml. led to an increased and more variable blank. The viscosity of the polystyrene solution increased to the extent that handling the solution became difficult.

The polymerization was not noticeably affected by the presence of tert-butyl catechol as an inhibitor in the styrene in amounts up to 100 p.p.m.

PROCEDURE

REAGENTS. Iodine Chloride. A 0.1 M (0.2 N) solution in carbon tetrachloride made by dissolving about 5 ml. of technical

Variation of Bla and Iodir	ank with ne Chlorid	Conditio le Addi	ons of tion	Polymerization
Catalyst	Time of Reflux	ICl Ad Temp.	ddition Time	0.1 M ICl Used
	Min.	° C.	Min.	M1.
Na	30	0	20	0.43, 0.42 0.38, 0.44 0.34, 0.28
Na	60	0	20	0.33, 0.31 0.28, 0.39 0.29
Na Na	30 60	30 0	20 60	0.40,0.60 0.38
40% Na-Hg 40% Na-Hg	30 60	0	20 20	$\begin{array}{c} 0.34 \\ 0.32, 0.34 \end{array}$
Na	60 60	0	20 60	0.18, 0.21
40% Na-Hg	60 45	0 0	120 20	1.52 0.21
40% Na-Hg	30 30	0 0	20 20	0.95 0.95
40% Na-Hg	45	0	20	0.14,0.21
	Variation of Bla and lodin 'Catalyst Na Na Na 40% Na-Hg 40% Na-Hg 40% Na-Hg 40% Na-Hg 40% Na-Hg	Veriation of Blank with and lodine Chlorid Catalyst Time of Refux Min. Na 30 Na 60 Na 40% Na-Hg 30 40% Na-Hg 30 40% Na-Hg 30 40% Na-Hg 30	Variation of Blank with Conditionand lodine Chloride Additionand contraction of Reflux Temp. Catalyst Time of Reflux Temp. Min. ° C. Na 30 0 Na 60 0 Ma-Hg 60 0 Na 60 0 Na 60 0 Na 60 0 Na 60 0 Ma 60 0 Na 80 0 40% Na-Hg 30 0 40% Na-Hg 30 0 40% Na-Hg 30 0 40% Na-Hg 30 0	Variation of Blank with Conditions of and loding Chloride Addition Catalyst Time of Reflux ICl Addition Temp. Catalyst Min. °C. Min. Ma 30 0 20 Na 60 0 20 Na 80 0 20 Ma 30 0 20 40% Na-Hg

Table IV.	Analysis of Known M	Aixtures
Vinylcyclohexene Added %	Vinylcyclohexene Found %	Error, Absolute %
11.13	11.18 11.18 11.19 11.21	+0.05 +0.05 +0.06 +0.08
5.51	5.42 5.42	-0.09 - 0.09
2.78	2.97 2.98 2.97 2.98	+0.19 +0.20 +0.19 +0.20
1.12	1.04 1.07 0.93 0.96	$ \begin{array}{r} -0.08 \\ -0.05 \\ -0.19 \\ -0.16 \\ \end{array} $

iodine chloride in 1 liter of technical carbon tetrachloride. The reagent can also be prepared from the elements by the method of Kemp and Mueller (1), substituting carbon tetrachloride for glacial acetic acid as the solvent.

Glacial acetic acid, c.p. grade. Sodium thiosulfate, 0.1 N, standardized against potassium iodate.

Potassium iodide, 15% aqueous solution.

Metallic sodium, technical grade.

Dioxane. Purified by prolonged refluxing with metallic sodium until the surface remains bright (usually 24 hours or more), followed by distillation from the sodium. The dioxane should not be allowed to stand more than 10 days before use.

METHOD. Dry the styrene sample by shaking with anhydrous sodium sulfate. Deliver 5 ml. of sample into a tared 50-ml. volumetric flask and weigh to 0.01 gram. Make up to the mark volumetric flask and weigh to 0.01 gram. Make up to the mark with dioxane. Pour the solution into a 300-ml. round-bottomed flask provided with a dry standard-taper ground-glass joint con-Quantitative transfer is not necessary. Add about 6 denser. grams of freshly cut sodium (the sodium should not be finely cut. but in 3 or 4 pieces). Heat to boiling on a hot plate and reflux for 1 hour. Shake the flask vigorously at intervals to break up the sodium into finely divided pieces.

Centrifuge a portion of the mixture, using about 10 ml. in each of two centrifuge tubes. Three to 5 minutes of centrifuging at moderate speed is adequate. Into a 125-ml. glass-stoppered Erlenmeyer flask (or ipdine flask) containing about 5 ml. of glacial acetic acid, pipet a 5-ml. aliquot of the clear solution. Cool the flask in an ice bath and pipet accurately 20 ml. of 0.1 M iodine chloride solution into the flask. Allow the solution to stand 20 to 30 minutes in the dark at 0 $^\circ$ C. Add 15 ml. of 15% potassium iodide solution, shake well, and titrate at once with 0.1 N thiosulfate.

Run a blank experiment using pure styrene containing no vinvlcyclohexene (but containing up to 100 p.p.m. of tert-butyl catechol if desired) with the unknown.

Test for completeness of polymerization by allowing the remaining solution to reflux for another hour, titrating another aliquot as above.

CALCULATIONS. A factor of 100/97 is included to correct for incomplete halogenation.

r cent		vinylcyclohexene	_ (A	(A	 B)	×	N	\times	27	. 0
	cent				S	X	0.97	7		

where

Pe

= volume of sodium thiosulfate required to titrate Å blank

volume of sodium thiosulfate required to titrate B unknown

normality of sodium thiosulfate =

S = sample weight in grams

ANALYSIS OF KNOWN MIXTURES OF VINYLCYCLOHEXENE AND STYRENE

Known mixtures of pure styrene and pure vinylcyclohexene were made up and analyzed by the procedure given above. From the results given in Table IV, which are typical, it is apparent that there is no systematic error in the determination. The discrepancies are apparently due to variations in the blank, since the values given represent various titrations, but only a single polymerization, for each sample.

PRECISION, ACCURACY, SENSITIVITY

The volumetric determination has a precision of $\pm 0.5\%$ (relative), but a constant error of -3% which can be corrected by a suitable factor.

The accuracy of the method is limited by the reproducibility of the blank. After one hour of polymerization, the blank corresponded to 0.30 ± 0.05 ml. of 0.1 M iodine chloride. A variation of 0.05 ml. in the blank corresponds to 0.27 mg. of vinvlcvclohexene in each aliquot portion or about 0.05% (absolute) in the original sample.

From the results in Table IV, the over-all accuracy appears to be $\pm 0.2\%$ (absolute). The sensitivity is likewise of the order of 0.2%.

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Spectrochemical Determination of Small Amounts of Aluminum in Steel

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A spectrochemical method is described for the determination of aluminum in steels with a range from 20 to 500 micrograms per sample. Colorimetric procedures proved unsuitable because of the presence of interfering ions which could not be completely eliminated. A method was developed employing a mercury cathode separation and a final spectrographic procedure of sparking a concentrated solution of aluminum.

A N INVESTIGATIONAL project at this laboratory required an accurate determination of trace amounts of aluminum in corrosion-resistant steels. A number of photometric procedures were attempted with the use of organic reagents including aurintricarboxylic acid (6, 11, 15, 16, 18, 21-25, 30-34), morin (7, 15), hematoxylin (13, 15, 17), and alizarin S (2, 5, 15, 29, 34). After intensive studies, constituting examinations of exact pH control, • interfering ions, and various chemical separations, colorimetric methods for the determination of aluminum were found impractical for the materials to be tested.

A spectrochemical procedure was then developed with satisfactory results. The aluminum was separated by a mercury cathode electrolysis (14, 22, 24) and the spectrographic procedure was employed with an iron salt added as an internal standard. A spark solution method (27) which has a high degree of reproducibility was found to be more suitable in this case than the usual arc method (4). A Bausch & Lomb large Littrow spectrograph was used and a quartz prism was found to have sufficient resolving power and optical efficiency. Densitometric measurements of the spectral lines were made for accurate determination of the aluminum content.

PREPARATION OF STANDARDS

STANDARD ALUMINUM SOLUTION (1 ml. = 0.020 mg. of alu-Dissolve 0.020 gram of pure aluminum metal in 10 ml. minum). of hydrochloric acid (1 to 1). When solution is completed, add 10 ml. of sulfuric acid (1 to 1) and evaporate to fumes of sulfuric acid. Cool, transfer to a 1000-ml. volumetric flask, and dilute to the mark.

INTERNAL REFERENCE STANDARD (1 ml. = 3.75 mg. of iron). Dissolve 3.750 grams of pure iron wire in 40 ml. of sulfuric acid (1 to 1). Cool the solution, transfer to a 1000-ml. volumetric flask, and dilute to the mark.

SPECTROGRAPHIC STANDARDS. Dissolve samples of a corrosion-resistant steel (18 Cr-8 Ni) containing no aluminum in covered 50-ml. beakers with 10 ml. of hydrochloric acid (1 to 1) and

10 ml. of sulfuric acid (1 to 4). Add increments of the standard aluminum solution to give a range from 0.002 to 0.05% aluminum. Carry out the aluminum separation according to the outlined chemical procedure. The spectrographic working curve is obtained from the values of these standards.

CHEMICAL PROCEDURE

Dissolve a 0.5-gram sample in a covered 50-ml. beaker with 10 ml. of hydrochloric acid (1 to 1) and 10 ml. of sulfuric acid (1 to When solution is complete, remove and rinse cover glass, and evaporate slowly to light fumes of sulfuric acid on an asbestos hot plate. Cool somewhat, add 10 ml. of distilled water, redissolve, and evaporate again to light fumes of sulfuric acid. Cool slightly, add 30 ml. of distilled water, and dissolve the salts on an asbestos hot plate.

Filter through a Whatman 11-cm. No. 40 filter paper into a mercury cathode cell containing approximately 25 to 30 ml. of clean mercury, rinsing beaker and washing the filter paper several times with distilled water, and reserve the filtrate. Transfer the times with distilled water, and reserve the filtrate. filter paper containing the insoluble aluminum oxide to a platinum crucible, char, and ignite the residue. Add a small measured amount (approximately 0.25 gram) of sodium carbonate and fuse over a Meker burner. Cool, transfer the crucible to a 100-ml. beaker containing 50 ml. of boiling distilled water, and continue boiling until the fused mass is completely dissolved. Rinse the orweible with distilled water, transfer the solution to the reserved crucible with distilled water, transfer the solution to the reserved filtrate, and adjust the volume to 200 ml.

Electrolyze at 7 volts and 2.5 to 4 amperes for at least 2 hours or until solution is colorless. When electrolysis is complete, drain the mercury and rinse the electrodes with distilled water into the electrolyzed solution.

Filter through a Whatman 11-cm. No. 40 filter paper into a 250ml. beaker, rinsing the cell and washing the filter paper several times with distilled water, and evaporate on a hot plate to 20 to 25 ml. Transfer the solution to a 50-ml. beaker, rinsing carefully with 10 ml. of distilled water, and continue evaporation to 3 to 4 ml. Cool, add 1.0 ml. of internal standard solution, adjust volume to 5.0 ml. with distilled water in a 10-ml. mixing flask, and mix well. The solution is now ready for spectrographic analysis. PRECAUTIONS. All reagents must be tested spectrographically

for aluminum. All glassware should be Pyrex. It is advisable to run a control through the entire procedure.

This may be prepared by adding a known quantity of standard aluminum solution to a steel in which this element is found to be absent.

DESCRIPTION OF MERCURY CATHODE CELL

The cell consists of a 250-ml. beaker with a glass stopcock leading from the lower edge. A wire fused into the petcock, through the side, is terminated to a platinum wire which is in contact with

Table I. Analyses of Synthetic Standards

	$\Delta \log I$		Maximum Devia- tion from		$\Delta \log I$		Maximum Devia- tion from
Al Added %	$\left(\frac{\Lambda_{\rm f}}{F_{\rm e}}\right)$	Al Recovered %	Amount Added %	Al Added %	$\left(\frac{AI}{F_{0}}\right)$	Al Recovered %	Amount Added %
	Al = 3961.527 Å.	Fe = 3927.922 Å	ι.		Al = 3944.034 Å.	Fe = 3927.922 Å.	
0.002	$ \begin{array}{r} - & 6 \\ - & 6 \\ - & 7 \end{array} $	0.0025 0.0025 0.0020	0.0005	0.010	$^{+1}_{+1}_{+1}$	0.0100 0.0100 0.0100	0.000
0.004	-2 - 2 - 2 = 0	0.0033 0.0033 0.0040	0.0008	0.015	+ 5 + 7 + 9	0.014 0.015 0.016	0.001
	$^{0}_{+2}$ + 3 + 3	0.0040 0.0046 0.0048 0.0048		0.020	$^{+11}_{+12}_{+12}_{+12}$	0.019 0.020 0.020 0.020 0.020	0.001
0.005	+ 2 + 3	0.0046 0.0046	0.0005		$^{+12}_{+13}$	0.020 0.020	
	+ 3 + 5	0.0050 0.0055		0.025	$^{+16}_{+19}$	0.023 0.026	0.002
0.006	+ 4 + 5 6 + 7 + 8	$\begin{array}{c} 0.0052 \\ 0.0055 \\ 0.0058 \\ 0.0058 \\ 0.0058 \\ 0.0060 \\ 0.0065 \end{array}$	0.0008	0.030	+19 +22 +22 +23 +23 +23 +25	0.026 0.029 0.029 0.030 0.030 0.033	0.003
0.008	+10	0.0075	0.0005		+25	0.033	
0.010	+13 +14	0.0092 0.0095	0.0010	0.040	$^{+28}_{+28}_{+31}$	0.038 0.038 0.042	0.002
	+15 + 15 + 16 + 18	0.0100 0.0100 0.0105 0.0110		0.050	$+34 \\ +34 \\ +35$	0.050 0.050 0.051	0.001
0.015	+23 +24 +24 +24 +24 +24 +24	$\begin{array}{c} 0.0145\\ 0.0150\\ 0.0150\\ 0.0150\\ 0.0150\\ 0.0150\\ 0.0150\\ \end{array}$	0.0005				21-22

the mercury. About 25 to 30 ml. of mercury are sufficient to form a satisfactory layer. A platinum gauze anode, 2.5 cm. (1 inch) in diameter and 5 cm. (2 inches) long, is held above the mercury layer and adjustments up and down in conjunction with a rheostat will vary the voltage and current flow. The mercury is agitated by a steady flow of air through a capillary tube reaching to the bottom of the mercury layer.

SPECTROGRAPHIC PROCEDURE

The carbon electrodes used in the spectrographic procedure are prepared by cutting carbon rods 0.78×30 cm. ($^{5}/_{16} \times 12$ inches) into 5-cm. (2-inch) lengths. The ends of the electrodes are polished by using a Jarrel-Ash cutter and they are then heated in a muffle at 510° C. for 1 hour. The electrodes are sparked for 75 seconds.

One drop of the solution, prepared by the above chemical procedure, is placed on each of two flat-top carbon electrodes which are sparked for 75 seconds immediately after the solution has been absorbed (β , β ?). No condensing lens or prespark is used in recording the spectra. A Bausch & Lomb large Littrow spectrograph is used with an uncontrolled condensed spark source. This high-tension spark generator consists of a 0.45-kv.a. step-up transformer delivering 15,000 volts from alternating current supply at 110 volts, 60 cycle. A 0.005-microfarad condenser produces a heavy condensed spark. A self-induction coil aids in elimination of air lines. The maximum inductance of 20 microhenries is used. The optical stand is placed 38 cm. (15 inches) from the slit and the spark gap is set at 3 mm.

Eastman No. 33 plates, 10×25 cm. $(4 \times 10 \text{ inches})$, are used. The plates are developed 4 minutes in D-19 at 18° C., fixed for 15 minutes, washed from 20 to 30 minutes, and dried. The calibration of the plate is based on the method described by Pierce and Nachtrieb (19)—i.e., the use of a direct current arc between iron electrodes and a rotating logarithmic step sector. The densities of the iron reference line 3927.922 Å. and the aluminum line 3961.527 Å. (12) are read on a Leeds & Northrup recording microphotometer when the aluminum content is from 0.002 to 0.012%, while the aluminum line 3944.034 Å. is read when the aluminum content is from 0.012 to 0.050%. The aluminum content is determined by the use of a working curve drawn by plotting $\Delta \log I$

prepared according to the method outlined under spectrographic standards.

DISCUSSION

The colorimetric procedures employing morin (7, 15), hematoxylin (13, 15, 17), and alizarin S (2, 5, 15, 29, 34) were found to be of little value because of erratic results due to the unsuitability of the material to be analyzed. A great deal of investigation was carried out using aurintricarboxylic acid (6, 11, 15, 16, 18, 21-25,30-34) as a color reagent. It was discovered that an exact control of pH was necessary before the addition of the aluminum

Sample No.	Al Recovered	Maximum Deviation
	%	%
1755	0.002 0.003 0.003	0.001
1756	$\begin{array}{c} 0.014 \\ 0.015 \\ 0.015 \\ 0.015 \end{array}$	0.001
1757	$\begin{array}{c} 0.021 \\ 0.021 \\ 0.022 \end{array}$	0.001
1758 .	- 0.022 0.023 0.023	0.001
Alloy 1	0.003 0.003 0.003	0.000
Alloy 2	0.003 0.003 0.003	0.000
Alloy 3	0.005 0.006 0.006	0.001
Alloy 4	0.006 0.006 0.006 0.006	0.000
B.S. 101b	0.002 0.003	0.001

All results rounded off to three places.

color reagent and after the reduction in color intensity with ammonium carbonate (21, 32). With this control excellent results were obtained with pure solutions. However, erratic results were produced on actual samples, due mainly to interfering ions (15, 18, 22, 24).

In the analysis of a steel, when a color development is the final product, it is either necessary to remove ions producing interfering colors or to separate the element to be determined. Where trace amounts are concerned it is not practical to precipitate such minute quantities of aluminum as the oxine (1, 3, 9, 10, 23, 28) or phosphate (26), and a separation of the interfering substances by precipitation (20) would cause losses due to adsorption (7). A mercury cathode electrolysis (14, 22, 24) was found to produce the most satisfactory separation but trace amounts of iron and chromium as well as titanium, vanadium, zirconium, columbium, tungsten, and manganese which are not eliminated, interfered singly or in toto with the various color reagents (15, 18, 22, 24). Iron and vanadium are especially sensitive to aurintricarboxylic acid, forming a lake of the same color as that produced by aluminum.

In view of the foregoing difficulties, a spectrochemical procedure was developed by separating the aluminum with a mercury cathode electrolysis (14, 22, 24), after incorporating the alumina by fusion with sodium carbonate (14) and then sparking the concentrated solution using a large Littrow spectrograph with a quartz prism. No interference was found due to impurities present when the aluminum lines 3961.527 or 3944.034 Å. and the iron reference line 3927.922 Å. were employed. This was established by adding quantities of these ions in amounts far exceeding those present under actual operating conditions. Because of slight contamination of aluminum in most reagents and in view of the trace amounts sought, it was necessary to check all reagents. The reagents were found satisfactory, although they contained very small traces of aluminum. Inasmuch as the same amount of reagents was used in constructing the working curve as was needed



for the complete chemical procedure, no correction was necessary for the aluminum present. Small amounts of aluminum were present in the carbon electrodes and sparking the electrodes for 75 seconds was found sufficient to remove all the aluminum impurity, as a further exposure showed no aluminum to be present.

Figure 1 demonstrates the working curves when using the aluminum line 3961.527 Å. for aluminum ranging from 0.002 to 0.012% and the aluminum line 3944.034 Å. for aluminum ranging from 0.012 to 0.050%. The method of least squares was used in constructing the straight-line portion of both curves.

It will be noticed that there is a curvature in the lower portion of curve 2 in Figure 1. This curvature begins at the value of 0.004% aluminum where the aluminum and iron lines are of equal density. This change in slope from 0.002 to 0.004% aluminum may be construed as being a factor of relatively high proportion of spectral background in relation to the density of the spectral lines at these lower limits.

Table I indicates the reproducibility and accuracy obtained by using synthetic standards prepared by adding increments of standard aluminum solution to a corrosion-resistant steel containing no aluminum. The reproducibility of a number of samples analyzed is shown in Table II.

Further investigation is being conducted now at this laboratory for the determination of zirconium by a similar procedure.

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This paper is not to be construed as an official method of the Navy Department.

Spectrophotometric Determination of Titanium in Steels

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Absorption spectra have been determined for the hydrogen peroxide complexes of titanium and vanadium in the presence of 1 gram of iron, in perchloric-phosphoric acid solution. These spectra furnish the basis for improved rapid, accurate methods for the determination of from 0.5 to 6 mg. of titanium in iron, steel, vanadium steel, and stainless steel, without separating the titanium or using hydrofluoric acid; accuracy approaching one part per hundred may be obtained. Details are given for a method of determining metallic and combined titanium in steel, which has given good reproducibility.

THE desirability of a more rapid method of accurate analysis for titanium in steels has been emphasized by recent interest in the effects of metallic versus combined titanium on hardenability, in titanium-stabilized stainless steels, and in welding steels containing small amounts of vanadium and titanium. Spectrophotometric analysis appeared to offer an opportunity to eliminate time-consuming separations.

The standard procedure for titanium analysis in steel includes a cupferron separation from the bulk of the iron, prior to the addition of hydrogen peroxide and comparison of the intensity of the yellow color (1, 2). However, some recent methods omit such a separation (6, 8, 9) and, for example, decolorize the iron by the addition of phosphoric acid. In the presence of much of colored ions such as chromium, nickel, or iron, the visual colorimetric determination of titanium is difficult. The large amounts of chromium in stainless steels may be separated by sodium carbonate plus sodium peroxide (12), mercury cathode electrolysis (δ) , boiling perchloric acid and sodium chloride (13), or filtration of chromic acid out of 70% perchloric acid solution (16). If the interfering element vanadium is present in the steel, it may be separated by sodium carbonate fusion (4).

Some popularity has been achieved by other colorimetric reagents for titanium, such as gallic acid (15), thymol (10), and chromotropic acid, 1,8-dihydroxynaphthalene-3,6-disulfonic acid (5). In general, these require preliminary separation of titanium. Considerable interest has been evinced in the ratio of metallic to combined titanium in steel (7, 11), and methods for separating the two have suggested the use of various dilutions of hydrochloric acid (3, 14, 17).

EXPERIMENTAL WORK

The apparatus and reagents have been described (18).

A series of synthetic standard titanium steels was prepared by adding varying amounts of titanium solution to 1 gram of N.B.S. iron 55a. These were then treated as described in Method A, below, and the absorption spectra measured from 360 to 600 m μ . Figure 1 shows that the peak absorption is at 400 m μ , and it is narrower than in the absence of phosphoric acid, where the peak is at 410 m μ . Figure 2 indicates that even in the presence of 1 gram of iron, a linear relation exists between titanium concentration and optical density at 400 and at 460 m μ .

To investigate interference by vanadium, a series of synthetic standard vanadium steels was prepared by adding varying amounts of vanadium solution to 1 gram of iron 55a. These were then treated as described in Method A, and the absorption spectra measured from 360 to 620 m μ , as shown in Figure 3. Even in the presence of 1 gram of iron, Beer's law is valid at 400 and 460 m μ , as shown in Figure 4.

SIMULTANEOUS DETERMINATION OF TITANIUM AND VANA-DIUM IN STEEL. It was observed that when 1 gram of steel is treated as in Method A, the presence of 1 mg. of titanium gives a density of 0.269 at 400 m μ , and 0.134 at 460 m μ . Under similar conditions, 1 mg. of vanadium gives an optical density of 0.057 at 400 m μ , and 0.091 at 460 m μ . If x represents the number of milligrams of titanium, y the number of milligrams of vanadium,



Figure 1. Absorption Spectra of Titanium-Peroxide Complex

In phosphoric-perchloric acid solution containing 1 gram of iron



Figure 2. Linearity of Titanium Concentration-Density Relation

In presence of 1 gram of iron



Figure 3. Absorption Spectra of Vanadium-Peroxide Complex

In phosphoric-perchloric acid solution containing 1 gram of iron

and the two absorb independently of each other, the following simultaneous equations can be set up:

$$\begin{array}{l} 0.269 \ x + 0.057 \ y = D_{400} \\ 0.134 \ x + 0.091 \ y = D_{460} \end{array}$$

These can be solved to give:

$$x = 5.40 \ D_{400} - 3.38 \ D_{460}$$
$$y = 15.9 \ D_{460} - 7.54 \ D_{400}$$

It can be seen that small errors in reading density will affect the vanadium result more than the titanium.

As a test of the above equations, several synthetic vanadiumtitanium standard steels were prepared and analyzed by Method A, measuring the density of each solution at 400 and at 460 $m\mu$. Table I shows the accuracy of the results; as was expected, the vanadium errors are the greater. As a further test, several standard cast irons of known titanium and vanadium content were analyzed by Method A. Table II shows the extremely accurate

Table I. Simultaneous Determination of Titanium and Vanadium in Synthetic Standard Steels

(1 gram of standard 55a plus varying amounts of V and Ti, with 10 ml. of HClO4 and 4 ml. of 1:1 H ₂ PO4, diluted to 50 ml.)						
Sample	Ti Added	V Added	D400	D460	Ti Found	V Found
	%	%			%	%
1	0.050	0.050	0.172	0.116	0.054	0.052
2	0.050	0.400	0.366	0.430	0.052	0.406
3	0.100	0.200	0.370	0.298	0.100	0.195
			0.389	0.311	0.104	0.200
4	0.200	0.200	0.640	0.436	0.201	0.210
			0.649	0.440	0.200 ·	0.211
5	0.300	0.200	0.902	0.570	0.295	0.228
6	0.100	0.600	0.600	0.660	0.101	0.598

Table II. Analysis of Standard Cast Irons Containing Titanium and Vanadium

Sample	D408	D488	Ti Found %	Error %
Std. 6d, 0.139% Ti and 0.209% V	0.393	0.215	0.139	0.000
Std. 7c, 0.067% Ti and 0.042% V	0.392	0.215	0.139	0.000
8td 74 0.114% Ti and 0.018% V	0.207	0.180	0.068	+0.001 0.000
	0.322	0.177	0.114	0.000
Std. 82, 0.048% 11 and 0.011% V	0.142	0.078	0.049	+0.001 +0.001
			Av.	0.0004



Figure 4. Linearity of Vanadium Concentration-Density Relation

results obtained for titanium; however, the vanadium results proved to be rather high. This subject was not pursued further, since the major interest was in titanium.

Although the molybdenum-peroxide complex shows an intense peak at 330 m μ it is impossible to make measurements in that region, in the presence of 1 gram of iron, because of the strong absorption of ferric perchlorate in the ultraviolet.

Table	111.	Determination	of Titanium	in S	Synthetic	Standards	o
		Stainless Steel	without Sepa	iratin	ig Titaniur	n	

	(0.5 gram	of Std. 101b plu	s varying amounts	of titani	um)
Ti	Added	D400	Ti Recovered		Error
	%		%		%
	0.00 0.10 0.20 0.30 0.40 0.50 0.60 0.60 0.70 0.80	$\begin{array}{c} 0.040\\ 0.180\\ 0.320\\ 0.453\\ 0.580\\ 0.722\\ 0.855\\ 0.997\\ 1.132 \end{array}$	0.103 0.206 0.304 0.397 0.501 0.600 0.704 0.803	- Av.	$\begin{array}{c} 0.003\\ 0.006\\ 0.004\\ -0.003\\ 0.001\\ 0.001\\ 0.004\\ 0.003\\ 0.003\\ 0.003\\ 0.003\\ \end{array}$

DETERMINATION OF TITANIUM IN STAINLESS STEELS. In view of the great monochromaticity available, the possibility presented itself of an accurate determination of titanium in stainless steel, without separation from the nickel, chromium, iron, etc. A series of synthetic standard titanium stainless steels was prepared by adding varying amounts of titanium solution to 0.500gram samples of N.B.S. standard 18-8 steel 101b. These were then analyzed by Method B, described below. Table III shows the high accuracy of the results obtained, using the experimental finding that under these conditions 1 mg. gives an optical density of 0.272 at 400 m μ , and subtracting as a blank the density 0.040 given by 101b itself. To investigate possible interference by columbium and tungsten, a similar series was prepared from standard 123a (0.002% Ti, 0.75% Cb, 0.11% W) and analyzed by Method B; Table IV shows that the results are accurate even in this case. Further, adding up to 0.5% of columbium to standard steel 121 caused an error of less than 0.01% of titanium.

Three standard stainless steels of known titanium content were analyzed by Method B. Table V shows that the corrected results for 121 and 121a are good, but those for 123a indicate a rather high relative error, with absolute error only 0.004%.

Table IV	V. Determina	ation of	Titanium	in Syntheti	ic Stand	lards of
0.75%	Columbium,	0.11%	Tungsten	Stainless	Steel,	without
		Separa	ting Titani	um		

	(0.5 gran	a of Std. 123a j	plus varyin	g amounts of tita	nium)
	Ti Present	D400		Ti Found	Error
	%			%	%
	0.002	0.036		0.007	0.005
	0.202	0.312		0.210	0.008
	0.402	0.582		0.409	0,007
	0.602	0.802		0.014	0.012
	0.802	1.100		0.810	0.013
				A	v. 0.009
-					
	Table V.	Analysis of	Standard	Titanium Stainle	ess Steels
	Table V.	Analysis of Certified	Standard	Titanium Stainle Ti Found	rss Steels Ti Corrected
	Table V.	Analysis of Certified Titanium	Standard D489	Titanium Stainle Ti Found Uncorrected	Ti Corrected for Mo and V
	Table V. Steel	Analysis of Certified Titanium %	Standard Deee	Titanium Stainle Ti Found Uncorrected %	Ti Corrected for Mo and V %
	Table V. Steel Std. 121	Analysis of Certified Titanium % 0.394	Standard <i>D</i> 466 0.547	Titanium Stainle Ti Found Uncorrected % 0.403	Ti Corrected for Mo and V % 0.395
	Table V. Steel Std. 121	Analysis of Certified Titanium % 0.394	Standard Dece 0.547 0.542	Titanium Stainle Ti Found Uncorrected % 0.403 0.398	ess Steels Ti Corrected for Mo and V % 0.895 0.390
	Table V. Steel Std. 121 Std. 121s	Analysis of Certified Titanium % 0.394 0.361	Standard D400 0.547 0.542 0.489	Titanium Stainle Ti Found Uncorrected % 0.403 0.398 0.360	ess Steels Ti Corrected for Mo and V % 0.395 0.390 0.351 0.252
	Table V. Steel Std. 121 Std. 121a Std. 122a	Analysis of Certified Titanium % 0.394 0.361 0.002	Standard D400 0.547 0.542 0.489 0.492 0.036	Titanium Stainle Ti Found Uncorrected % 0.403 0.398 0.360 0.362 0.026	ess Steels Ti Corrected for Mo and V % 0.395 0.390 0.351 0.353 0.007
	Table V. Steel Std. 121 Std. 121a Std. 123a	Analysis of Certified Titanium % 0.394 0.361 0.002	Standard D488 0.547 0.542 0.489 0.492 0.036 0.034	Titanium Stainle Ti Found Uncorrected % 0.403 0.398 0.360 0.362 0.026	ess Steels Ti Corrected for Mo and V % 0.395 0.390 0.351 0.353 0.007 0.006
	Table V. Steel Std. 121 Std. 121a Std. 123a	Analysis of Certified Titanium % 0.394 0.361 0.002	Standard Date 0.547 0.542 0.489 0.492 0.036 0.034	Titanium Stainle Ti Found Uncorrected % 0.403 0.398 0.360 0.362 0.026 0.025	ess Steels Ti Corrected for Mo and V % 0.395 0.380 0.351 0.353 0.007 0.006

DETERMINATION OF METALLIC AND COMBINED TITANIUM IN STEEL. Reproducible results for metallic and combined titanium in steel were obtained by Method C, as shown in Table VI, even when 2 to 1 hydrochloric acid was substituted for the 1 to 1 acid. It was found important to use close-textured filter paper for the separation; medium-textured paper allows some of the finer particles to pass through. Since most of the combined titanium in steel is present as titanium carbonitride, the validity of the method was tested by adding 30 and 40 mg. of titanium carbonitride to 1-gram samples of iron 55a, and analyzing for metallic (or soluble) titanium as in Method C. Only a negligibly small fraction of the carbonitride was soluble in the dilute hydrochloric acid under these conditions. Method C omits use of phosphoric acid to decolorize iron. Although not necessarily advantageous this is a permissible variation, since ferric perchlorate is nearly colorless. However, in this case, titanium-free steels give a blank of density 0.026 at 410 m μ for the acid-soluble portion, and this blank must be subtracted from all such readings. Optical density at 410 mµ resulting from 1 mg. of titanium under these conditions is 0.304, so that slightly greater sensitivity is attained.

METHODS IN DETAIL

METHOD A, FOR LOW-ALLOY IRON AND STEEL. Dissolve 1.000 gram of sample in 10 ml. of 1 to 1 nitric acid plus 10 ml. of 70% perchloric acid, by warming in a 125-ml. Phillips beaker. Evaporate to fumes of perchloric acid, and continue heating vigorously until the fumes become transparent two thirds of the way up the beaker. Cool rapidly in water, in order to minimize per-oxide formation. Add 25 ml. of water to dissolve the salts, then 4 ml. of 1 to 1 phosphoric acid. Destroy any yellow color due to chromate by adding 3 or 4 drops of sulfurous acid, or more if necessary. To remove silica and graphite, filter through a 9cm. Whatman No. 40 paper into a 50-ml. volumetric flask. Wash thoroughly with several small portions of water, dilute to

Table VI. Determination of Metallic and Combined Titanium in Steel

		A. So	lution in 1	:1 HCl	B. So	lution in :	2:1 HCl
				Sum of metallic and			Sum of metallic and
Sample	Total Titanium %	Metallic titanium %	Combined titanium %	combined titanium %	Metallic titanium %	Combined titanium %	d combined titanium %
Std. 82 (0.048% Ti)	0.048 0.047	0.000 0.000	0.048 0.048	0.048 0.048	0.000 0.000	0.049 0.049	0.049 0.049
GMO	0.059 0.060	0.000 0.000	0.059 0.057	$\begin{array}{c} 0.059 \\ 0.057 \end{array}$	$0.001 \\ 0.001$	$0.059 \\ 0.057$	0.060 0.058
GMP	0.101 0.102	0.003	0.095 0.095	0.097 0.098	0.001 0.001	$0.097 \\ 0.097$	0.098 0.098
GMR	0.189 0.189	$\begin{array}{c} 0.002 \\ 0.003 \end{array}$	$\begin{array}{c} \textbf{0.183} \\ \textbf{0.182} \end{array}$	0.185 0.185	0.005 0.004	0.184 0.182	0.189 0.186
GMS	$0.350 \\ 0.352$	$\begin{array}{c} 0.010\\ 0.012 \end{array}$	0.335 0.339	0.345 0.351	0.011 0.011	$0.341 \\ 0.342$	0.352 0.353

the mark, and mix thoroughly. Measure the optical density at 400 and 460 m $_{\mu}$ of a 3-ml. portion to which one drop of 30% hydrogen peroxide has been added, using as a blank a similar portion to which one drop of water has been added. Even in the presence of varying amounts of vanadium, the percentage of ti-tanium in the steel is equal to 0.540 D_{400} - 0.388 D_{400} . If vanadium and molybdenum are known to be absent, then the percent-age of titanium is simply $D_{400}/2.69$. If the vanadium and molybdenum percentages are known, the titanium percentage is equal to $D_{400}/2.69$ minus one tenth of the molybdenum percentage factors are calculated from the optical densities at 400 mµ.

METHOD B, FOR STAINLESS STEEL. Dissolve a 0.500-gram sample in 15 ml. of 1 to 1 hydrochloric acid plus 2 ml. of nitric acid in a 125-ml. Phillips beaker. Add 10 ml. of 70% perchloric acid; evaporate, fume, and cool as in Method A. Add 20 ml. of water to dissolve the salts, 4 ml. of 1 to 1 phosphoric acid, and 5.0 ml. of saturated sulfurous acid, to reduce the chromium com-Warm gently 10 or 15 minutes to expel excess sulfurous pletely. acid, filter through a 9-cm. No. 40 paper into a 50-ml. volumetric flask, wash thoroughly with several small portions of water, and dilute to the mark. Measure the optical density at 400 m μ of a peroxidized portion against an unperoxidized portion. Then the percentage of titanium is $D_{400}/1.36$ minus one tenth of the molybdenum percentage minus one fifth of the vanadium percentage.

METHOD C, FOR METALLIC AND COMBINED TITANIUM IN STEEL Transfer a 1.000-gram sample to a 125-ml. Phillips beaker, add 25 ml. of 1 to 1 hydrochloric acid, and dissolve by moderate 25 ml. of 1 to 1 hydrochloric acid, and dissolve by moderate heating. After one hour (by which time action has ceased) filter through a 9-cm. No. 42 paper, and wash carefully with 5 to 95 hydrochloric acid. Catch filtrate and washings in a 250-ml. Phillips beaker, and add 10 ml. of perchloric acid and about 5 ml. of nitric acid. Evaporate, fume strongly, and continue as in Method A, except for omitting the phosphoric acid, and measuring the optical density at 410 m μ . Then in the absence of much vanadium or molyhdamum the parentzer of metallic titanium vanadium or molybdenum, the percentage of metallic titanium in the steel is $(D_{410} - 0.26)/3.04$. A density of 0.026 is obtained when 1 gram of a titanium-free steel is analyzed by this procedure.

The combined titanium is determined as follows: Return the insoluble residue and paper from the first filtration to the original 125-ml. Phillips beaker. Add 7 ml. of perchloric acid and about 30 ml. of nitric acid, and digest at moderate heat until all organic matter is destroyed. Then evaporate to fumes of perchloric acid and fume vipercurve for 2 minutes. On the provide the state of and fume vigorously for 3 minutes. Cool in water, add 25 ml. of water and 3 drops of sulfurous acid, and filter through a 9-cm. No. 40 paper into a 50-ml. volumetric flask. Wash thoroughly with several small portions of water, dilute to the mark, mix well, and determine the optical density at 410 m μ . Then $D_{410}/3.04$ gives the percentage of combined titanium in the steel.

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Use of Enzyme in Riboflavin Determination

Free and Combined Riboflavin

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Fluorometric determination of riboflavin in certain products of natural origin by a method involving adsorption on Florisil without preliminary enzyme digestion gives low results, which are due to nonadsorption of a fraction of the riboflavin on Florisil. Evidence is

N THE fluorometric determination of riboflavin by a method employing a Florisil column the authors have observed that higher results are obtained on many natural products when enzyme incubation is included than when this step is omitted (Table I). The microbiological data clearly support the higher values.

Table I. Riboflav	in Values with	and without Enzy	yme Treatment
Sample	Fluor With enzyme	rometric Without enzyme	Microbiological (8)
	×10.	r/g.	×/0.
Dried brewers' yeast Yeast extract	30.1 145	15.5 77.6	33.1 138 212
Dried liver	91.1	58.1	90.7
Enriched white bread Dried skim milk	2.23 12.4	1.92 11.0	2.54 12.0

Other workers have indicated that the use of enzyme gives higher results. Peterson, Brady, and Shaw (5), for example, found that the use of clarase yields increased riboflavin values for pork products. McLaren, Cover, and Pearson (4) used a takadiastase-papain mixture on meats. Cheldelin, Eppright, Snell, and Guirard (2) recommended the use of enzymes on many products. The data appearing in the literature indicate that enzymes facilitate the extraction of riboflavin. The authors have investigated a number of aspects of the enhancement of riboflavin values by the use of enzyme and believe they have evidence that the increase in values observed in their laboratory is not due to an extraction effect of the enzyme but rather to the release of riboflavin from a bound form. This does not imply that the enzyme does not aid in extraction of riboflavin from certain products.

The method used in these studies is similar to that of Andrews (1).

The sample is extracted in a volumetric flask with 0.1 N sulfuric acid for 1 hour in a boiling water bath, followed by incubation for 1 hour with 0.3 gram of polidase at pH 4.5 and 48° C. When no enzyme treatment was used the reaction was still adjusted to pH 4.5. If a significant amount of pigment is present, the mixture is at this point treated with potassium permanganate and hydrogen peroxide. It is then made to volume and filtered, and an aliquot is passed through a Florisil column (12 cm. \times 8 mm.). The column is washed with water and the riboflavin eluted with 20% pyridine in 2% acetic acid. The fluorescence of the eluate is measured and compared to that of a known amount of riboflavin added to the unknown. A blank is obtained by the addition of solid sodium hydrosulfite.

To determine whether the higher riboflavin values when enzyme is used are a result of a more efficient extraction, the authors extracted samples with 0.1 N sulfuric acid and filtered the extract. This filtered extract was then given enzyme treatment

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presented that nonadsorption of part of the riboflavin is not due to physical factors alone but also to a difference in character between adsorbed and nonadsorbed riboflavin. The nonadsorbable, "combined" riboflavin is converted to the adsorbable form by enzyme.

and carried through the usual procedure. The values obtained by enzyme treatment of the filtered extract as compared to those from enzyme treatment of an unfiltered sample are shown in Table II. The evidence definitely indicates that extraction by enzyme is not a factor in the increased values.

The authors then sought to learn why part of the riboflavin escapes determination when enzyme treatment is omitted. Either part of the riboflavin fluoresces to a different degree than the remainder or it is lost on the Florisil column.

To test the first possibility the fluorescence of extracts not receiving enzyme treatment was determined without use of the column. The data obtained are compared with results by the usual method in Table III. Values compare very favorably, indicating no change in fluorescence upon enzyme treatment. Thus it appeared that loss of riboflavin occurred on the Florisil column, either by nonadsorption on the column or, if adsorbed, by nonelution with the pyridine mixture. If riboflavin is not adsorbed it should be capable of being recovered in the drippings from the column. To determine whether this would be the case, an aliquot of the extract obtained without enzyme treatment was put through the column, the drippings were collected together with the washings, and the adsorbed riboflavin was eluted with pyridine mixture. It was found that the fluorescence of the unadsorbed drippings plus the washings represent the difference between values obtained with and without enzyme treatment (Table IV).

The excellent agreement between the calculated and determined total riboflavin shown in Table IV eliminates the possibility that riboflavin may be adsorbed and not eluted.

In the authors' initial experiments the amount of riboflavin found in the unadsorbed drippings and that eluted from the column were variable for a given sample. Apparently the riboflavin passing through the column was not entirely unadsorbed

Table	11.	Riboflavin	Values	Obtained	by	Enzyme	Treatment	of
		Filte	ered and	Unfiltered	Ext	ractsa		

Sample	Unfiltered Extract	Filtered Extract
	×/g.	y/g.
Dried brewers' yeast Enriched white bread Dried skim milk	30.1 2.23 11.7	29.6 2.28 12.2

 $^{\rm a}$ Filtered and unfiltered extracts incubated with 0.4% polidase for 1 hour at pH 4.5 and 45° C.

Table III. Comparison of Riboflavin Values Using No Enzyme and No Column with Those Using Enzyme and Column

Sample Enzy	me and Column	and No Column
	2/0.	r/g.
Dried yeast Dried yeast Liver extract	30.1 93.1 299	30.1 91.9 300

Table IV. Comparison of the Sum of Riboflavin Fractions with the Determined Total

	Ribe	oflavin	Total Ri	boflavin	
Sample	Adsorbed on column	Unadsorbed on column	Calcu- lated	Deter- mined	
	y/a.	r/g.	γ/g.	γ/q .	
Dried yeast	6.7	24.9	31.6	30.1	
Yeast extract	56.7	46.3	103	111 300	
Dried skim milk	9.65	2.51	12.2	12.4	
Dried whey	44.2	3.2	47.4	48.4	
Enriched white bread	1.90	0.55	2.20	2.20	

Table V. Occurrence of Riboflavin in Drippings from Florisil Column

			Enzyme	Treatment	
			1	2	18
	Fraction of drippings	None	houra	hoursa	hours
		γ	γ	γ	γ
1.	Original 10-ml. aliquot ^b				
-	+15 ml. of boiling water	0.23	0.60	0.16	0.17
2.	Next 25 ml. of boiling water	2.79	1.30	0.46	0.15
3.	Next 25 ml. of boiling water	1.65	0.38	0.24	0.02
4.	Next 25 ml. of boiling water	0.74	0.15	0.08	0
5.	Next 25 ml. of boiling water	0.37	0.15	0.08	0
6.	Next 25 ml. of boiling water	0.23	0.16	0	0
7.	Next 25 ml. of boiling water	0.11	0.15	0	0
8.	Next 25 ml. of boiling water	0.07	0.17	0	0
Tot	tal drippings (200 ml.)	6.2	3.1	1.0	0.34
Elu	ate from column	4.8	8.3	10.7	10.7

Incubated with 0.4% polidase at pH 4.5 and 45° C.
 Prepared from yeast extract. A 10-ml. aliquot contained 11.9 micro-grams of total riboflavin by direct determination.

and the amount depended upon the thoroughness of the washing. They therefore studied the effect of extent of washing upon the amount of riboflavin held on the column (Table V). Boiling water was used for washing, since it was found much more efficient than water at room temperature in clearing the column of unadsorbed riboflavin. Under this severe washing there is a significant amount of unadsorbed riboflavin even after a 2-hour incubation with enzyme.

Hoffer, Alcock, and Geddes (3) found riboflavin to be incompletely adsorbed from extracts of flour. These workers demonstrated that such factors as concentration, volume, clarity of extracts, and the particular lot of Florisil used affected the adsorption characteristics of riboflavin. Rubin and De Ritter (7) interpreted the action of enzyme in improving the adsorption of riboflavin on the basis of producing greater clarity in the extracts.

On the other hand, in a preliminary report (6), the authors advanced the suggestion that riboflavin exists in certain extracts not only as free riboflavin but also combined in a form which is not adsorbed, or is more weakly adsorbed, on Florisil. The enzyme then acts to split this combined riboflavin to an adsorbable form.

If there is interference with adsorption of riboflavin from extracts of natural products, such as liver and yeast, pure riboflavin added to these extracts should not be quantitatively recovered in the pyridine eluate after Florisil adsorption. The results of experiments to test this point are shown in Table VI. The good recovery of added riboflavin shows that the adsorptive capacity of the Florisil is unimpaired and argues against any assumption of significant interference with the adsorption of free riboflavin from such extracts. In the case of the yeast extract (Table VI) only 52% of the riboflavin originally present was adsorbed on the column; however, 91% of the added pure riboflavin was adsorbed. Furthermore, the drippings and washings were fractionated as illustrated in Table V; the added riboflavin did not alter the pattern of riboflavin occurrence in the drippings. The most plausible explanation for these data is that the riboflavin which is not adsorbed on the Florisil is different from free riboflavin.

The suggestion of Rubin and De Ritter (7) that the enzyme simply acts to produce clearer extracts may well be considered with such low-potency materials as cereals where rather large samples must be taken for analysis. However, in the case of veast and liver extracts the extracts filtered at pH 4.5 are clear even though incubation with enzyme is omitted. Incubation of these clear extracts with enzyme with no further filtration results in the same increase in riboflavin adsorption as previously indicated.

Rubin and De Ritter (7) tested the adsorption on Florisil of riboflavin phosphate and riboflavin succinate and concluded that these forms are fairly completely adsorbed. However, their data show only 86% of the phosphate to be adsorbed on a single column, as against 100% of free riboflavin. In their experiments the column was washed with only 25 ml. of hot water. Since the authors have shown that a more drastic washing is necessary to remove the unadsorbed riboflavin completely, Rubin and De Ritter's data on riboflavin phosphate cannot be regarded as casting doubt upon the existence of combined riboflavin in extracts of natural products. On the other hand, their data do indicate that even in pure solution the adsorption behavior of riboflavin phosphate differs from that of free riboflavin.

It is of interest to consider what significance the behavior of combined riboflavin might have in riboflavin determination. When a Florisil column is used in estimation of riboflavin in natural products treatment with enzyme is indicated. Methods which omit the enzyme step when using a column risk the loss of the combined riboflavin. It has been the authors' experience that when the hydrosulfite blank is low, substantially the same results are obtained when fluorescence of the extract is read directly as when enzyme treatment and column are included (Table III). However, when considerable color occurs in the extract poor results are obtained without use of the column.

Yeast was found to contain a larger proportion of combined riboflavin than any other material tested, values up to 80% of the total having been determined.

Table VI. Recovery of Riboflavin Added to Extracts of Natural Products

	No Adde	d Ribo-	10 Micro Riboflavi		
	Riboflevin	Ribo- flavin	Ribo-	Ribo- flavin	Recovery of Riboflavin
Sample	in drippings	from column	in drippings	from	from Column
	γ	γ	γ	γ	%
Yeast extract Liver extract	5.38 2.89	5.74 11.7	5.42 3.09	$\begin{array}{c} 14.8\\22.0\end{array}$	91 103

^a No ensyme treatment used, extracts at pH 4.5, columns washed with 100 ml. of boiling water.

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Lead in Smelter Products

A Rapid Polarographic Method

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An improved quantitative method for lead in smelter products has been devised in which preliminary separations are unnecessary for the materials investigated. An acceptable degree of accuracy is obtained and the time required is reduced considerably. Diffusion current constants for lead in 1 N hydrochloric acid and in alkaline tartrate are reported.

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THE isolation and determination of lead in complex materials such as flue dusts and slags are tedious if the usual precipitation as sulfate and determination by the molybdate titration are used. For accurate results the lead sulfate must be purified prior to titration, which further complicates the analysis. The method presented in this paper simplifies the decomposition of the material and obviates preliminary separations.

EXPERIMENTAL

A manual polarograph was used in the greater part of the investigation. Diffusion currents were measured with a Leeds & Northrup Type P galvanometer, and a Shallcross Ayrton shunt having nine sensitivity settings. The galvanometer was equipped with a telescope and a scale calibrated by means of known currents; the sensitivity was determined by the usual method (2) immediately after each set of determinations.

The potentiometric bridge consisted of 6.7 meters of B. & S. No. 20 Nichrome wire, wound uniformly on a 20.3-cm. cylinder. The hardness of Nichrome permitted the use of an efficient sliding copper contact which could be replaced when worn. The uniformity of the winding was checked at 15.2-cm. intervals by the Wheatstone bridge method; the error did not exceed 0.1% at any point. Bridge settings could be read to 0.001 volt. The potential drop was standardized frequently against a Weston cell.

Once the shape of the curve had been determined, it was found sufficient in subsequent analyses to record four points of the linear portion of the residual current and a single point at the limiting current. Extrapolation of the residual current to the voltage corresponding to the final point yielded excellent results. A Model XII Sargent Heyrovský polarograph was used in part of the preliminary determinations of the nature of the plot of current against voltage. The manual polarograph is satisfactory even in this capacity if the deflections corresponding to small voltage increments are plotted directly; the time required to obtain a complete curve in this manner compares favorably with that needed to complete and process a photographic record. The greater precision of current and voltage determinations with the manual instrument, moreover, is of considerable importance for investigational purposes.

The dropping electrode assembly is shown in Figure 1. The 20-ml. electrolytic cells were designed to permit removal of oxygen from solutions prior to attachment of the cell to the dropping electrode, thus permitting the analysis of a solution while others were being degassed. An upturned side arm received the salt bridge of the saturated calomel electrode described elsewhere (1). The electrolytic cell was closed with a one-hole stopper carrying a short glass tube wide enough to permit the insertion of either the nitrogen-inlet capillary or the dropping electrode. Rubber sleeves on the dropping electrode and on the salt bridge prevented diffusion of air during the determination. Tank nitrogen saturated with water vapor was used without further purification. Sodium sulfite was found unsatisfactory. In all cases measurements were made with the cell in a water thermostat at $25^\circ = 0.1^\circ$ C

0.1° C. The dropping electrode assembly was the same as that described by Lingane and Laitinen (4). Provision was made, however, to permit the raising and lowering of the entire assembly without changing the height of the mercury column. It was also found advantageous to make the connection of the dropping electrode to the lower end of the stand tube rigid by means of a paraffin-filled metal jacket around the connection, as shown in Figure 1. The capillary consisted of a 7-cm. length of Sargent Heyrovský tubing with an internal diameter of 0.05 mm. A mercury column height of 76.4 cm. was maintained throughout. The rate of mercury flow, m, was determined with the capillary tip immersed in water at 25° C. Four determinations of m over a period of 4 months gave a value of 1.540 ± 0.002 mg. per second. The drop time was about 4.2 seconds at 0.55 volt and 3.8 seconds at 0.95 volt. The resistance of the entire assembly including the calomel cell was approximately 300 ohms. The half-wave potentials reported were corrected for the IR drop in the assembly.

A 10 millimolar solution of lead was prepared by dissolving 2.072 grams of 99.9% lead metal in 50 ml. of 4 M nitric acid and diluting to 1 liter. The supporting electrolytes used were 1 N hydrochloric acid and alkaline tartrate, a medium 0.5 M in so-dium tartrate and 0.1 N in sodium hydroxide; these solutions were made from reagent grade materials, and were accurate to 2%, an adequate tolerance for such media. The maximum suppressors consisted of a 0.2% solution of gelatin containing toluene as a preservative, and a 0.1% solution of sodium methyl red. A dust of accurately known lead content was not available; it was found necessary, therefore, to prepare such a sample. Its composition and consistency were approximately those of the flue dust used in part of the investigation. This "synthetic" dust consisted of lead in the form of lead dust, assayed lead oxide, and lead dioxide to which were added zinc oxide, arsenic trioxide, antimony trioxide, ferric oxide. The mixture was ground in a ball mill until homogeneous.

PROCEDURE

DECOMPOSITION OF SAMPLE AND PREPARATION FOR ANALYSIS. Thoroughly mix a 0.2-gram sample of the smelter product with 2 grams of reagent grade sodium peroxide in a 12.5-cm. (5-inch) Pyrex test tube; place an additional 0.3 gram of peroxide on top of the mixture. Fuse the material by rotating the test tube slowly in a Bunsen flame, being careful not to make the initial application of heat too rapid. After the melt has become homogeneous in color, a period of 3 to 5 minutes, remove the test tube from the



remove the test tube from the flame and allow it to cool, during which time the test tube cracks. Break the test tube into a beaker. Add enough water to cover the material, but not more than 50 ml. Allow to stand until the material has completely separated. from the glass fragments (about 15 minutes); otherwise a clear solution may be unobtainable in the subsequent treatment.

Add 25 ml. of concentrated hydrochloric acid rapidly, stirring to aid complete solution of the yellow precipitate commonly obtained. Chlorine is evolved, and a clear yellow solution results. Dissolve about 3 grams of tartaric acid

Figure 1. Dropping Electrode Assembly

Table I.	Analysis of	Representative	Smelter	Products
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		Pola	rograp	hic Method	LTT I
Material Analyzed	Volumetric Method, % Lead ^a	1 N HCl, % lead	No. of detns.	Alkaline tartrate, % lead	No. of detns.
Synthetic standard dust, (ac- tual lead content, 49.81%) Blast furnace flue dust High-lead zinc fume Primary, conper-sande slime	$\begin{array}{r} 49.0 \ \pm \ 0.6 \\ 49.2 \ \pm \ 0.2 \\ 49.3^{b} \end{array}$	$\begin{array}{r} 49.6 \ \pm \ 0.3 \\ 50.4 \ \pm \ 0.3 \\ 49.6 \ \pm \ 0.7 \end{array}$	5 7 3	$\begin{array}{r} 49.4 \ \pm \ 0.6 \\ 48.3 \ \pm \ 0.7 \\ 46.7 \ \pm \ 0.4 \end{array}$	5 8 3
fume Blast furnace slag	24.1 ^b 4.71 ^b 4.44 ^b ,d	° 'e	::	25.1 = 0.3 4.07 = 0.08	5 3 5

^a Precipitation as lead sulfate with no purification, and titration with molybdate using external indicator, unless otherwise stated.
^b Plant assay.
^c Wave in HCl not well defined.
^d Lead sulfate freed from calcium sulfate.

in the acid solution to prevent the precipitation of antimony upon dilution. A slight precipitate causes no difficulty in analysis; a heavy precipitate, however, makes sampling difficult and may retain lead.

Dilute the solution to 100 ml. in a volumetric flask. Taking into account the fact that the resulting solution is approximately 3 N in hydrochloric acid, mix aliquots of the solution via approximately proper supporting electrolyte (see following paragraph). Maxi-ma may be suppressed by the addition of gelatin, an end con-centration of 0.01%. Sodium methyl red may be substituted for gelatin in the alkaline tartrate medium.

SELECTION OF SUPPORTING ELECTROLYTE. Lead waves are well defined in 0.1 N potassium chloride, 1 N hydrochloric acid, 1 N nitric acid, 1 N sodium hydroxide, and in various tartrate media (3). In complex materials such as are encountered in smelter product analysis, the choice of a suitable electrolyte depends upon the nature and relative proportion of elements other than lead. In any case the limiting current must be well defined, and the residual current must be linear for a sufficient voltage span to permit extrapolation. The present authors recommend span to permit extrapolation. The present authors recommend 1 N hydrochloric acid as a medium in cases where the prior deposition of constituents does not interfere with normal development of the lead wave. Alkaline tartrate (a medium 0.5 M in sodium tartrate and 0.1 N in sodium hydroxide) is often applicable where the constituents of the sample do not permit the use of hydrochloric acid. If 1 N sodium hydroxide is used with an external reference electrode, it is advisable to employ an inter-mediate agar plug and salt bridge (1) to avoid contamination of the agar bridge of the calomel electrode. ANALYSIS. Transfer the prepared solution to an electrolysis

cell. Remove dissolved air with nitrogen; 15 to 20 minutes' de-gassing time is usually sufficient for 15-ml. samples. Using either a mercury pool anode or an external reference electrode, electrolyze the solution from about 0.10 to 0.60 volt vs. the saturated calomel electrode if hydrochloric acid is the supporting electrolyte, or from about 0.50 to 1.00 volt'if alkaline tartrate is used.

RESULTS

The ratio of diffusion current to concentration, i_d/C , for lead in 1 N hydrochloric acid at 25° C. was found to be 6.47 = 0.05microampere liters per millimole (eleven determinations). Gelatin (0.01%) was present as a maximum suppressor in six of the determinations; well-defined waves with no significant change in the relative diffusion currents were also obtained in the absence of gelatin. Since the capillary used in this investigation had a constant, $m^{2/3}t^{1/6}$, of 1.69 mg.^{2/3} sec.^{-1/2}, the more fundamental "diffusion current constant", may be calculated as 3.83. Although this constant is directly applicable to practical analyses with different capillaries, a deviation of the constant has been noted (5) among capillaries whose values of $m^{2/3}t^{1/6}$ differ widely. As yet there is no standard $m^{2/3}t^{1/6}$ to which data can be reduced for comparison. In order to compare the constant determined in this investigation with that of 3.86 previously reported on the basis of an $m^{2/3}t^{1/6}$ value of about 2.31 (5), reference was made to the empirical relationship found by Lingane and Loveridge (5). The present constant 3.83 referred to an $m^{2/3}t^{1/6}$ value of 2.31 thus becomes approximately 3.76.

The i_d/C ratio for lead in alkaline tartrate at 25° C. was found to be 4.22 ± 0.03 (four determinations). The diffusion current constant is 2.52, $m^{2/3}t^{1/6}$ being 1.67. When reduced to the capillary constant referred to above, the value obtained, 2.48, is comparable to that of 2.39 previously reported (3).

The half-wave potential for lead was found to be -0.43 volt vs. S.C.E. in 1 N hydrochloric acid, and -0.75 volt in alkaline tartrate. The voltage span required for full development of the diffusion current in both media was about 0.25 volt; this differs from the span of 0.4 volt in alkaline tartrate found by Lingane (3).

The results obtained are summarized in Table I.

The blast furnace flue dust and the high-lead zinc fume were chosen as representative of high-lead samples. The primary copper-anode slime fume was representative of products high in antimony and containing a great variety of substances. The blast furnace slag was included as representative ('material low in lead and high in silica.

DISCUSSION

The absolute accuracy of the method cannot be evaluated except with reference to the synthetic standard dust, the only sample of accurately known lead content. It is significant that the polarographic analysis of the standard dust was accurate to better than 1%. In some cases in which there is poor agreement between volumetric and polarographic results, it is likely that the latter may be more reliable, considering the method of decomposition and preliminary separations involved in the volumetric method. This assumption is supported by the low result obtained in the molybdate titration of the synthetic standard dust, and by the precision of the polarographic analyses. In the case of the blast furnace slag, the agreement between the two methods was improved considerably when the lead sulfate was reprecipitated before titration.

No explanation is offered for the discrepancy in the polarographic blast furnace flue dust analyses using hydrochloric acid and alkaline tartrate as supporting electrolytes. The polarographic analysis of the high-lead zinc fume illustrates the fact that each mixture presents a distinct problem as far as selection of electrolyte is concerned.

The time required for polarographic analysis is less than that for the molybdate titration. The preparation of a sample for the former analysis, for instance, involves only a brief 5-minute fusion whereas the usual acid treatment for the volumetric method requires about an hour. Once the polarographic method is placed on a routine basis, it is estimated that not more than 40 minutes of actual work are required for each sample, as compared with about 70 minutes for the volumetric method.

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Pore-Size Distribution in Porous Materials

Pressure Porosimeter and Determination of Complete Macropore-Size Distributions'

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A method for determining the macropore-size distribution in a porous solid, as well as the derived distributions for some typical porous materials, is presented. A glass dilatometer placed in a thermostated high-pressure bomb is used to measure the small changes in volume of a mass of mercury, in which the porous material under investigation is immersed, when the mercury is subjected to varying external pressure.

DETERMINATION of total pore volume is a routine measurement in most laboratories dealing with porous materials. The value usually is calculated as the difference of two specific volumes (reciprocal density). Thus the internal pore volume is the difference between the reciprocals of real density and particle density; the intergranular (void) volume is the difference between the reciprocals of bulk density and particle density; and the sum of pore and void volumes is the difference between the reciprocals of bulk and real densities. [The nomenclature of McBain (10) is followed in identifying the several densities, assuming (with some error) that real and true densities are equal.] The total internal pore volume is then calculated from observa tions of the real and particle densities, determined, for example, by the usual pycnometric method using water and mercury, respectively, as the displacement liquids.

In processes involving diffusion rates and the availability of internal surface to large molecules, a knowledge of total pore volume is less important than a knowledge of the fraction of total pore volume contributed by pores in a given size range—i.e., of the distribution of pore sizes. It is convenient to classify the internal pores of porous materials roughly in two ranges. Present usage (\mathscr{B}) applies the name "micropores" to those having radii smaller than 100 Å.; "macropores" to those larger than 100 Å. The division of the pore volume of a given porous material into micro- and macropores implies the existence of a distribution in size, yet little work has been done in the determination of such distribution functions.

Rabinowitsh and Fortunatow (12) have determined the respective fractions of micro- and macropores in a number of porous solids by means of the Kelvin equation. Pore-size distributions in the micro region have been determined qualitatively using the Kelvin equation by Kubelka (8) whose work is largely invalidated by neglect of adsorption. The adsorption equation of Brunauer, Deming, Deming, and Teller (3) may be of some use in this connection, but is open to the criticism that it does not satisfactorily combine the simultaneous effects of adsorption and capillary condensation. Jellinek and Fankuchen (7) have used the scattering of x-rays at very small angles to evaluate pore size (or particle size) but assumed a constant average size. The unpublished work of Shull (14) on low-angle x-ray scattering takes into consideration a pore-size distribution; but, this method not only cannot conveniently be used for pores larger than perhaps 500 Å. in radius, but the results in terms of pore size may also be open to question. This paper presents a method for determining the macropore-size distribution in a porous solid as well as the derived distributions for some typical porous materials.

Washburn (16) has pointed out the fact that surface tension opposes the entrance into a small pore of any liquid having an ¹ First part of paper on "Pore-Size Distribution in Porous Materials".

Second part is found on page 787.

angle of contact greater than 90° (the common phenomenon of capillary depression); that this opposition may be overcome by the application of external pressure; and that the pressure required to fill a given pore is a measure of the size of the pore. Henderson, Ridgway, and Ross (6) have used this principle in a very limited way, and Loisy (9) has proposed the use of the same principle in a study of pore-size distributions.

The relation (quoted by Washburn) giving the pressure required to force liquid into a pore of given size is

$$pr = -2 \sigma \cos \theta \tag{1}$$

where p is the pressure, r the pore radius, σ the surface tension, and θ the contact angle. It may be derived as follows: In a pore of circular cross section, the surface tension acts along the circle of contact over a length equal to the perimeter of the circle. This force is $2 \pi r \sigma$. Normal to the plane of the circle of contact, the force tending to squeeze the liquid out of the pore is $-2\pi r \sigma \cos \theta$. (The negative sign arises from the fact that the angle between the direction of action of the surface tension and the positive normal to the plane of contact is $\pi - \theta$. Since $\theta > 90^\circ$, the term $-2\pi r \sigma \times \cos \theta$ is intrinsically positive.) Opposing this force is the applied pressure acting over the area of the circle of contact with a force equal to $\pi r^2 p$. At equilibrium these opposing forces are equal: $-2\pi r \sigma \cos \theta = \pi r p$ whence Equation 1 follows immediately.

From this relation it appears that a porous material under zero pressure will "absorb" none of any nonwetting liquid in which it is immersed. When the pressure is raised to some finite value, the liquid will penetrate and fill all pores having radii greater than that calculated from Equation 1. [The authors have arbitrarily excluded from the category of "pores" all those openings having radii greater than that given by 1 for p = 25pounds per sq. inch (1.75 kg. per sq. cm.). This is the lowest pressure to which their samples are subjected and corresponds to a radius of about 43,000 Å., which is below the limit of resolution of the unaided eye.] As the pressure is increased the amount of liquid "absorbed" increases monotonically at a rate proportional to the differential pore volume due to pores of size corresponding to the instantaneous pressure. Thus, a given pore-size distribution gives rise to a unique pressuring curve; and, conversely, a given pressuring curve affords a unique determination of the pore-size distribution.

SOURCES OF ERROR

Deviation from the assumed circular cross section is an important source of error. It should, however, be noted that this assumption appears in Equation 1 only through the ratio, 2/r, of perimeter to area. For noncircular cross sections, this ratio will still be of the order of the reciprocal of some average radius although the constant, 2, may change. The effect here will be only to change the radii calculated from Equation 1 for various pressures by a constant factor. The shape of the distribution curve and order of magnitude of the calculated radii will not be appreciably different.

The question of the correct contact angle between liquid and solid is uncertain. The authors have adapted this experimental method to the use of mercury as the working liquid, inasmuch as mercury has a contact angle greater than 90° for most solids, and have measured contact angles for mercury on a large variety of materials by the height-of-sessile-drop method (11), obtaining values ranging from 135° to 142° (1). While the surfaces used were in equilibrium with air at normal humidity, and the contact angles thus measured are probably high because of adsorbed moisture, it would seem that the internal surfaces of the porous materials must be similarly contaminated; and that the measured contact angle is close to the true value required in application of Equation 1. The authors have assumed an average contact angle of 140° in this study. Differentiation of Equation 1 and elimination of p give

$$\frac{\Delta r}{r} = -\Delta \theta \, \tan \, \theta \tag{2}$$

as the fractional error incurred in calculated pore radius by an error of $\Delta\theta$ in contact angle. For θ in the neighborhood of 140°, $\Delta r/r$ for a 1° error in contact angle is only about 1.5%. This error is probably smaller than that caused by taking the perimeter to cross-sectional area ratio as 2/r, and moreover operates in the same manner in its ultimate effect on the distribution curve.

If θ is not in the neighborhood of 140°, the only effect is the same magnification or reduction in the scale of pore-radius values, although the size of the error may be considerably more serious. Table I shows the variation in calculated pore radius with applied pressure for contact angles of 140° (used in this investigation), 112° (found by Washburn for mercury on glass, 15), and 180° (the extreme case).

The pore radius calculated by this method is the radius of the opening to the pore. If there exist in the material pores which are considerably larger than the largest entrances to them, these pores will be measured as of the size of the largest opening. Inasmuch as availability of internal surface is determined by the size of opening to a pore, however, this is an advantage in that it gives the total volume of pores available to penetrants of any given





Pressure Porosimeter

size. In point of availability, if one is concerned with molecules 20 Å. in diameter, it is less important to know that a certain pore has a diameter of 40 Å. than that the largest entrance to it is only 15 Å. In this connection, see (13).

PRESSURE POROSIMETER

Experimentally, the essential problem is to measure the small changes in volume of a mass of mercury, in which the porous material under investigation is immersed, when the mercury is subjected to varying external pressure. The volume changes are measured electrically in a glass dilatometer placed in a thermostated high-pressure bomb and subjected to fluid pressure up to 10,000 pounds per sq. inch (700 kg. per sq. cm.). (Using $\theta = 140^{\circ}$ and $\sigma = 480$ dynes per cm, Equation 1 gives 107 A. as the pore radius in equilibrium at 10,000 pounds per sq. inch. Thus, investigations up to 10,000 pounds per sq. inch just cover the macropore range.)

The dilatometer is of the usual one-piece type. Samples varying from 1 to 20 grams are normally charged, and the capillary tubing has a cross-sectional area of about 0.04 cc. per cm. Larger or smaller capillary tubing may be used for very porous or slightly porous material.

The dilatometer is provided with a device for observing the height of mercury in the capillary when enclosed in an opaque metal bomb. A metal wire is strung taut along the inside of the capillary tubing and made one arm of a resistance bridge. The length of exposed wire is then equal to the length of capillary not filled with mercury. Since the mercury column will act as a conductor of effectively zero resistance, shorting out more or less of the wire as the mercury is raised or lowered, the resistance of the wire-mercury conductor is a measure of the mercury height.

Table I.	Variation of Pore Radius with Pressure for Several Values of
	Contact Angle

Pressure, P.s.i.	Pore R 140°	adius for Contact Ar 112°	gles of: 180°
	Å.	A.	Å.
$\begin{array}{c} 25\\ 100\\ 200\\ 300\\ 400\\ 500\\ 700\\ 1,500\\ 2,000\\ 3,000\\ 4,000\\ 5,000\\ 6,000\\ 6,000\\ 7,000\\ 8,000\\ \end{array}$	42.680 10,670 5,330 2,670 2,135 1,520 1,520 1,520 1,520 1,520 1,520 1,520 1,520 1,520 2,14 178 152 133	$\begin{array}{c} 20.840\\ 5,210\\ 2,600\\ 1,740\\ 1,300\\ 1,040\\ 744\\ 521\\ 347\\ 280\\ 174\\ 130\\ 104\\ 87\\ 74\\ 65\end{array}$	$\begin{array}{c} 55, 680\\ 13, 920\\ 6, 960\\ 3, 480\\ 2, 780\\ 1, 990\\ 1, 392\\ 928\\ 696\\ 464\\ 348\\ 278\\ 232\\ 232\\ 199\\ 174\\ \end{array}$
9,000 10,000	107	58 52	135

Figure 1. Mercury Dilatometer

If the tubing is of uniform diameter and the wire of uniform resistance, then the change in resistance of the wire-mercury conductor will be a direct measure of the change in volume of the mercury.

Figure 1 is a diagram of the dilatometer. The wire is looped over a bridge fused across the junction of capillary to bulb, and passes up through the capillary and out through side holes in the tubing. The ends are separately anchored between cushioned nuts threaded on an insulating screw. Another nut provided with locknut is threaded on the inner end of the screw, so that when this nut is tightened the screw is backed out of the tube and the wire thereby stretched taut. The smooth glass bridge allows the tension to equalize over both branches and obviates separate tightening. The authors have used No. 32 platinum wire. Platinum is used because it is the only common metal with an air-stable surface not attacked by mercury, and this size is a compromise between sturdiness and flexibility.

The dilatometer is calibrated directly in cubic centimeters per ohm by taking coordinated readings of resistance and weight of mercury buretted from a stopcock sealed temporarily to the bottom of the dilatometer, while the latter is held at 0° C. in an ice bath. For convenience, only those dilatometers exhibiting a constant cubic centimeter per ohm conversion factor are retained for use. Dilatometer 5, for example, had an average conversion factor of 0.608 cc. per ohm with an average deviation over its useful length of 0.002 cc. per ohm.



Figure 2. Filling Pistol for Dilatometer

The dilatometer is filled with sample through its open bottom, sealed off, and placed in the filling pistol as shown in Figure 2. The pistol is evacuated at about 10^{-s} mm. of mercury for 30 minutes, during which time the mercury is poured back and forth several times between the reservoir and the barrel of the pistol. Finally, the pistol is up-ended with the dilatometer head down, isolated from the vacuum line, and the vacuum broken by removing the stopcock plug. Atmospheric pressure forces mercury through the dilatometer head and fills the entire vessel with mercury.

In operation, the filled dilatometer is placed in a highpressure bomb with one end of the resistance wire grounded and the other brought through an insulated lead in the bomb head. (The high-pressure insulated lead is a product of the American Instrument Company, Silver Spring, Md.) Pressures up to 2000 pounds per sq. inch are supplied from a full cylinder of nitrogen and read on a dial gage (±10 pounds per sq. inch) calibrated against a dead weight gage. Pressures from 2000 to 10,000 pounds per sq. inch are generated by forcing oil into the bomb with a hand-operated Bosch fuel-injection pump and read directly on the dead weight gage. The initial 2000 pounds per sq. inch of gas pressure provide a cushion at the top of the bomb which prevents oil from the Bosch pump from spilling over into the top of the dilatometer at the higher pressures and consequent fouling of the capillary tube.

Pressuring is stopped from time to time and coordinated readings of pressure and resistance are made. With some materials there is a measurable rate of penetration and time is allowed for the resistance to rise to its equilibrium value. When the pressure is rapidly applied there is a noticeable rise in temperature and time is allowed for the system to cool and the resistance to fall to its equilibrium value. Corrections to the observed gage pressure are made by adding atmospheric pressure plus the average mercury height in the dilatometer. Table II gives typical data for five porous materials investigated. The final pressuring curve is obtained by plotting against observed pressure (corrected), p, the volume of mercury "absorbed" per gram of porous material, $V_0 - V$. Typical pressuring curves are shown in Figures 3 and 6.

The compressibility of mercury and the change of resistance with pressure of platinum are both negligible in this pressure range. This supposition was satisfactorily checked by filling the dilatometer with mercury only and pressuring to 10,000 pounds per sq. inch.

PORE-SIZE DISTRIBUTION

Let the total volume of all pores having radii between r and r + dr be

$$dV = D(r)dr \tag{3}$$

where D(r) is the distribution function for pore size. From Equation 1, assuming constant σ and θ ,

$$dr + rdp = 0 \tag{4}$$

Eliminating r and dr from Equations 1, 3, and 4 gives

T

$$dV = D(r) \frac{2\sigma\cos\theta}{p^2} dp = -D(r) \frac{r}{p} dp$$
(5')

The volume measured by the dilatometer is the volume of al pores having radii greater than r—i.e., the total pore volume, V_{\bullet} , decreased by the volume, V, of pores smaller than r. Thus the pressuring curves plot $V_{\bullet} - V$ as a function of p. The slope of the pressuring curve, $\frac{d(V_{\bullet} - V)}{dp} = -\frac{dV}{dp}$ is then an experimentally determinable quantity and Equation 5' may now be rewritten in the form

$$D(r) = \frac{p}{r} \frac{d(V_0 - V)}{dp}$$
(5)

in which all the terms on the right are known or determinable.

Values of the derivative in Equation 5 required to evaluate D(r) are readily obtained by graphical differentiation. For a number of values of p, the pressuring curve is differentiated to obtain $d(V_0 - V)/dp$, r is calculated from Equation 1, and D(r) is calculated from Equation 5. Plotting D(r) against r gives the distribution curve.

Curve A of Figure 3 is the pressuring curve for a sample of diatomaceous earth (Celite catalyst carrier Type 296 furnished







Distribution Functions for Diatomaceous Earth and Figure 4. **Fritted Glass**

by Johns-Manville Corp.) heated to 550° C. for 16 hours. By differentiating and applying Equation 5, the circled points in the plot of Figure 4 were obtained. The points appear to form a modi-fied Maxwellian distribution, and an attempt was made to fit a curve of the form

$$D(r) = A\left(\frac{r^2}{r_0^3}\right)^n \exp\left(-\frac{r^3}{r_0^3}\right) \tag{6}$$

to these points. Equation 6 contains three arbitrary constants-A, n, and r_0 —for adjustment to the experimental points. The methods may be applied. The method chosen here was to deter-mine the three constants from three salient features of the curve. Inspection of the plotted points affords an estimate of r_{\pm} , the pore radius corresponding to the peak of the distribution; D_{\pm} , the value of D(r) at this point; and V_0 , the pore volume determined from either the densities or the extrapolated value for $V_0 - V$ as → ∞ p

By equating dD(r)/dr to zero, it is found that

$$r_m = r_0 \sqrt{n} \tag{7}$$

Placing this value of r_m in Equation 6 gives

$$D_{\mathbf{m}} = A \left(n/e \right)^{\mathbf{n}} \tag{8}$$

Integrating Equation 3 from zero to infinity with D(r) given by Equation 6 gives

$$V_0 = Ar_m \Gamma(n + \frac{1}{2})/2\sqrt{n} \tag{9}$$

Eliminating A from Equations 8 and 9 gives

Table II. Physical Data on Some Porous Materials

					Pore Radius
					Dia-
			Macro-	Total	tribu-
	Vo-Vat P	ressures of:	pore	Pore	tion
100	200 500	1000 2000	5000 Vol-	Vol- Macro- Surf	ace ^c V/S func-
p.s.i.	p.s.i. p.s.i.	p.s.i. p.s.i.	p.s.i. ume	ume pores Are	a ratiod tion"
	Cc. pe	r gram	Cc./g.ª	Cc./g.b % Sq. m	./a.
Diatomaceous earth 0.132	0.460 0.918	1.013 1.040	1.045 1.049	1.14 92 4.2	5430 4580
Coors porous plate 0.00	0.003 0.093	0.152 0.162	0.172 0.173	0.172 100 1.6	2150 1860
Pyrex UF fritted glass 0.00	0.012 0.159	0.168 0.169	0.169 0.169	0.175 97 0.69	5100 4190
Activated clay 0.003	0.002 0.009	0.071 0.123	0.166 0.195	0.518 27 223	46 <501
Pelleted gel 0.003	0.040 0.108	0.133 0.152	0.168 0.178	0.657 37 323	40 <501
Pyrex UF fritted glass 0.00 Activated clay 0.00 Pelleted gel 0.00	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.168 0.169 0.071 0.123 0.133 0.152	0.169 0.169 0.166 0.195 0.168 0.178	0.175 97 0.69 0.518 27 223 0.657 37 323	$\begin{array}{cccc} 5100 & 4190 \\ 46 & < 50 \\ 40 & < 50 \end{array}$

^a Equals V₀-V at 10,000 p.s.i.
^b Calculated from real and particle densities.
^c BET method, using N₁ at its normal b.p.
^d Radius of uniform circular cylinder having BET surface and volume equal to total pore volume (Å.).
^e From r = frD(r)dr/fD(r)dr(Å.).
^f Estimated from Figure 7.

$$\frac{n/e)^{\mathfrak{m}}\sqrt{n}}{\Gamma(n+\frac{1}{2})} = \frac{r_{\mathfrak{m}}D_{\mathfrak{m}}}{2V_{\mathfrak{m}}} \tag{10}$$

which may be solved for n. Equations 7 and 8 then serve to find r_0 and A.

For the diatomaceous earth of Figure 4, r_{-} and D_{-} were estimated to be 4100 Å. and 17.5×10^{-5} cc. per Å., respectively. Table II gives $V_{e} = 1.045$ cc. From these data, n = 0.58, $r_{e} = 5380$ Å., and $A = 4.16 \times 10^{-4}$ cc. per Å. The upper curve of Figure 4 is a plot of Equation 6 with these values for the constants. This distribution may perhaps be regarded as the "normal" distribution for pores in a porous solid, and the indicated agreement between the postulated distribution and that found experimentally is satisfactory. The area under this curve is the total pore volume, V.

The average pore radius is defined as

(

$$\overline{r} = \int_{0}^{\sigma_{0}} rD(r)dr/V_{0}$$
(11)

Given the numerical function, D(r), r may be calculated by some process of numerical integration. A value for an average pore radius may also be obtained from the measured volume per surface ratio for the pores. Table II gives values for the pore volume calculated from measured densities, surface area by the BET method (4), average pore radius calculated from these values, and average pore radius calculated from Equation 11.



Figure 5. Distribution Function for Porous Plate

In the case of the "normal" distribution of Equation 6, Equation 11 may be reduced to

$$\overline{r} = \frac{\Gamma(n+1)}{\Gamma(n+\frac{1}{2})} r_0 \tag{12}$$

For the diatomaceous earth, \bar{r} calculated from Equation 12 is 4990 Å. compared with 5430 and 4580 obtained by the other methods.

The average pore radius calculated from Equation 11 is always less than that calculated by assuming a geometric model for the

Average

pores and using the volume/ surface ratio, providing the porosimeter has measured essentially all of the total pore volume-i.e., providing there is no significant micropore volume. This presumably is because r in Equation 11 refers not to the radius of the pore but to the radius of the largest opening to the pore. This value of r is necessarily not greater than the true pore radius, and is, in general, smaller. Thus a comparison of the last two columns of Table II affords a qualitative measure of "ink-bottle" pores in

those cases where "% macropores" is near 100. The paper following this one will discuss the "ink-bottle" pore shape phenomenon in connection with the hysteresis observed during depressuring (δ) .

NONNORMAL AND INCOMPLETE DISTRIBUTIONS

Curve B of Figure 3 is the pressuring curve for a fine-pore fritted glass (Pyrex fritted glass, ultrafine porosity, kindly furnished by Corning Glass Works), and the lower curve of Figure 4 shows the derived distribution function. No information on the particle size classification prior to sintering is available from the manufacturers, but this distribution is probably not "normal". (An attempt was made to fit these points to a displaced Gaussian distribution, but the best fit is rather poor. The curve drawn is merely a smooth curve through the points.) The sharp cutoff on both sides of the peak seems to indicate that a relatively narrow range of particle sizes is retained for sintering, with a consequent narrow range of pore sizes. The average pore diameter of 8400 Å. is in good agreement with the manufacturer's statement that filtrates through this porous body are usually bacterially sterile.

Curve C of Figure 3 is the pressuring curve for another ceramic material, Coors porous plate (No. 760, Coors Porcelain Co., Golden, Colo.), the derived distribution for which is plotted in Figure 5. The sharp drop in frequency of occurrence of pore sizes at about 3000 Å. is remarkable. Thus, pores of radius 3500 Å. are present to the extent of only 3% of the pores of radius 2700 Å. The distribution to the left of the peak is a great deal wider and appears Maxwellian. One is tempted to presume that the derived distribution is a part of a wider and "normal" parent distribution such as is shown dotted in the figure, and such as might be obtained by a very efficient classification process that removes the large-pore portion. Advice from the manufacturers, however, indicates that this presumption is incorrect.



Pressuring Curves for Activated Clay and Silica Alumina Figure 6. Gel

The method is not restricted to macropore structure. While this investigation is limited to pressures up to 10,000 pounds per sq. inch (down to 100 Å. in pore radius), the principle applies down to pore sizes so small that the concepts of surface tension and contact angle break down-i.e., to where the pores are no longer large compared to the atomic dimensions of mercury. Thus, in materials to whose pore volume there is a significant contribution from micropores, the entire distribution is not derivable from pressuring only to 10,000 pounds per sq. inch; but pressuring to 50,000 pounds per sq. inch (corresponding to r =20 Å., the probable lower limit) would give valuable data for elucidating micropore size distributions. Nevertheless, pressuring curves up to 10,000 pounds per sq. inch even for materials



Figure 7. Distribution Functions for Materials of Figure 6

largely microporous are of value even without the distribution. Such data will be presented and discussed in a later paper (5).

Partial distributions for two microporous materials, an activated clay and a pelleted silica-alumina gel, are shown in Figure 7, taken from the pressuring curves of Figure 6. The pelleted gel shows a superposition of two distributions (one incomplete here); one is the micropore distribution, the other a macrodistribution presumably due to pelleting of relatively large gel particles. The clay catalyst shows only a continuous distribution extending well into the micro region. Table II shows that the area under the incomplete peaks (micropore volume) in both cases must be 3 to 4 times the area under the curves to the right of r = 100 Å. With this in mind, one can estimate the approximate average pore radius at about 50 Å. for both samples.

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Macropore-Size Distributions in Some Typical Porous Substances

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Macropore-size distributions in typical porous substances have been measured, using the pressure porosimeter described in the previous paper. Substances investigated include fuller's earth, diatomaceous earths, silica-alumina gels, flint quartz, porous iron, activated clay pellets and porous desiccants.

POROUS materials are characterized by two related quantities: a particle density which is appreciably lower than the real or true density of the material, and a surface area which is greater than the observable geometric surface area. Porous materials differ widely in each of these characteristics; for example, the particle density of some diatomaceous earths is only 20% of the true density, and some activated carbons have surface areas 500,000 times the external geometric area, while the particle

"Second part of paper on "Pore-Size Distribution in Porous Materials." First part is found on page 782.

Table I.	Variation	of Macro	porosity	Measured	at	Low	Pressures
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			-						
		Volume Pores, Co	of Merce. per G	ram X	moved f 10 ⁻⁴ at	rom (- Mm. of) and F Hg Pres	orced in sure Inc	to (+)
	Material	550	660	860	1070	1300ª	1460	1560	1660
2 6 5 3 16	Coors porous plate Activated clay Fuller's earth Diatomaceous earth Type M fritted glass	$ \begin{array}{r} -2.4 \\ -3.3 \\ -10 \\ -56 \\ -300 \end{array} $	$-2.2 \\ -2.7 \\ -37 \\ -150$	-1.2 -1.3 -3.4 -22 -66	-0.3 -0.3 -1.8 -10 -22	0 0 0 0	+0.9 +0.8 +2.3 +28 +210	+1.6 +1.4 +2.8 +51 +330	+1.8 +4.0 +136 +420

^a Atmospheric pressure plus mercury height in dilatometer.

Table II. Physical Properties of Porous Materials

		Mesh	Surface		Density		Po	ore Volum	ee	Average
	Material	(Tyler)	Areaa	Bulk	Particleb	Real	Total	Macro	Macro	Diameterd
			Sq. m./g.		Gram/cc.			Cc./g.	%	Å.
				Clay	Type					
6	Activated clay	4-6	223	0.68	1.111	2.614	0.518	0.195	38	93
5	Fuller's earth	5-7	129	0.55	0.860	2.660	0.405	0.105	71	244
3	Diatomaceous earth	4-6	4.2	0.32	0.631	2.265	1.14	1.049	92	11,000
	Diatomaceous earth	4-8	< 1	0.29	0.470	4.341	1.7	1.0	00	
]	Desiccar	nt Type					
10	Bauxite	8-14	228	0.88	1.575	3.622	0.360	0.124	34	63
11	Silica gel	8-14	669	0.81	1.547	3.675	0.388	0.123	32	89 24
	8				C 1					
			A	tivated	Carbons					
8	Columbia carbon	6-8	1397	0.42	0.754	1.897	0.802	0.344	43	23
1	DAICO CAIDON	1 14	000	0.00		1.000	0.000	0.000		00
				Gel 1	ype					
13A	Silica-alumina gel	4-8	280	1.00	1.558	2.369	0.228	0.0019	0.8	33
13C	Silica-alumina gel	4-8	467	0.69	1.126	2.377	0 463	0.0100	$\frac{1.1}{2.2}$	40
13D	Silica-alumina gel	4-8	372	0.64	0.962	2.378	0.620	0.0180	2.9	67
13E 13F	Silica-alumina gel	4-8	409	0.55	0.860	2.402	0.657	0.0282	3.8	73
13G	Silica-alumina gel	4-6	201	0.68	1.050	2.343	0.527	0.147	28	105
			Misc	ellaneou	s Materia	la				
1	Flint quarts	4-6	< 1	1.53	2.610	2.641	0.0044	0.0044	100	
2	Coors porous plate	8-20	1.6	1.00	1.801	2.612	0 172	0.173	100	4,300
15	Fritted glass	8-14	0.69	0.87	1.608	2.237	0.175	0.169	97	5,100
								_	_	

Calculated from low-temperature nitrogen adsorption isotherms by means of the Brunauer, Emmett, Teller

backmack from tow-comperative introgen austription resting to means of the Diffuence, particle method (3).
 b Bulk densities by hand tapping in a 250-cc. graduate, particle density by mercury displacement, real density by water displacement.
 Total pore volumes obtained from difference between reciprocals of particle and real densities; macropore volume of mercury absorbed at 10,000 p.s.; pressure.
 Average pore diameters calculated from pore volume and surface area measurements.

density of a porous filter plate may be 70% of its real density, and its surface area is only 1000 times its geometric area.

The pores within a granule of porous material may also vary widely in absolute dimensions, from those readily seen by the naked eye (106 Å. in diameter) to those with diameters of only 4 or 5 Å. It is obvious that the large pores contribute very little to the total surface area of the material. Wicke (11) estimated that the surface area contributed by pores averaging 20 Å. in diameter in a sample of charcoal is 1500 sq. meters per gram, while the surface area contributed by a practically equal volume of pores averaging 20,000 Å. in diameter is only 1.7 sq. meters. This ratio of surface area contribution by large and small pores will vary from one material to another, depending upon the poresize distribution.

Although these large or macropores contribute little to the total surface area, they may serve an important function as distributing arteries to the smaller or micropores (2, 4, 10). The rate of adsorption or catalytic action is intimately tied up with

> the diffusion velocity of the reactants into the porous material and this is governed in part by the quantity and size distribution of the macropores.

A rough value for the average diameter of the pores of a material may be calculated from total pore volume and surface area measurements (5). Thus, assuming uniform cylindrical pores we have:

Pore diameter = $\frac{4 \times \text{pore volume}}{4 \times \text{pore volume}}$ surface area

The values in the last column of Table II were calculated from this relationship. It is obvious that with materials having a wide range of pore sizes such values have little significance.

Pore diameters may also be calculated from adsorption data by means of the Kelvin equation (1). Adsorption values at high relative pressures, corresponding to condensation in macropores, are, however, extremely difficult to obtain and extrapolations from lower relative pressures are of dubious utility.

Persorption studies are also of little help in macropore-size studies because of the lack of a variety of molecules of the necessary dimensions.

The penetration of porous solids by mercury may be easily demonstrated with simple apparatus at pressures under 20 pounds per sq. inch. The data in Table I were obtained with a 40-cc. glass bulb dilatometer attached to a 2mm. bore capillary arm. In these reasurements the samples were evacuated, covered with mercury, thermostated at 40° C., and the position of the mercury level noted. The pressure on top of the mercury in the dilatometer was lowered by means of a Hy-Vac pump or in-



Figure 1. Macropore Volume of Fuller's Earth and Activated Clay Pellets



Figure 2. Macropore Volume of Porous Desiccants

creased with a bulb aspirator. These data show clearly the great difference in the volume of the very large pores of these porous materials.

The pressure porosimeter previously described (9) was used in this work. The materials were obtained from the following sources: (1) flint quartz from New England Quartz Co., New York, N. Y.; (2) Coors porous plate No. 760 from Coors Porcelain Co., Golden, Colo.; (3) diatomaceous earth, Celite catalyst carrier Type 296, C-20883, from Johns-Manville Corp., New York, N. Y.; (4) diatomaceous earth, Celite catalyst carrier Type VI, C-20882, from Johns-Manville; (5) fuller's earth, extruded pellets from Attapulgus Clay Co., Philadelphia, Pa.; (6) activated clay, extruded pellets, from Filtrol Corp., Los Angeles, Calif.; (7) activated clay, extruded pellets after service in catalytic cracking unit; (8) activated carbon, Columbia pellets, from Carbide and Carbon Chemical Corporation, New York, N. Y.; (9) activated carbon, Darco granules from Darco Corporation, New York, N. Y.; (10) bauxite, granules from Aluminum Ore Co., Pittsburgh, Pa.; (12) silica gel, granules from Aluminum Ore Co., Baltimore, Md.; (13) silica-alumina gels, laboratory and plant samples; A, B, C, D, and E are nonpelleted; F and G are pelleted; (14) porous iron, briquet, from Metals Disintegrating Co., Inc., Elizabeth, N. J.; (15) fritted glass, UF porosity from Corning Glass Works, Corning, N. Y.; (16) fritted glass, M porosity from Corning Glass Works, Corning, N. Y.

In all determinations the porous samples were heated for 16 hours at 540° C. with the exception of the fritted glass, Coors porous plate, porous iron, activated carbon, carbon on activated clay, and diatomaceous earth samples. These latter were ovendried at about 150° C. The samples were evacuated for 0.5 hour at 0.001 mm. of mercury pressure at room temperatures prior to covering with mercury. Weight of the samples varied from 1 to 20 grams, depending upon the dilatometer and macroporosity.

The macropore volumes calculated from particle and real densities are based on particle densities determined at a total absolute pressure of about 17 pounds, while the base pressure in the highpressure dilatometer was about 25 pounds. This difference in pressure is negligible except with materials having a large number of very large pores—e.g., diatomaceous earth. The data of Table I give a measure of this variable. Unavoidable jarring of the dilatometer prior to the initial resistance reading is also a source of error with materials having very large pores.

Samples were exposed to atmospheric conditions for only a short time prior to sealing in the dilatometer, but they must have contained some adsorbed water.

These materials had received widely varying temperature and other processing treatments during their preparation. It is not claimed that these individual samples are truly representative of their types.

RESULTS

The data obtained are presented in Figures 1 to 10 in which the volume of mercury absorbed in cubic centimeters per gram of porous solid is plotted against applied pressure. Pore diameters $(140^{\circ} \text{ contact angle})$ corresponding to the pressures shown are also indicated in these figures. Although macropore-size distributions are not explicitly exhibited in these curves, such distributions are implied in their shapes, and are in fact derivable by methods previously outlined (9). The physical properties of all these materials are tabulated in Table II.

ACTIVATED CLAY AND FULLER'S EARTH. Both materials had been extruded and cut to form small pellets. The activated clay had been acid-leached prior to extrusion and had been partially deactivated by service in a catalytic cracking unit. The total surface areas of these samples were approximately equal, but the distribution of macropores varies widely (Figure 1). The absence of extremely large pores in the fuller's earth and the large quantity of small macropores are clearly shown.

POROUS DESICCANTS. These materials have been heated much higher than they would have been for commercial utilization, but the relative positions of the curves of Figure 2 probably would not be changed. The absence of many macropores in the silica gel is noteworthy. The total pore volumes of these materials are within 7% of each other but their surface areas differ by about 400%.

Although the data presented by Henderson, Ridgway, and Ross (6) for their sample of bauxite are very sketchy and they give measurements at 30 and 900 pounds per sq. inch pressure only,



Figure 3. Macropore Volume of Diatomaceous Earths and Activated Carbons

we may make a comparison between their value of 0.29 cc. per gram for the total pores not filled at 900 pounds per sq. inch pressure and the authors' value of 0.32 cc. per gram obtained from a total pore volume of 0.36 cc. per gram less the 0.04 cc. per gram value obtained at 900 pounds per sq. inch. Similar values for fuller's earth, however, are not so close. Their value was 0.57cc. per gram; the authors', 0.78 cc. per gram. There may be a considerable difference between the authors' samples and those used by Henderson, Ridgway, and Ross.

DIATOMACEOUS EARTHS AND ACTIVATED CARBONS. These materials are considered together because of their utilization as catalyst carriers. The diatomaceous earth samples had been fired at a high temperature, judging by their physical appearance. Unfired diatomaceous earths with reported surface areas of about 30 sq. meters per gram would be expected to have substantially different macropore volumes from the two samples whose data are reported here. As is pointed out under the discussion of hysteresis, the diatomaceous earth, sample 4, was not materially colored by absorbed mercury when removed from the test but contained appreciable quantities of mercury within the pellet. This indicates the absence of any small macro ink-bottle pores and this fact is borne out by the low surface area and the flatness of its curve in Figure 3. The complete distribution curve for diatomaceous earth, sample 3, has already been presented (9).

A marked difference in the distribution of macropores in the two activated carbons is also shown in Figure 3. The distribution of very large macropores in the two samples is essentially the same, but there are very few small macropores in sample 8.

SILICA-ALUMINA GELS. The silica-alumina gels presented in Figure 4 show the relatively wide distribution of macropores within samples prepared by different methods. The absence of any flattening of these curves at high pressures is noteworthy as indicating a relatively small proportion of macropores.

The definite increase in macropore volume with decrease in particle and bulk density may also be noted from the data in Table II.

SILICA-ALUMINA GEL AND FLINT QUARTZ. Although fint quartz because of its low total pore volume would not normally be classed as a porous material, the data in Figure 5 show that it has a few relatively large pores. The macropore volume at 4000 pounds per sq. inch pressure is equal to the total pore volume calculated from particle and true densities. The silica-alumina gel sample with a total macropore volume practically equal to that of the flint quartz has a uniform distribution of macropores.

POROUS IRON. The porous iron sample was obtained from a small experimental briquet. Material was not available for the usual particle and real density measurements, the particle density value shown in Table II having been obtained from the weight and geometric volume of the briquet, while the true density is a







Figure 5. Macropore Volume of Flint Quartz and Silica-Alumina Gel



handbook value for iron. The low value for the calculated percentage of macropores, 80%, is no doubt due either to the destruction of very large pores when the briquet was granulated or to the presence of a large number of very large pores.

EFFECT OF METHOD OF PREPARATION. Macropores may be incorporated in individual particles during the course of preparing the sample. This is shown in Figure 7 in which the macropore distribution of pelleted gel (13F) particles may be contrasted with that of gel particles (13E) which had not been ground and reconsolidated by pelleting.

EFFECT OF CARBON DEPOSITION. When hydrocarbons are cracked on clay catalysts a deposition of carbon is left in the pores of the catalyst particles. The data plotted in Figure 8 show that small amounts, 1.2%, of such carbon exert only a minor plugging effect in the macropores. This carbon was deposited by cracking light gas oil at 800 °F. followed by thoroughly purging out the cracked products with nitrogen. The sample was pumped out at room temperature in the usual manner prior to covering with mercury.

EFFECT OF MESH SIZE ON MACROPOROSITY. In most of the determinations reported here the granules or particles were between 4- and 14-mesh, usually relatively narrow-mesh sizes. The effect on macropore volume of granulating to smaller mesh sizes is shown in Figure 9. Reducing the size of the high-macropore-volume activated clay granules from 4- to 6-mesh to 20- to 28-mesh decreased the macropore volume, while similar size reduction of the low-macropore-volume silica alumina gels increased the macropore volume. These effects may be explained by assuming that some large pores are actually destroyed in the case of the clay catalyst, while with the gel catalyst more macropore volume is available in the smaller granules because some such pores are actually blocked off from contact with the mercury in the larger particles.



Figure 7. Macropore Volume of Silica-Alumina Gels Prepared by Different Methods



Figure 9. Effect of Mesh Size on Macropore Volume of Activated Clay and Silica-Alumina Gels

HYSTERESIS. The appearance of the samples after the 10,000 pounds per sq. inch measurements varied widely. The gels, with the exception of those that had been pelleted, contained very little mercury, while the fuller's earth, activated clay, pelleted gels, bauxite, activated carbon, diatomaceous earth, and activated alumina samples contained considerable quantities of mercury. For example, the activated clay pellets contained 148% by weight of mercury after each pellet had been bounced to remove any that was loosely held. Pellets subjected to 2000 pounds per sq. inch pressure were light gray in color, while samples removed after a 10,000 pounds per sq. inch test were very dark gray. Pellets cut in half showed that the mercury was uniformly dispersed throughout the particle.

Diatomaceous earth, material No. 4, was substantially different

Table III.	Hysteresi	is in Macropo	prosity Det	erminations		
	Macropore Volume					
Materia	1	Occupied by mercury at 10,000 p.s.i. pressure	Occupied p.s.i. pres p.s.i.	by mercury at 25 sure after 10,000- measurements		
		Cc./g.	Cc./g.	Percentage of total macropore volume		
6 Activated cli 10 Bauxite 4 Diatomaceou 8 Activated ca 9 Activated ca 13G Pelleted silic gel	ay 16 earth 17bon 17bon a-alumina	0.191 0.124 1.49 0.344 0.685 0.147	$\begin{array}{c} 0.130 \\ 0.068 \\ 1.47 \\ 0.285 \\ 0.551 \\ 0.090 \end{array}$	68.1 54.8 98.8 82.8 80.6 61.3		
13E Silica-alumin 15 Fritted glass	a gel	0.0282 0.161	0.0001 0.0436	0.4 27.1		



Figure 8. Effect of Carbon Deposition on Macropore Volume of Activated Clay Pellets



Figure 10. Hysteresis in Macropore Volume Measurements

from both the activated clay and the gel catalysts. Upon removal from the 10,000 pounds per sq. inch test the individual granules were only very slightly darker but very much heavier than when charged, some samples having increased as much as 1600% in weight. When halved with a knife a globule of mercury appeared, the individual halves having practically the same appearance as halves which had never been in contact with mercury. When the two sections were again halved more mercury globules appeared.

In addition to the varying appearances of the samples after the test, it was noted that, with most of the samples, upon releasing the pressure after a 10,000 pounds per sq. inch test the desorption curve did not follow the absorption curve. Two examples of this phenomenon are presented in Figure 10. With some of the samples the desorption of the mercury at the lower pressure occurred slowly but seemed to approach a definite equilibrium.

Measurements of the hysteresis encountered with the various materials used in this investigation are presented in Table III, in which the volume of mercury remaining in the pores of the materials after reducing the pressure from 10,000 to 25 pounds per sq. inch is shown. The last column of this table presents values which are a direct measure of the number or quantity of pores from which the mercury is not desorbed. The very large difference between the pelleted and nonpelleted silica alumina gels, 13G and 13E, as well as the extremely high value for the diatomaceous earth is worth noting.

If the pores of these materials were either uniform in diameter or V-shaped one would expect the mercury to flow out when the applied pressure is released. If, however, there are pores with small mouths, the so-called ink-bottle pores (7, 8), they would not be expected to empty when the pressure is released.

ACKNOWLEDGMENT

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Rapid Method for Determination of Copper in Steel Especially Suitable for Foundry Control

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A method is described for the rapid and accurate determination of copper in plain and alloy steels for foundry control. The total time for the analysis is approximately 15 minutes. Its accuracy makes it suitable as a standard method for copper in steel up to 1.3% with a maximum error of less than ± 0.02 . The method involves precipitation of copper as cuprous thiocyanate from a perchloric acid solution and subsequent titration of the cuprous thiocyanate by the Andrews method, using chloroform and potassium iodate.

N THE manufacture of electrical steel the advent of copper-bearing steel scrap makes mandatory a rapid analytical method for the determination of copper. For the purpose of foundry control such a method must permit a determination to be made within 15 minutes and must be reasonably accurate.

Direct electrolytic procedures, as established by Frediani and Hale (7), Silverman, Goodman, and Walter (20), and Levine and Seaman (14), require a minimum of 40 minutes to 2 hours after solution of the metal, as well as a correction if molybdenum is present.

No volumetric procedures for the direct determination of copper in the presence of iron were found by the writers, although Lundell (15) in the titration of nickel using potassium thiocyanate and silver nitrate, states that copper would titrate as nickel. If such a method were devised for copper, the necessary correction for nickel would introduce another step and make the method too lengthy.

Direct colorimetric and polarographic methods were not investigated. Spectrographic procedures were not considered, since no spectrograph was available.

Indirect methods-that is, methods which involve a preliminary separation of the great bulk of the iron from the copperwere studied. All involve solution of the metal and subsequent precipitation of the copper with hydrogen sulfide (15, 19, 23), sodium thiosulfate (15, 19, 23), sodium thiocyanate (2, 3, 15, 23), aluminum metal (19), organic precipitants (27), or internal electrolysis (17). Final determination of the per cent copper present can be accomplished by various methods: electrolytically, colorimetrically, by ignition to the oxide of the sulfide precipitate, by precipitation with α -benzoinoxime and subsequent ignition to the oxide, by titration to the removal of the blue color complex by potassium cyanide, by titration of the reduced salt with potassium bromate using chloroform [Jamieson's modification of Andrews method (1, 10)], by titration of the oxidized salt of copper with the iodide-thiosulfate procedure, and by titration of cuprous thiocyanate with iodate (23).

In the procedures reviewed for the separation of copper from iron, solution of the metal by dilute sulfuric acid is recommended. The action of this acid results in the formation of ferrous iron. metallic copper, and cuprous copper. In this condition the copper can be quantitatively precipitated. The time required to dissolve the metal varies with the metal and its particle size, but in most cases complete solution cannot be effected in less than 15 minutes.

This fact established a pattern that it was found necessary to follow: (1) dissolve the metal in nitric acid in order to effect its immediate solution, (2) fume with perchloric acid to remove the nitric acid. (3) add sulfurous acid to reduce the iron and copper. (4) add sodium thiocyanate to precipitate the copper and permit its separation from iron, and (5) titrate the cuprous thiocyanate by the Andrews method.

Step 1 affords practically instantaneous solution of the metal. Step 2 removes the oxidizing acid and replaces it with a nonoxidizing acid (perchloric is nonoxidizing in the cold). Step 3 reduces the copper to a form in which it will precipitate and the 'iron to a form in which it will not interfere with the precipitation. This step could have been effected by stannous chloride, but there was danger of the latter hydrolyzing during filtration and causing erroneous results. In step 4 sodium thiocyanate causes almost immediate precipitation of copper, when the solution is properly buffered, and the precipitate is not contaminated by sulfur as would be true if hydrogen sulfide or sodium thiosulfate were used. Step 5 was adopted because the copper was in the ideal form for this titration and it was deemed more accurate in the reaction of cuprous to cupric ion. Other procedures were used successfully after the copper was oxidized to the cupric form, but were not adopted, as the oxidation of the copper introduced one extra step that was felt unnecessary.

REAGENTS REQUIRED

Nitric acid, 15 N, chemically pure, reagent grade. Perchloric acid, 70 to 72%, chemically pure, reagent grade. Hydrofluoric acid, concentrated, chemically pure, reagent

grade. Hydrochloric acid, 12 N, chemically pure, reagent grade. Sodium thiocyanate, c.P., 5%, water solution. Gelatin, 2%, water solution.

Sulfur dioxide, C.P., saturated water solution.

Sodium acetate, C.P., reagent grade.

Chloroform, c.p., reagent grade. IODINE MONOCHLORIDE SOLUTION. Dissolve 10 grams of 5 ml. of distilled water. Add 75 ml. of hydrochloric acid and 5 ml. of chloroform. Put in glass-stoppered bottle and adjust exactly to a very faint iodine color in the chloroform layer by shaking and adding dilute potassium iodide or iodate as the case may require. When not in use keep the solution of iodine monochloride in a cool, dark place.

POTASSIUM LODATE, C.P., standard solution. Dissolve 1.1784 grams in 1 liter of distilled water. One milliliter is equivalent to 0.02% of copper based on a 1-gram sample. (This salt is sufficiently pure to use as a primary standard.)

PROCEDURE

Dissolve a 1-gram sample of steel in a mixture of 5 ml. of perchloric acid and 5 ml. of nitric acid in a 300-ml. Berzelius beaker. Add 2 drops of hydrofluoric acid to remove silica. Fume gently to remove nitric acid and until iron perchlorate salts precipitate. Do not heat these salts to decomposition, as sparingly soluble iron oxide is formed. Cool slightly and dilute with approximately 20 ml. of distilled water. Add 10 ml. of sodium thiocyanate, boil, add 100 ml. of sulfurous acid and 5 grams of sodium acetate, boil, add a few drops of a gelatin solution, and stir. Cool in an ice bath and add ice to the solution. When chilled, filter through a Shimer filter tube, using a filter pad made from a mixture of a Shifter filter tube, using a lifer pad made from a mature of one each of thoroughly pulped No. 40 and No. 41, 12.5-cm. Whatman's filter paper. Wash with cool, oxygen-free, distilled water until free of sulfur dioxide. Remove the filter pad and insert it into a separatory funnel containing 25 ml. of chloroform, 60 ml. of hydrochloric acid, 40 ml. of cool, boiled, distilled water, and 3 drops of iodine monochloride solution. Shake the solution and pad vigorously and titrate the solution with potassium io-date solution until the pink color in the chloroform layer dis-appears, which is the end point of the titration. Add the iodate solution gradually, and shake the solution vigorously after each addition.

RESULTS

Table I indicates the optimum precision of the method. These results were obtained without regarding the time element.

Table II shows results obtained under conditions similar to foundry control when the time factor is important.

	Table I. Deterr	ninatio	n of Co	pper		
Bureau of Standards Standard No.	Type of Material	No. of Analy- ses	Deviati % Cu Maxi- mum	on from Present Aver- age	% Cu Found	% Cu Pres- ent
21c 111a 32c 15b 65b 20c 35a	Acid open hearth Nickel-molybdenum Chromium-nickel Basic open hearth Basic electric Acid open hearth Acid open hearth	4333445	$\begin{array}{c} 0.010\\ 0.001\\ 0.003\\ 0.003\\ 0.007\\ 0.005\\ 0.011\\ \end{array}$	$\begin{array}{c} 0.006\\ 0.000\\ 0.002\\ 0.002\\ 0.001\\ 0.003\\ 0.002\end{array}$	$\begin{array}{c} 0.044\\ 0.079\\ 0.097\\ 0.147\\ 0.206\\ 0.258\\ 0.265\\ \end{array}$	0.050 0.079 0.099 0.145 0.205 0.255 0.267
Synthetic Standards	Bureau of Standards Std. Sample 13d plus Grams of Copper					
1 2 3 4 5 6	0.00128 0.00255 0.00383 0.00510 0.00893 0.01275	7 5 5 6 5 5	$\begin{array}{c} 0.010 \\ 0.005 \\ 0.004 \\ 0.010 \\ 0.011 \\ 0.017 \end{array}$	$\begin{array}{c} 0.002\\ 0.002\\ 0.001\\ 0.005\\ 0.001\\ 0.001\\ 0.001 \end{array}$	$\begin{array}{c} 0.148 \\ 0.275 \\ 0.403 \\ 0.527 \\ 0.894 \\ 1.297 \end{array}$	0.150 0.277 0.404 0.532 0.893 1.296

PRECAUTIONS

For the purpose of expediting the results, the amount of perchloric acid specified is such that the residual acid left will be adequately buffered by the amount of sodium acetate added. If the solution is fumed too vigorously, insoluble iron salts are formed, yet if the solution is not fumed adequately the resulting solution will be too acid for the copper to precipitate quantitatively. Experience will quickly establish the proper fuming point.

The precipitate of cuprous thiocyanate is very finely divided

and the filter pad must be packed comparatively tight to prevent loss of the precipitate.

The wash water must be cool and free from oxygen.

If the precipitate and filter pad are not washed free of sulfur dioxide, erroneously high results will occur.

The chloroform-hydrochloric acid mixture should be cool and must not contain any oxidizing substance.

Other insoluble thiocyanates must not be present.

CONCLUSION

The procedure outlined gives accurate results within the required time. Its limitations are well under the maximum error of $\pm 0.02\%$, which is adequate for most work. The faults may be overcome when a better coagulant is found and a better filtering mechanism is devised.

	Table	II. Deterr	nination	of Coppe	down	
	(Ac	id Open-He	arth Steel	l Used)		
Bureau of Standards Standard No.	No. of Analyses	Maximum Time, Minutes	Deviation Cu P Mar.	n from % resent Av.	Average % Cu Found	% Cu Present
20c 35s	64 4+	16 15	0.013 0.007	$\begin{array}{c} 0.004 \\ 0.004 \end{array}$	$\substack{\textbf{0.251}\\\textbf{0.263}}$	$0.255 \\ 0.267$
^a Analyst A. ^b Analyst B.						

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THE views presented in this article are those of the writers and are not to be construed as the official views of the Navy Department.

Determination of Water Content in Oils

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RECENT publications (1, 2, 4) have definitely shown the Karl Fischer reagent to have great merit for the determination of water. Insufficient emphasis, however, has been placed upon pitfalls that may be encountered in adapting this reagent and technique to a new control method. Properly employed, with due regard to necessary precautions in manipulation, the Karl Fischer method lends itself readily to accurate and rapid water determinations. Improperly used, erroneous results and lack of reproducibility become the rule rather than the exception.

The adaptation of this method to the determination of moisture in oils (insulating and lubricating, both new and used) is possible only with careful and painstaking adherence to a predetermined uniform technique. Since the variable limits to be encountered in this field are water contents of 5 to 200 p.p.m., the general procedure of McKinney and Hall (5) recommending sample sizes between 50 and 150 mg. of water cannot be pursued. The titration of a variable multiphase system as undertaken by Aepli and McCarter (1) leaves much to be desired. The excellent visual titration method proposed by Flowers (3) is usable only with clear, colorless oils and requires a well trained, practiced operator.

Flowers' method consists of a visual titration using from 10 to 200 grams of sample and a titration solvent consisting of 10 ml. of absolute methanol and 50 ml. of dried benzene. To quote, "it has been found necessary to hold the duration of each determination within narrow limits. A stopwatch should be used to time the titration of the blank and the titration of the sample." When samples larger than 30 ml. in volume are used a multiphase system results. For large samples and dark oils the end point becomes difficult to see. With the lighting arrangement and titration care suggested and with a little practice it becomes possible for a trained observer to carry out accurate determinations by this procedure.

Some of the major difficulties that must be considered in the formulation of a satisfactory technique for this determination are:

The actual quantities of water encountered are exception-1 ally small if samples of convenient size are to be used.

2. Many samples are dark colored, limiting the use of a visual titration method.

The Karl Fischer reagent and its decomposition products 3. are generally immiscible with the majority of samples encountered. Addition of methanol alone does not alleviate this condition.

4. The quantity of water present in most solvents that may be employed as titration media is apt to be much greater than that present in the sample itself, necessitating relatively large blanks.

Samples of high water content may be heterogeneous.

The authors' interest in this problem was aroused some time ago because of the difficulties encountered by laboratories cooperating with Committee D-9, Section N, Subcommittee IV, of the A.S.T.M. The work so far accomplished indicates that the Karl Fischer method can be employed satisfactorily for this determination but that adherence to the recommended technique must be unfailing.

REAGENTS AND APPARATUS

Eimer & Amend Karl Fischer reagent and standard water in methanol were used throughout. To enable the use of larger volumes of reagent and thus minimize errors of measurement, the freshly mixed, strong Karl Fischer reagent should be diluted with sufficient anhydrous c.p. methanol and pyridine (best grades available) in ratio 3 to 1, so that the final strength will approximate 1 ml. of Karl Fischer reagent = 2.0 mg. of water. As titration solvent a mixture of anhydrous chloroform and

methanol was found most suitable. Technical chloroform was

found to contain appreciable amounts of moisture. The major portion (to cut down on size of blank) was removed by adding 0.37 kg. (1 lb.) of 6- to 16-mesh freshly dried silica gel to a 11.3-kg. (25-lb.) can of chloroform and letting stand for 3 or 4 days with occasional agitation. The chloroform decanted was found to (contain less than 5 p.p.m. of water. A good grade of c.p. methanol (conforming to A.C.S. specifications) was used. Methanol containing more than 0.02% water (determined by Karl Fischer titration) was rejected, in order to keep the solvent blank at a The solvent blank is compensated for automatically minimum. in the method employed. The use of benzene, ethyl ether, petroleum ether, naphtha, methanol, isopropanol, carbon tetra-chloride, and tetrachloroethane was investigated. The chloroform-methanol system was the only one found satisfactory under all conditions. All titrations carried out in this medium resulted in homogeneous single-phase systems. All types of oils investi-gated as well as the reagent and its decomposition products are soluble in the quantity recommended and troublesome multi-phase liquid-liquid, liquid-solid, or liquid-liquid-solid systems are not encountered.

The qualitative unit alone of the Fisher Senior titrimeter (Catalog No. 9-312) employing the polarized platinum-platinum electrode system was used for indicating the potentiometric end point. The end point is fully as sensitive as that of the dead-stop method of Wernimont and Hopkinson (6). Titrations were carried out in flat-bottomed, extraction-type Pyrex flasks of 250-ml, capacity. The setup was essentially the same as that of Almy et al. (2). A split, two-holed, machined Bakelite stopper was used to prevent contamination by atmospheric moisture.

A stop watch was essential for ascertaining the end points.

PROCEDURE

Best results are obtained with rigid adherence to the following details:

Place 100 ml. of dehydrated chloroform and 25 ml. of anhy-drous methanol in the 250-ml. titration flask and set on the stand with Bakelite stopper, stirrer electrode, and buret for Karl Fischer reagent in position. Adequately protect the buret containing the reagent in position. Adequately protect the buret containing the Karl Fischer reagent from atmospheric moisture with silica gel or other suitable drying medium. Use a Castaloy buret regulator (Eimer and Amend Catalog No. 3-886) to give a consistently uniform dropping rate. Add 15 to 20 drops of Karl Fischer re-agent, turn on stirrer, and then adjust the cathode ray tube (magic eye) control so that the eye is closed. Continue adding the reagent 5 drops (0.1 ml.) at a time. After each addition the eye will open and then slowly close. The end point is reached when the aver remains steadily open for a minimum of 30 seconds when the eye remains steadily open for a minimum of 30 seconds after the reagent has been added. This initial end point represents a blank for the titration solvent and the volume of reagent used need not be recorded. Immediately after this blank is reached, pipet 25 ml. of standard water in methanol into the flask. Do not permit the flask to remain open to the atmosphere longer than necessary. Again titrate to an end point, recording the volume of Karl Fischer reagent used. Do not readjust the eye control but leave it as initially set for all subsequent titrations.

In titrating the standard water solution add approximately 80% of the required Karl Fischer reagent rapidly (add 10 ml. if the reagent is of the above recommended strength and if the "1 ml. equals 1 mg." standard water solution is used). Complete the titration by 5-drop additions until the 30-second end point is again reached. The water equivalent of the reagent then may be accurately calculated. Duplicate runs should check to within 0.1 ml. Discard the titrated solution, again add chloroform and methanol to the flask, titrate to a 30-second end point, add the unknown oil sample, and retitrate using 5-drop increments. Samples weighing 40 to 60 grams yield most consistent results. These samples may best be taken by filling a 175-ml. (6-ounce) screw-cap bottle with the sample, weighing to the nearest 0.5 gram, pouring an estimated 50-gram sample into the flask, and ascertaining the exact weight used by difference.

DISCUSSION

Unlike most recent publications on this technique, the authors recommend direct titration with the Karl Fischer reagent. It is

Table I. Decompos	sition of Reagent
Excess Reagent Added	Total Decomposition Time
(after Reaching End Point)	(with Agitation)
ML	Sec.
0.15	175
0.30	295
0.45	425
0.40	400

well known that the Karl Fischer reagent deteriorates on standing. The iodine-consuming reaction, noted by Almy (2) even in completely sealed systems, is accelerated by impurities present in the pyridine. This decomposition necessitates adequate control of the rate of titration for utmost reproducibility. In the commonly used back-titration methods excess Karl Fischer reagent is added to the sample being titrated and the excess reagent is determined by use of standard water in methanol. During the period while the excess Karl Fischer reagent is in contact with the solution its decomposition adds an unknown factor to the problem. The magnitude of the decomposition will depend upon the nature of other materials already present in solution and the length of time required for back-titration.

Obviously, in a direct titration method there will be no excess Karl Fischer reagent until all the water present has reacted. Use of a completely closed titration vessel in this laboratory indicated that in the presence of nothing but methanol and its own decomposition products, decomposition of the reagent did occur, as indicated in Table I.

Titrating with 0.1-ml. increments thus yields an adequate end point before decomposition of the reagent enters the picture.

Because of the nature of this reagent, the authors feel it is inadvisable to attempt to obtain 1-drop end points. Precision of this magnitude is obtainable only with extremely rigid control of conditions. Even with completely closed systems, slight variations in the length of time required to add samples are sufficient to prevent duplication of end points to this degree. Back-titration is dangerous because an additional step is added to the procedure, the titration time is extended, and the effect of decomposition of the reagent and contamination by atmospheric moisture is accentuated.

Actually, in order to assure a perfectly homogeneous titration medium the weight ratio of chloroform to sam-

and the second start of	a way of the literation of the second	
	Table II. Light Oil	of a great state of the second
Weight of	H.O. Found	Deviation from
Sample	nio round	Average
Grama	P.p.m.	P.p.m.
48	61.8	+16.8
60	52.1	+7.2
49 69	57.1 45.1	+12.2 +0.2
67	41 7	- 3 2
50	46.0	+ 2.9
40	70.0	+25.9
72	32.0	- 12.9
59	44.0	- 0.3
42	54 8	T 9.2
74	31.1	-13.8
56	54.0	- 0.9
44	44.9	0.0
52	44.2 20.0	- 0.7
70	32 9	-12.0
47	48.9	+ 4.0
64	41.2	- 3.7
54	30.5	-14.4
56	45.9	+1.0
56	40.3	- 4.0 + 1.0
69	43.0	- 1.9
28	46.2	+ 1.3
66	42.5	- 2.4
46	54.0	+ 9.1
07 65	42.0	- 2.9
62	45.3	+ 0.4
-	44.0	,
A v .	44.9	

ple taken should be 2 to 1. If conditions necessitate the use of oil samples larger than 70 grams, more chloroform should be used in the titration solvent than that recommended above.

Tables II and III represent the data obtainable. A precision of 10% (of the water content) is assured. This precision should be satisfactory, considering the small quantities involved.

In Table II are listed the data for a series of 30 analyses of a light oil.

The samples were taken from a single container and run on successive days, using different strengths of Karl Fischer reagent. Results indicate that there is not a progressive increase in moisture content. Because occasional results are erratic, it is strongly recommended that at least 3 samples be titrated each time and that obviously high results be discarded.

T	able III. Transformer	r Oil
Weight of Sample Grams	H2O P.p.m.	Deviation from Average P.p.m.
	New Transformer Oi	il
77 56 54 44 50 52 41 Av.	$\begin{array}{c} 25.2\\ 34.5\\ 31.4\\ 30.2\\ 29.0\\ 27.9\\ 26.6\\ 29.3 \end{array}$	$ \begin{array}{r} - 4.1 \\ + 5.2 \\ + 2.1 \\ + 0.9 \\ - 0.3 \\ - 1.4 \\ - 2.7 \end{array} $
	Used Transformer Oi	il
47 40 51 84 79 Av.	123.0 118.0 98.0 93.0 102.0 106.8	+16.2 +11.2 - 8.8 -13.8 - 4.8

About 20% of the results obtained deviate from the average by more than 10 p.p.m. The same care was used in handling all samples. No relationship between magnitude of the error and atmospheric humidity could be found, indicating that the exposure while transferring from weighing bottle to titration vessel could not be causing the abnormally high results. The abnormally low results are just as unexplainable. A satisfactory procedure, in the authors' laboratory, has been to run at least 3 samples of all unknowns. The average of all 3 is used if no determination is far off from the other 2.

If any single determination is definitely much higher or lower than the other two it is discarded and the average of the two closer determinations used. If the eight values in Table II, deviating by 10 or more p.p.m. are eliminated, the average of the remaining 22 determinations is 45.8 p.p.m. Using this average and redetermining the deviations the average deviation becomes 6.1%.

The data in Tables III are on samples recently received on a round robin from the A.S.T.M. The precision implied by these results is sufficiently adequate for routine testing of such oils.

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Determination of Ether Vapor in Gaseous Mixtures

Separation and Determination in Gaseous Mixtures Containing Ethylene and Determination of Dissolved Ethylene in Ethyl Ether

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A method for the separation and determination of ether vapor in gases containing ethylene consists of absorption of the ether vapor by hydroferrocyanic acid suspended in 3 to 2 sulfuric acid contained in a single gas pipet. The subsequent determination of oxygen in the dissolved gases recovered is unaffected by previous use of the hydroferrocyanic acid reagent, providing a gas mixture of similar composition has previously been shaken with the reagent.

SINCE ethylene is usually formed in the processes employed for the manufacture of ether, a good method for determining dissolved ethylene is desirable in a complete examination for all possible impurities. It was found that the solution of the problem could be based upon the formation of a compound of low vapor pressure containing ether of crystallization, in particular upon the compound formed between ether and hydroferrocyanic acid (1, 2).

PREPARATION OF REAGENT

Hydroferrocyanic acid was prepared (4) by dissolving 56 grams of potassium ferrocyanide crystals in 100 ml. of hot water, adding 300 grams of crushed ice together with a piece of solid carbon dioxide, adding 400 ml. of concentrated hydrochloric acid, and immediately filtering the white precipitate through a Buch-ner funnel containing some dry ice. The solution was kept at 0° C. during the operation. The filtrate, which soon turned blue, was discarded. The active reagent for ether was then prepared by adding the entire yield of free unwashed acid to 150 ml. of concentrated sulfuric acid under a well ventilated hood. Acconding to Chrotien (3) a stable addition compound with sulfuric acid is formed in the cold. The mixture became warm, evolved hydrogen chloride and possibly some carbon monoxide, and part of the solid went into solution. After further degassing by shaking and suction, 100 ml. of water were added and the mixture was well stirred. A fine white precipitate formed which re-mained in suspension. The mixture was stored in a glass-stoppered bottle and allowed to stand at room temperature. proximately 100 ml. of this suspension of hydroferrocyanic acid in sulfuric acid were decanted into a small single Hempel gas pipet, leaving any coarse crystals behind. If the tubing of the gas pipet other than the capillary tubing was of large diametere.g., 12 mm.—and the precipitate was occasionally stirred by in-troduction of nitrogen through the capillary no trouble was ex-perienced with clogging. The reagent kept well in such a pipet without any special precaution to exclude oxygen.

ANALYSES OF SYNTHETIC GASEOUS MIXTURES

Synthetic gaseous mixtures containing ether vapor, ethylene, and hydrogen were prepared in order to check the accuracy of the analytical separation of ether vapor from ethylene. The admixture of air or oxygen was avoided and mercury was used as the retaining liquid. On analysis of this mixture ether vapor was determined by the hydroferrocyanic acid suspension contained in a Hempel pipet as described above, using 5 passes and shaking the pipet. Ethylene was determined by absorption with 100%sulfuric acid containing nickel sulfate and silver sulfate as catalysts (7), and hydrogen was obtained by difference.

It was found that once the reagent had been saturated with the other gases in the mixture, it became specific for ether vapor. A measured volume of oxygen shaken with the previously saturated reagent was recovered quantitatively. The reagent after stand-

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ing in a single Hempel pipet in contact with air for several weeks showed little if any visible change and was still available for the quantitative absorption of ether vapor. For ether vapor concentrations under 10% the reagent may be used continuously, but for higher concentrations the reagent must be allowed to stand in the pipet for a few hours between analyses if quantitative recovery is desired. Gases recovered in the boiling out method (5) rarely contain more than 3% of ether vapor. The data in Table I illustrate the value of this reagent.

Moreover, the use of the hydroferrocyanic acid reagent to determine the partial pressure of ether vapor in mixtures of ethylene and nitrogen saturated with ether vapor at a low temperature e.g., 0° C.—gave values which agreed with the published values (6) for the vapor pressure of ether at the same temperature. The volume per cent of ethylene in the residual gas as determined by fuming sulfuric acid was found to agree with the value obtained in the original gaseous mixture before saturation with ether vapor, showing that the separation was accurate.

There should be no difficulty in determining small amounts of ether vapor in ethylene—for example, a few tenths of 1%—since the hydroferrocyanic acid reagent is more effective for smaller concentrations of ether vapor. The size of the sample of the volatile solvent can be increased to 500 ml. or a much larger

Table I. Analyses of Synthetic Gaseous Mixtures Containing Ether Vapor, Ethylene, and Hydrogen Found Deviation Constituent Present % % % 6.6 6.6 0.0 Ether vapor Ethylene^a Hydrogen^a 80.0 13.4 80.0 13.4 0.0 $0.0 \\ -0.1 \\ +0.1$ Ether vapor Ethylene Hydrogen 6.6 80.0 13.4 $\begin{array}{r} 6.6 \\ 79.9 \\ 13.5 \\ \end{array}$ 42.4 42.9 14.7 42.3 +0.1Ether vapor 43.0 14.7 -0.1 Ethylene Hydrogen 42.3 42.8 14.9 0.0 Ether vapor Ethylene Hydrogen 42.3 -0.2 + 0.243.0 Ether vapor 42.3 42.1 -0.243.0 Ethylene Hydrogen 43.0 +0.0

^a Triplicate analyses of this mixture gave the same results, but a fourth showed slight deviations as indicated in Table II.

Table II. Recovery of Ethylene and Nitrogen Dissolved in or Mixed with 500 Ml. of Ether

		(0 0., 100 mi		
				Deviation, Ml. of
Nitrogen	Ethvlene	Ethvlene	Deviation.	Ethvlene/100
Addeda	Added	Recovered	Ethylene	Ml. of Ether
Ml.	Ml.	Ml.	Ml.	
0.00	40.00	39.20	-0.80	-0.16
0.00	43 08	41.50	-1.58	-0.32
0.00	41.80	41.05	-0.75	-0.15
0.00	71.80	70.80	-1.00	-0.20
32.00	38.60	38.50	-0.10	-0.02
31.90	39.70	39.50	-0.20	-0.04
32.00	40.00	39.90	-0.10	-0.02

" Nitrogen when added was recovered in each case quantitatively.

volume if the size of bulb A (5, Figure 1) is increased. A gas buret of special design with graduated tubing of small diameter at the lower end would make possible precise determination of a at the lower end would make possible precise determination of a very small volume of ether vapor. The authors made no deter-minations of amounts of ether vapor less than 6.6 volume %, though results indicated that the 0.5 to 3.0% of ether vapor commonly present was satisfactorily removed by the hydroferrocyanic acid reagent (Table II).

Solutions containing ether and known amounts of dissolved ethylene and nitrogen were then prepared and analyzed by the boiling out method (5). The ether vapor was removed from the recovered gases by the hydroferrocyanic acid reagent and the ethylene determined by the method mentioned above. It will be noted in Table II that with a moderate partial pressure of ethylene (55 volume % or less) in the dissolved gases recovered the determination of ethylene is quantitative. The removal of ether vapor in this manner thus makes possible the subsequent determination of ethylene by customary methods and also the determination of total dissolved gas if ethylene is present.

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Determination of Dissolved Gases in Volatile Liquids

A Boiling-Out Method

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A highly satisfactory method for the recovery of gases dissolved in ether and other volatile solvents has been devised, based upon the principle of boiling out in a partial vacuum, using a reflux condenser cooled by dry ice, removing the small amount of residual solvent vapor by chemical means, and transferring the recovered gases to a gas buret for measurement and analysis. .The low temperature employed minimizes the risk of side reactions. Results can be obtained with an absolute accuracy of about 0.03 volume % or better, referred to the volume of the liquid sample for all concentrations of dissolved fixed gases in ether such as air, nitrogen, and oxygen, and for moderate partial pressures of the more soluble gases such as methane in the gaseous mixture recovered.

NE of the oldest methods for the recovery of dissolved gases in aqueous solvents is the so-called boiling-out proc-Many of the methods (1, 3, 6-9) used for the determination ess. of dissolved gases may be regarded as modifications of this procedure. In the present case the dissolved gases in a volatile solvent such as ether are removed by boiling out and evacuation, using an efficient reflux condenser, cooled by a suitable refrigerant. The small amount of solvent vapor remaining is removed by a selective absorbent contained in a gas pipet, thus avoiding the necessity of fractional distillation. The advantages of the present method are: applicability to volatile solvents, minimizing of side reactions and of the decomposition of unstable solvents, use of large samples with consequent greater accuracy, simpler technique, and less expense.

The sublimation method (2) suitably modified was also investigated by the authors and found to have several important advantages-namely, quantitative removal of solvent vapor from the gases recovered, elimination of possible side reactions, avoidance of the decomposition of unstable solvents and of the formation of constant-boiling mixtures, special suitability for the testing of boiled-out solvents for freedom from dissolved gases, and

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better adaptability for semimicroprocedure. However, the method is more complicated and the apparatus and materials are more expensive than in the boiling-out method. At the low temperatures suited for the sublimation of the solvent, some gases, such as carbon dioxide and propylene, may be left in the sublimate. A higher vacuum is required, liquid air or preferably liquid nitrogen is often needed, and large samples are not feasible. The very ingenious method of Swanson and Hulett (8), though well adapted to the determination of dissolved gases in aqueous solutions, is not generally available for the determination of dissolved gases in highly volatile solvents.

APPARATUS FOR THE BOILING-OUT METHOD

The apparatus which is shown diagrammatically in Figure 1 resembles in several respects that of Lorah, Williams, and Thomp-son (3). It is made entirely of Pyrex and consists essentially of a boiling out bulb, A, of 1000-ml. capacity, provided with abulbed reflux condenser, B, which is connected by means of the tube, i_1 , to the Geissler-Van Slyke (11) pump, C, D. i_1 has an internal diameter of 8 mm., is provided with the hump, h, and slopes toward the condenser. The mercury-sealed ground-glass joints, j_2 and j_3 , permit removal of the tube for cleaning. The Geissler-Van Slyke mercury pump includes the expansion cham-ber, C, of about 170-ml. capacity, the trap, D, of about 30-ml. capacity, and a three-necked 500-ml. Woulff bottle, E. The upper bulb of the sampling pipet, F, has a capacity of 100 ml. and the lower bulb a capacity of 100 to 300 ml. or more. The entire apparatus is mounted on a rigid steel frame not shown. sembles in several respects that of Lorah, Williams, and Thompentire apparatus is mounted on a rigid steel frame not shown.

PROCEDURE FOR DETERMINATION OF GASES IN SYNTHETIC SAMPLES

In order to carry out the determination of dissolved gases the Woulff bottle, E, is filled with purified mercury, the three stop-pers of E are securely wired down, and a suitable mercury-filled gas buret is attached at a. All stopcocks and ground joints are lubricated with a special dextrin-glycerol-mannitol lubricant (5) insoluble in ether. In the examination of synthetic samples, pipet F previously calibrated is evacuated by means of a good oil pump and charged with a measured amount of well boiled-out ether of analytical reagent quality and measured amounts of the desired gas or gases. Before ether is admitted to the evacuated pipet, F, tube t_1 is lowered well below the undisturbed surface of the ether and filled with ether by gentle suction on tube t_4 , bringing the first few milliliters of ether into tube t_4 and closing stopcock S_6 . After introduction of the measured amount of well boiled-out ether into F by appropriate adjustment of S_6 , this stopcock is turned so that the unused ether in tubes t_3 and t_4 can be removed. A leveling bulb is now attached to t_4 by pressure tubing, and all air in t_3 and in the pressure tubing is displaced by mercury. The gas is then brought into solution in the ether in Fby pressure exerted on raising the leveling bulb and by shaking. The charged pipet F_i is then attached at j_1 and the annular spaces of j_1 . j_2 , and j_3 are filled with mercury. After all air is expelled from the buret and capillary tube, t_3 , the

After all air is expelled from the buret and capillary tube, t_3 , the entire Geissler-Van Slyke pump, C, D, is filled with mercury above S_3 but below j_3 by application of compressed air at S_5 . A layer of mercury is placed at the bottom of the jacket of the bulbed condenser, B, to protect the rubber stopper. The jacket is then filled with solid carbon dioxide and acetone. With stopcock S_1 open to A, but stopcocks S_8 , S_7 , closed, the apparatus is thoroughly evacuated through S_2 . Stopcock S_2 is now closed and the previously prepared synthetic sample is introduced at S_1 . By means of the Geissler-Van Slyke pump, C, D, operated by compressed air and vacuum at S_5 , the evolved gas slightly contaminated with ether vapor is gradually transferred to the buret. If any liquid ether appears in pump chamber C, stopcock S_4 is turned so that all liquid ether, but no gas, may be transferred to trap D. By means of a coil of slightly heated resistance wire wound around the lower third of the distillation bulb, the frost that collects on the bulb is kept melted for the most part, until no further bubbles of gas collect at the tip of the mercury pump on the upward stroke.

ANALYSIS OF GASEOUS MIXTURE RECOVERED

The gases normally present are nitrogen and oxygen. Small amounts of methane, carbon dioxide, hydrogen, and ethylene

Table I.	Recovery	of	Tank	Nitroge	en Dissolved	in	or	Mixed	with
			75	Ml. of	Ether				

	(0° C., 7	760 mm.)	Deviation MI of
Nitrogen	Nitrogen	Deviation	Nitrogen/100
Added	Recovered		Ml. of Ether
Ml.	Ml.	Ml.	
16.49	16.51	+0.02	$ \begin{array}{r} +0.03 \\ -0.01 \\ -0.11 \\ +0.12 \\ +0.07 \end{array} $
18.01	18.00	-0.01	
19.67	19.59	-0.08	
17.22	17.31	+0.09	
15.42	15.47	+0.05	



Figure 1. Apparatus for Recovery of Dissolved Gases from Volatile Liquids

Table II. Recovery of Carbon Dioxide-Free Air Dissolved in or Mixed with 300 MI. of Ether

	(0° C., 7	'60 mm.)	Deviation, Ml. of Air/100
Air Added	Air ^a Recovered	Deviation	Ml. of Ether
Ml.	Ml.	Ml.	
75.00	75.04	+0.04	+0.01
81.97	81.92	-0.05	-0.02
68.45	68.49	+0.04	+0.01
27.02	27.10	+0.08	+0.03
73.15	73.20	+0.05	+0.02
^a Air recovere	d contained in each c	ase 20.9 or 21.0%	oxygen.

Table III. Recovery of Tank Oxygen Dissolved in or Mixed with 300 MI. of Ether

	(0° C., 3	760 mm.)	Deviation Ml of
Oxygen Added Ml.	Oxygen Recovered Ml.	Deviation Ml.	Oxygen/100 Ml. of Ether
87.63 80.07 40.49	87.69 80.05 40.42	$+0.06 \\ -0.02 \\ -0.07$	+0.02 -0.01 -0.02

may also be present. The ether vapor, which constitutes 0.5 to 3% of the gaseous phase, and any traces of alcohol vapor are first removed by a pipet containing fuming sulfuric acid, or preferably 70% perchloric acid. Solutions formed by the reaction of perchloric acid dihydrate and liquid ether in the ratio of 2 to 1 by volume had a negligible vapor pressure (0 mm. of mercury) at 25° C. as measured in the Van Slyke manometric apparatus. No trouble with explosions was ever experienced in this connection, but the use of an explosion screen is recommended. The gases recovered are determined by customary methods, except that traces of hydrogen are estimated by the method of Zenghelis (12) slightly modified. Ethylene or other unsaturated hydrocarbon gases if present would be removed with the ether vapor. The separation of ether vapor from ethylene will be discussed in another paper (4).

RESULTS

The results for the recovery of dissolved nitrogen, air, oxygen, and methane are given in Tables I to IV, inclusive. The volumes of all gases and gaseous mixtures have been calculated to 0° C. and 760 mm. The ether contained in pipet F was in all cases at room temperature, about 25° C., and the gases were dissolved to as large an extent as possible. The quantitative recovery of the gaseous mixture added was regarded in some cases as sufficiently indicative of the success attained without further analysis. Recovery of the gases above mentioned is highly satisfactory.

INDEPENDENT CHECK ON TECHNIQUE OF SAMPLING

In order to make certain that the error in sampling was negligible, dry carbon dioxide-free air was passed at a slow rate for

Table IV.	Recovery of Methane-Tank Nitrogen Mixtures Dissolved
	in or Mixed with 500 Ml. of Ether

	(0° C.,	760 mm.)	
Gaseous	Gaseous		Deviation, Ml. of Gaseous Mixture/100
Addeda	Recovered ⁴	Deviation	Ml. of Ether
Ml.	Ml.	Ml.	
70.00	69.60 70.20	-0.40 -1.35	-0.08 -0.27
82.47	81.45 74.20	-1.02 -0.90	-0.20 -0.18
75.49	76.02	+0.53	+0.11
40.27	40.22	-0.05	-0.01
16.50	16.52 15 15	+0.02 -0.03	+0.00 -0.01

 \bullet In the first four experiments methane-nitrogen mixture contained 90% methane and in the last five 50% methane.

Table V. Comparison	of Results Obtained Van Slyke Methods	d by Boiling-Out and
	Gas at S.T.P. per M	l. of Ether at 24° C.
Barometric Pressure	Boiling out method	Van Slyke method
Mm. of Hg	Ml.	Ml.
737.5	0.0876	0.0875
739.6	0.090	0.091
741.0	0.0910	0 0915

many hours through analytical reagent ether contained in a 1liter flask immersed in a constant-temperature bath kept at 24°C. The total dissolved gas was then determined by the boilingout method and by the manometric method of Van Slyke (10). Preliminary experiments made with the Van Slyke apparatus had shown that the addition of 2.0 ml. of degassed 70 to 72% perchloric acid to 1.0 ml. of well boiled-out ether reduced the vaporpressure of the mixture to a negligible value and that perchloric acid was preferable to sulfuric acid or phosphoric acid for this purpose. The results are given in Table V.

The agreement between the results obtained by the two widely different methods is sufficient to warrant the conclusion that the error in the technique of sampling in the case of the boiling-out method is negligible.

PROCEDURE FOR ROUTINE DETERMINATION OF GASES IN ETHER OF UNKNOWN GAS CONTENT

In routine work on samples of unknown gas content, pipet Fmay be used as before for the volumetric measurement of the samples of ether, except that no gas of any sort is introduced into the evacuated pipet other than the gases originally present in the ether. If the apparatus is to be used exclusively for the routine examination of ether samples, ground joint j_1 and pipet F may be omitted and 20 cm. or more of 5-mm. glass tubing sealed on below stopcock S_1 . The samples may then be conveniently measured by difference in weight of the original container before and after removal.

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Observations on the Rare Earths

Extraction of Ytterbium from Rare Earth Mixtures with Sodium Amalgam

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UTSTANDING among recent developments in the separation of the rare earth elements are the methods involving direct reduction of certain of the trivalent rare earth ions to amalgams from aqueous solutions. Thus, by electrolytic reduction at a mercury cathode in alkaline acetate solutions containing potassium citrate and potassium carbonate, McCov (5, 6) prepared europium, ytterbium, and samarium amalgams in yields decreasing in this order. By this method, europium was readily removed from rare earth mixtures (6) and ytterbium was extracted with somewhat less efficiency (7). While McCoy was unable to obtain amalgams of the other rare earth elements by this procedure, he did obtain europium, ytterbium, and samarium amalgams by treating acetate solutions containing citrate and potassium carbonate with potassium amalgam (5, 6).

In an important series of papers, Marsh (8-11) showed that the same three elements could be extracted as amalgams by shaking acidic acetate (or chloride) solutions with dilute sodium amalgam, the vigorous reactions in acidic media resulting in more efficient reductions than the milder reactions in the alkaline media used by McCoy. Indeed, under such conditions, Marsh (8) was able to produce amalgams with lanthanum, cerium, praseodymium, neodymium, and gadolinium as well, although the tendencies toward amalgamation were far less with these elements than with

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europium, ytterbium, and samarium. Agitation of acetate solu tions with liquid sodium amalgam with maintenance of a suitable acidity permitted the separation of samarium from its neighbors (9), the separation of ytterbium and purification of lutecium (10), and the isolation of europium (11), all with comparatively high efficiencies.

Reduction procedures previously employed in this laboratory for the separation of ytterbium (1, 13, 14) depended upon the isolation of ytterbous sulfate, but since ytterbous sulfate is appreciably soluble (4), these procedures did not quantitatively remove ytterbium from the other rare earth elements. Application of the sodium amalgam extraction technique of Marsh to some of the authors' materials overcame this lack of quantitative ytterbium removal. While the observations of Marsh were substantiated in their major details, additional results on some phases of the method apparently not investigated by Marsh appeared worth reporting. In addition, a qualitative colorimetric test for ytterbium and a new method for the removal of sodium ion from rare earth mixtures are discussed.

MATERIALS AND APPARATUS

All rare earth materials used were from the stock accumulated at the University of Illinois. Other chemicals were of analytical reagent quality and were used without further purification.

Solid sodium amalgam was prepared from sodium metal and mercury by combination under oil (3). Liquid amalgams were

Direct reduction of ytterbic ion to ytterbium amalgam by sodium amalgam in acidic solutions has been verified as an excellent method for the removal of ytterbium from rare earth fractions and the purification of ytterbium and materials containing ytterbium. In dilute solutions, the efficiency of the extraction is inversely proportional to the coordinating tendency of the anion. In more concentrated solutions, acetates are preferable because of the formation of stable, amalgam-containing sludges in the presence of chloride or perchlorate. Ions, such as nitrate, which are reducible by sodium amalgam must be absent. For most satisfactory results, extractions should be made in the pH range 4 to 6. Dissolution of the amalgams to the green ytterbous ion in acid solution offers a qualitative colorimetric test for the detection of as little as 0.002 gram of ytterbic oxide in a mixture. Sodium salts which accumulate in rare earth materials in these procedures are effectively removed by precipitation of the rare earth elements with ammonium succinate.

prepared from the stock solid by addition of calculated weights of mercury.

All spectrophotometric measurements used for analysis were made with a Coleman Model 10S spectrophotometer equipped with a 10 m μ slit. This instrument was calibrated against pure ytterbium material (13) and against erbium and thulium materials previously analyzed by the National Bureau of Standards. Measurements of pH values were made with a Beckman Laboratory Model G pH meter, the glass electrode of which had been calibrated against a 0.05 M potassium acid phthalate solution.

EXTRACTION OF YTTERBIUM FROM SOLUTIONS CONTAINING VARIOUS ANIONS

Although Marsh found acetate solutions superior to chloride solutions (8), he reported no really comparative studies. Such studies seemed desirable, not only for establishing the optimum conditions for the extraction of ytterbium but also for determining the effects of acid strength and coordinating tendency of the anion upon the reducibility of the cation. The latter seemed of particular importance because the oxidation potentials of metals against their cations are often influenced by the presence of coordinating anions.

From a number of salts, the acetate, dichloroacetate, formate, chloride, and perchlorate were selected as being not only representative but also easy to prepare. The nitrate was excluded because previous experiments had shown that nitrate solutions, or even acetate solutions containing nitrate, yield no ytterbium amalgam when treated with sodium amalgam, probably because of preferential reduction of the nitrate. In addition, alkaline citrate solutions were studied to afford a comparison of the procedure with that of McCoy (5, 6, 7).

Ytterbium acetate, dichloroacetate, formate, chloride, and perchlorate solutions were prepared by digesting 1-gram portions of pure ytterbic oxide with excesses of 1 to 1 acids (concentrated acids diluted with equal volumes of water) on a steam bath until dissolution was complete, evaporating to dryness to remove most of the excess acids, and diluting to 300 ml. A citrate solution was prepared by mixing an acetate solution containing the equivalent of 1 gram of ytterbic oxide with a solution containing 8 grams of sodium citrate and then adding sodium hydroxide to pH 7.

These solutions were extracted with 0.7-gram portions of sodium as 0.1% amalgam for varying lengths of time by vigorously stirring the aqueous and amalgam layers together mechanically at a definite and reproducible rate. The acidities of the acetate, dichloroacetate, formate, chloride, and perchlorate solutions were maintained at pH 4 to 6 by periodic additions of 1 to 1 acids. No acid was added to the citrate solution. The amalgams (all still containing sodium) were withdrawn and completely decomposed by covering with dilute hydrochloric acid and aspirating air through them until mercurous chloride formed. From the resulting aqueous solutions and washings, ytterbium was recovered by oxalate precipitation and determined as oxide.

Plotted in Figure 1 are the yields, expressed as percentage of ytterbium initially present, for acetate, formate, chloride, per-

chlorate, and citrate solutions. Dichloroacetate solutions reacted with sodium amalgam but yielded practically no ytterbium amalgam.

It is apparent that the extent of extraction was inversely proportional to the coordinating tendency of the anion. With perchlorate, chloride, and formate solutions, amalgam formation was the same up to a maximum. Beyond this, however, the stability of ytterbium amalgam in contact with dilute acid increased from formate to perchlorate. Thus the reduction of ytterbic ion to the amalgam seems to be most easily effected in the presence of the most weakly coordinating anion, and coordinating anions appear to render ytterbic ion more resistant to reduction.

Acid strength was apparently without influence upon amalgam formation, since the results for perchlorate, chloride, and formate solutions were nearly the same. Citrate solutions were definitely inferior to the acidic solutions employed. The increased efficiency of Marsh's procedure over that of McCoy is thus indicated.

The appearance of the apple-green color of the hydrated ytterbous ion (indicated by arrows in Figure 1) corresponded closely with the point of maximum extraction. Direct reduction to the amalgam is apparently followed by dissolution of the ytterbium as the divalent material upon excessive contact between the aqueous and amalgam layers. In order to achieve maximum efficiency in actual extractions, amalgamation should therefore be continued only to the appearance of this green color.

The greater desirability of more concentrated solutions for larger scale separations indicated an extension of the extraction technique to these conditions. For this purpose, an oxide mixture, analyzing spectrophotometrically (15) to 69% Yb₂O₃, 6%Tm₂O₄, and 3% Er₂O₃ with undetermined amounts of yttrium and lutecium, was used as a source. Perchlorate, chloride, formate, and acetate solutions, each containing the equivalent of 10 grams of this oxide mixture in 125 ml., were each shaken with a total of 7 grams of sodium as 0.2% amalgam in a 1-liter separatory funnel. Acid was added during each extraction, and in all instances the amalgams contained sodium when withdrawn.

Because of the formation of stable sludges containing the amalgams, perchlorate and chloride solutions were unsatisfactory under these conditions of increased concentration. Acetate and formate solutions gave favorable results, but acetate solutions permitted the more ready separation of aqueous and amalgam layers. After five extractions, each of 1 to 2 minutes' duration, with fresh portions of sodium amalgam, 97% of the ytterbium initially present was removed from acetate and formate solutions. Although extraction at 50° C. was slightly more efficient than at room temperature, the differences were not large.

EXTRACTION OF YTTERBIUM ACETATE SOLUTIONS AT VARIOUS ACIDITIES

To test the effect of hydrogen-ion concentration upon extraction efficiency, acetate solutions containing the equivalent of 1 gram of pure ytterbic oxide in 50 ml. were extracted with 3 grams



Table I. Removal of Ytterbium from Mixtures

Inventory No.	Grams Original	of R2O3 Residue	Number of Extrac- tions	Con Tm I ^a	nposi 12O2 R ^a	tion a Y I ^a	as Per C b2O3 R ^a	ent C Lu I ^a	xide 201 Ra
LU-3 LU-4 LU-5 LU-6 LU-TM-1 T-4b TM-5° ^a I, initia	11.2 74.3 11.6 18.8 39.1 4.6 14.4 l material;	1.52 10.0 0.65 3.13 2.61 1.32 7.04 ; R, residu	5 11 5 4 8 5 3	1 1 3 6 26 47	9 4 17 20 55 88 88	36 61 87 75 87 65 45	<0.2 <0.3 4 5 <4 <1	63 37 12 22 7	91 95 81 74 40

Average atomic weight 156.
 Original mixture contained 7% (La, Y, Ho, Er)₂O_a.

of sodium as 0.1% amalgam until about two thirds of the sodium had reacted in each instance, the solutions being maintained at predetermined pH values by addition of glacial acetic acid. Ex-tractions in pH ranges of 4 to 5, 5 to 6, and 6 to 7 indicated the greatest efficiency and ease of control in the pH interval 5.0 to 5.5. In the pH range 4 to 6, 93.5 to 95.8% of the ytterbium initially present was removed in one extraction, but at higher acidities, premature decompositions of the amalgams gave less extraction. Precipitation of ytterbic hydroxide at pH 6.5 (12) limits extractions to more acid solutions.

SEPARATION OF YTTERBIUM FROM MIXTURES

Several lutecium- and thulium-rich mixtures were converted to acetate solutions by digesting the oxides for several days with dilute acetic acid on a steam bath. The nearly saturated acetate solutions were shaken with 3 to 11 portions of 0.1 to 0.8% sodium amalgam in a separatory funnel for 1 to 10 minutes per extraction, acetic acid being added periodically to maintain acidity. In each instance, the total quantity of sodium used amounted to 1 to 3 times the weight of ytterbium initially present.

The results are presented in Table I. Ytterbium and thulium analyses were made spectrophotometrically upon nitrate solutions (15). Lutecium contents were obtained by difference, since the arc spectra of these samples showed the presence of negligible quantities of rare earth elements other than ytterbium, thulium, and lutecium. The limit of detection of ytterbium by the spectrophotometric method was 0.2 to 0.3% of ytterbic oxide. None of the extracts showed spectrophotometric evidence of thulium.

These data substantiate the observations of Marsh (10). Acetate solutions apparently have sufficient latitude as to the extraction of ytterbium that precise acidity control can be sacrificed on a laboratory scale.

QUALITATIVE DETECTION OF YTTERBIUM

The apple-green color of the hydrated ytterbous ion produced in the decomposition of sodium-ytterbium amalgams with 1 to 2 N hydrochloric acid offers a method for the detection of ytterbium in rare earth mixtures.

To 5 ml. of the nearly neutral rare earth chloride solution in a test tube are added 5 ml. of 0.1% sodium amalgam. The mixture is shaken for about 15 seconds, and about 10 drops of concen-trated hydrochloric acid are added immediately from a buret. The mixture is again shaken for several seconds to remove the bulk of the sodium from the amalgam. As soon as the evolution of hydrogen diminishes, an apple-green color appears if 0.002 gram or more of ytterbic oxide is present. The duration of the green color depends upon the quantity of ytterbium present. Natural and synthetic mixtures yielded green colors lasting from 1 to 2 seconds for 0.002 gram of ytterbic oxide to 2 to 5 minutes for 0.1 gram. The color is most apparent after the bulk of the sodium in the amalgam has reacted.

Although samarium gives a momentary red color (samarous ion) under these conditions, this does not limit the applicability of the test, for mixtures containing appreciable quantities of both samarium and ytterbium are seldom encountered. The green colors of the trivalent praseodymium and thulium ions cannot be regarded as important interferences, for praseodymium-ytterbium combinations are uncommon and the thulium color is apparent only in fairly concentrated solutions. None of the other rare earth ions yields a color under these conditions.

The green color is also developed in acetate and sulfate solu-

tions, but the limit of detection (0.01 gram of ytterbic oxide) is not so favorable. Ions such as nitrate and bromate, which are reduced by sodium amalgam, must be absent, for in their presence ytterbium does not form an amalgam. Larger quantities of sodium amalgam may overcome this difficulty.

RECOVERY OF SODIUM-FREE RARE EARTH MATERIALS

Precipitation of the rare earth elements from extract and residue solutions with oxalic acid removed the bulk of the sodium ion, but appreciable quantities still remained, possibly because of the slight tendency of the relatively small trivalent ions of the heavier members of the rare earth series to form oxalato complexes containing sodium. The sebacate precipitation procedure of Whittemore and James (16) will eliminate sodium held in this fashion, but the precipitates are extremely light and voluminous and are difficult to ignite without loss due to puffing.

Better results are obtained by precipitating with ammonium succinate. A single oxalate precipitation, followed by dissolution of the resulting oxides in nitric acid and two successive succinate precipitations removed all but a trace (enough to yield a sodium flame test of 1 to 5 seconds' duration) of sodium from materials containing more than half their weight of sodium salts. Such succinate precipitates are crystalline, easily removed by filtration, and readily convertible to oxides by ignition. The success of succinate over oxalate precipitation may be due to the reduced tendency of the succinate ion to enter into the chelate rings essential to coordination among such dibasic acid radicals.

Succinate precipitation was best effected by adding three to four times the theoretical quantity of hot 10% ammonium succinate solution to a boiling, nearly neutral chloride or nitrate solution containing the equivalent of not more than 5% rare earth oxides. After digestion overnight on the steam bath, the precipitates were readily removed by filtration and were washed with 2% ammonium succinate solution.

Rough solubility measurements upon succinates prepared from purified rare earth materials indicated that approximately the equivalent of 0.05 to 0.2 gram of rare earth oxide per liter remained in the succinate mother liquors. Solubilities increase with increase in atomic number of the rare earth element. These solubilities are of the same order as the value of 0.0575 gram of yttrium oxide per liter reported for the solubility of yttrium succinate in boiling water (2). Microanalyses indicated the lanthanum and ytterbium precipitates to be La₂(C₄H₄O₄)₈.3H₂O and Yb₂(C₄H₄O₄)₈.9 H₂O, respectively.

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Glass Perforated Plate Distillation Column

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The distillation column described consists of perforated glass plates, downpipes, and plate spacers, which may be inserted without sealing into a glass column-tube. Plates may be inserted or removed as in a packed column, allowing operating characteristics to be varied over a wide range. The column is easily constructed.

PLATE columns (2, 5, 6) have been preferred for many fractional distillation operations in the laboratory because of their large throughput and relatively constant operating characteristics. However, except in the case of the metal sieve plate columns (5), the difficulties involved in their construction have resulted in general use of packed or film-type fractionating columns. The column described in this article employs glass perforated plates which may be easily constructed. These plates may be inserted or removed in a manner comparable to a packed column, allowing the operating characteristics to be varied over a wide range.

DESCRIPTION OF PERFORATED PLATE COLUMN

The column (Figure 1) consists of perforated glass plates, downpipes, and plate spacers (together with baffles in some cases), which may be inserted without sealing into a glass column-tube. Tolerances greater than 0.4 mm. in 25 may be permitted in the plate and spacer diameters, so that the column-tube may be a selected piece of stock tubing. (The selection was based on the outside diameter and the wall thickness at the ends of the tube.) The plates and spacers are held in place by means of a weight sealed to the spacer resting upon the top plate.

The plates are sintered-glass disks, 3 mm. thick and 25 mm. in diameter. When assembled in the column with the spacers, the effective diameter of the top surface is 22 mm. They are provided with 60 perforations, 0.85 mm. in diameter, at radii of 9, 7, 5, 3, and 0 mm., with 24, 19, 10, 6, and 1 hole, respectively. The plates are also provided with a 6-mm. downpipe hole located at a radius of 6.5 mm. The method of making these plates is described below.

The downpipes consist of pieces of 6-mm. tubing shaped as illustrated in Figure 1. The flared end of downpipe C is made by blowing a bubble, 8 to 10 mm. in diameter, flattening one side, and cutting it off at the desired height with an enery wheel. The flap on the bottom is formed by sealing the end and notching it. Except in the tests with the 15-plate column (Table III) the slots faced the wall of the column. The columns using these down-pipes employed a bottom downpipe with a liquid seal. Down-pipe *E* was used in the final test with the 48-plate column (Table IV, B). The weir notch is cut half-way through the rolled rim and is 2 mm. wide. The lower edge of this weir is 1 to 2 mm. above the surface of the plate. When placed in the plate the weir is positioned to face the wall of the column. The bottom end is constricted by fire-polishing and then expanded to 1.5-mm. inside diameter by pushing a rod of this size through while it is still hot. The bottom end is 4 mm. above the plate below. The spacers are made of short lengths of 25-mm. tubing, se-lected to fit the column-tube, 28 mm., as closely as possible without binding. The columns with 50-mm. plate spacing employ a set of three spacers (Figure 1, *B*). Each spacer is 12 mm. long with three knobs sealed to the top, making the effective length approxand cutting it off at the desired height with an emery wheel. The

three knobs sealed to the top, making the effective length approximately 16 mm. In some tests the plates are baffled by sealing a plate of glass in the center of the spacer resting upon the plate. The baffle and spacer are at least 3 mm. higher than the overflow The baffle and spacer are at least 3 mm, higher than the overflow weir. Figure 1, C, shows a baffle permitting flow around both ends. Weirs 5 mm, high are provided at the ends of this baffle. Figure 1, D, shows an around-the-end baffle; the clearances at the ends are 1 to 2 mm. The spacers used in the 48-plate, spaced 26 mm., column (Figure 1, E) are constructed from a 23-mm. length of tubing. This tube is slotted 5 mm. from the bottom, leaving two sections of wall, 4 mm. wide, for support. The out-side edges of these sections are grooved half-way through. The top of the spacer is slotted in the same manner but at right angles top of the spacer is slotted in the same manner but at right angles to the bottom slots. The slotted section is cut away, leaving two

prongs, which are beveled so that the upper, outside edge does not contact the wall of the column-tube.

The weight used in holding the plates and spacers together con-

The weight used in holding the plates and spacers together con-sists of a short piece of 8-mm. tubing filled with mercury. This is sealed to the spacer resting upon the top plate (Figure 1, F), so that it does not interfere with the liquid or vapor flow. The column is best assembled by dropping the plates (and downpipes) with a spacer resting on the top individually into the column, which is filled with water. The column is held at an angle, so that the downpipe slides into the position desired. The spacer keeps the plate perpendicular to the axis of the tube: angle, so that the downpipe slides into the position desired. The spacer keeps the plate perpendicular to the axis of the tube; otherwise the plate falls askew and tends to wedge in the spacer on the plate below. A more rapid method of assembling is to allow water to flow up through the column at a rate just sufficient to float the plates. The plates and spacers may then be stacked in from the top down. Variations in dimensions of the pieces make it difficult to adjust the water rate correctly. The column is dismantled by floating the pieces out in the reverse manner. is dismantled by floating the pieces out in the reverse manner. The plates and spacers cannot be dropped in or out of a dry tube, as they invariably become wedged.

CONSTRUCTION OF PERFORATED PLATES

The die shown in Figure 2 is used in forming the plates. The three 0.6-cm. (0.25-inch) plates (B, D, E) are drilled with holes corresponding to the perforations and the downpipe hole of the plate. The scale of the die is 15% greater than that of the final plate to allow for shrinkage during the firing. The perforating pins, G, 1 mm. in diameter, and F, 7 mm. in diameter, are soldered into the holes drilled in plate E. The fourth plate, C, 2 mm. thick, is drilled with a 40-mm. hole in the center and is used to hold the ring mold, H, containing the powdered glass, during the perforating operation. H consists of a ring 3 mm. long, whose inside diameter is about 20% larger than the column-tube diameter into which the plate is to be inserted. The outside diameter of the ring mold is such that it may be pressed into the centering hole in

plate C. All four plates are aligned by means of the guide rods, A. The powdered glass is made by grinding scrap Pyrex in a ball mill until it is approximately 350-mesh and finer. The powder is mill until it is approximately 350-mesh and finer. The powder is moistened with water until a coherent mass is obtained. This moistened glass is pressed into the ring mold, *H*, which rests upon a piece of filter paper, and the upper surface wiped smooth with a metal plate. After removal of the filter paper the glass is coated with lubricating oil, the upper surface covered with a piece of tissue paper, and the mass perforated in the die. Plates C and D are lifted off the die together and wiped apart. The perforated mass, after removing the tissue paper, is pushed out of the mold, allowed to dry in the air for 15 minutes, then baked at 600 °C. for 15 minutes in a muffle furnace open to the air, so as to burn out the oil. The powdery disk is rubbed lightly on both sides, to smooth the surfaces and remove any foreign matter, and the holes are blown clear.

The disk is given a final firing in a muffle furnace at 925° C. for 5 to 6 minutes. The firing time, which varies a little with each batch of glass and the manner of forming it, is determined in the following manner: After the disk is placed in the furnace it is observed periodically. During the firing the disk will curl up and then flatten out. It is removed from the furnace 2 minutes after it has flattened out. The disk so formed will be nonporous and about as strong as a solid piece of clear glass. It will have shrunk about 15%. The lines and holes are very sharp and there is no amorant distortion arount for a disk terms of the strength is no apparent distortion except for a slight amount at the outer edge of the downpipe hole. During the firing the disk is sup-ported by a piece of porous clay plate which, in turn, rests upon a piece of refractory material resistant to thermal shock. In general, the clay plate can be used for only one firing, after which it tends to break apart.

The downpipe hole is drilled true and the plate ground to fit the column-tube in which it is to be inserted.

COLUMN DESIGN

SPACERS. The spacers are designed for the purpose of holding the plates apart (and level), retaining the liquid on the plate, and preventing vapor leakage around the sides. Spacers with knobs on both top and bottom allow considerable vapor leakage due to irregularities in the column-tube internal diameter. Spacers without knobs drain the liquid from the plates by "wick action", causing the plates to run dry at relatively high distillation speeds. They would presumably "short out" the liquid which runs down between the column-tube and the spacer.

Spacers consisting of a short piece of tubing with knobs on the bottom edge cause the plate to run dry at low speeds, but this is not serious if the spacer is 12 mm. long, and there is practically no vapor leakage. Spacers consisting of short pieces of tubing with knobs on the top retain the liquid on the plate at very low distillation speeds. There is some vapor leakage around the sides, but this is small if the length of the spacer tube is sufficient for the liquid on the plate to splash over it. This type of spacer is preferred because, in addition to retaining the liquid on the plate at low speeds, it assists in assembling the column. (The spacer with knobs on the bottom permits the plate to fall askew when it is being assembled, sometimes causing the plate to wedge in the column.) No difference in plate efficiency was observed with either of the latter two types.

It was found necessary to make the spacer (without knobs or prongs) between 12 and 25 mm. long. Spacers shorter or longer than this would invariably wedge in the column. Consequently, for plate spacings greater than 30 mm., two or more spacers are necessary. For spacings less than this the single spacer (Figure 1, E) is used. This spacer is simpler to construct than those with knobs sealed on; in addition, the supporting prongs are perfectly level. The wall supports for the bottom slots are set at right angles to the prongs and their outside edges notched to ensure that the liquid which runs down the prongs from the plate above mixes with the liquid on the plate. The prongs are beveled to prevent contact with the plate edge and column-tube wall and decrease the amount of liquid running off the plates by way of the prongs.

These spacers have the disadvantage of retaining some liquid between them and the column wall. However, this liquid has shown no noticeable effect on the distillations made with these columns. It may be that there is sufficient circulation due to wick action to prevent it from being stagnant. This effect is being considered in future work.

DOWNPIPES. The downpipes are constructed to make them independent of their alignment.

A downpipe utilizing a well in the plate below, while having better operating characteristics, would require careful positioning during the assembling. There is the further possibility that some of the plates might get out of line during the handling of the column. The well also has the disadvantage of cutting down the active area of the plates. The important factors of the downpipe are its scaling, stability, and reflux capacity. In order to put this column on the line it is necessary for the plates to be sealed by liquid running from the top plate down.

The downpipe consisting of a 4-mm. tube with a rod inside (column 1a, Table I) was found to be self-sealing at moderate

Table I. Preliminary Tests with Benzene-Ethylene Dichloride

Four plates, spaced 50 mm., were used in all cases except column 4 which had 3 plates, spaced 70 mm. The downpipes shown in Figure 1, C, were used except for column 1. Column 1 employed 4-mm. tubes, open at the end, with a 1-mm. rod inside. The tests were made over the range 55 to 65 mole % benzene and the plate efficiencies based on an assumed relative volatility of 1.08.

Column	Weir Height, Mm.	Plat Di M 0.1	e Effic stillati loles p 0.25	iency, on Ra er Min 0.4	%ª te, n. 0.7	Holdup r M Actual	oer Plate, (l. Theo- retical	Drop per Plate, Mm. of Water
1ab	1	55	60	55		0.9-1.5	1.6-2.7	12-25
2be	5	70	65	65	11	1.9-2.9	2.9-4.9	
2cd 3ab	5 12	75 85	(60) 75	65 70	70	2.5-3.0	3.0-4.3	
3b°	12	70	65	65	85	9 48-9 0	9745	16 95
4.9.0	20	85	75	70	00	5 5_4 5	8561	10-33

^a Efficiencies for baffled plates c, d, f were calculated as if top plate was

^a Efficiencies for ballet and the set of the set of

/ Bottom 3 plates baffled, around-the-end baffle (Figure 1, D). Baffles arranged at right angles to each other.



Figure 1. Inserted Plate Column Arrangements

December, 1945

		Tabl	e 11.	15-Plate	, Spaced 5	0 Mm.,	Column	a	
Distilla	tion Rate ^b	M Per	ole Cent	No. of Plates	Plate Efficiency	Holdup p Actual	er Plate Theo- retical	Pres- sure Drop per Plate	Av. Height of Liquid i Downpipe
Mol./mi	n. L./hr	. <i>x</i>	y		%	Ml.	Ml.	water	Mm.
				Carbon Te	trachloride-	Benzene			
0.05	0.3	21.2	56.6	13.5	90	2.1	2.3	15	23
0.09	0.5	$20.5 \\ 21.7$	55.7 54.9	$13.3 \\ 12.6$	89 84	2.2	$2.5 \\ 2.7$	15	23
0.28	1.6	23.0 26.2	53.5 52.8	11.5	77 (66)	$2.5 \\ 2.5$	3.3	18	25
0.40	2.3	23.5	52.8	10.9	73	2.6	3.6	20	27
0.55	3.2	23.9	50.9	9.9	66	3.0	4.6	0.4	20
0.62	3.6	23.7 23.7	50.0 50.0	9.6	64 64	2.8	4.8	29	37
			7	-Heptane-	Methyl Cy	clohexane	-		
0.13	1.1	37.2	59.6	11.5	77				0.0 2.1
$0.21 \\ 0.33$	1.8	33.7	55.6 53.6	11.4	76 62		11		
0.50	4.3	35.6	52.1	8.5	57 54				
4 Same	U. 08 0. U 00. I 00. I 04								
• Mean	sured at b	ottom of	colum	n.					
e Heig	nt above p	nate Delo	w.						



distillation rates but was unsatisfactory because of its low capacity. The downpipe consisting of a 6-mm. tube with a flap over the bottom (Figure 1, C) was used in all the tests except with column Ia and the final ones with the 48-plate column (Table III, B). This downpipe requires that the column be put on the line by flooding the top of the column and then scaling the plates by turning the still heat off and on. It has the disadvantage that if any plate unseals the column goes off the line and the liquid condensate floods out the top of the column. No trouble was ever occasioned by a plate unsealing when the overflow weirs were 10 mm. or higher. These downpipes were also satisfactory for smaller weir heights at high distillation rates; however, they would invariably unseal at distillation rates less than 1 liter per hour unless very carefully made. Unsealing is caused by the liquid overflow entraining a vapor bubble into the downpipe. If the vapor bubble is large enough the downpipe would become vapor-locked and the liquid flow stop. In some cases the liquid would back up in the downpipe, sucking in a vapor bubble and unsealing the plate.

The downpipe with a constriction at the bottom (Figure 1, E) was found to be stable at all distillation rates and weir heights. Its important characteristic is that it is self-sealing at high distillation rates, the limiting rate being determined by the degree of constriction. A constriction of 1.5-mm. inside diameter, used here, self-seals at 2 liters per hour when used with *n*-heptanemethyl cyclohexane and has approximately the same capacity as the other type (Figure 1, C). The notched weir used with this downpipe has better operating characteristics than the horizontal overflow weirs. The liquid overflow does not entrain any vapor bubbles and there is less buildup of liquid on the plate with increasing distillation rate. It also takes up less space, making it easier to use with baffled spacers.

EXPERIMENTAL

The various columns were tested using the arrangements shown in Figure 1.

The four- and three-plate column, used for the preliminary tests, was insulated by a single glass heating jacket. The 15and 48-plate columns were insulated by the heating jacket previously described (β). The 48-plate column assembly is pictured in Figures 3 and 4. The heat was supplied by either a bare wire immersion heater or by an external heating element wrapped about a 120-mm. length of 30-mm. tubing sealed at an angle to the bottom of the still flask.

All tests were made at total reflux. Equilibrium samples were collected by allowing the reflux to flow both over and through the top and bottom receivers (only the bottom receiver shown in Figure 1, A). The distillation rate, in liters per hour of liquid at the boiling point, was determined at the bottom of the column



The rate in moles per minute was calculated using 85, 95, and 140 ml. per mole for benzene-ethylene dichloride, carbon tetrachloride-benzene, and n-heptane-methyl cyclohexane, respectively. The operating holdup (not including nondrainable liquid) was determined by the method of Oldershaw (7). The pressure drop through the column was measured by a manometer tube attached to the sampling line of the bottom receiver.

tube attached to the sampling line of the bottom receiver. The ethylene dichloride and benzene used in the preliminary tests (Table I) were unpurified reagents. The benzene, carbon

tetrachloride, and methyl cyclohexane (Tables II and III) were purified by fractionation in a 25-mm. column packed with 120 cm.



Figure 3. 48-Plate, Spaced 26 Mm., Column



The compositions of the various samples were determined from their refractive indices as measured by an Abbe refractometer. The data of Rosanoff and Easley (8) on benzene-ethylene dichloride and carbon tetrachloride-benzene and of Bromiley and Quiggle (1) on *n*-heptanemethyl cyclohexane were used in calculating the mole per cent.

The number of plates were determined by Fenske's equation (3):

 $n = \log \{ [(y)/(1 - y)] \times$ $\lfloor (1-x)/(x) \rfloor \rbrace \div \log \alpha$

where x = liquid leaving the bottom plate, mole % more volatile

> y =liquid entering the top plate, mole % more volatile

= relative volatilα ity

For the systems benzeneethylene dichloride and n-



Figure 4. Close-Up of 48-Plate Column

Indicating spray height with 1- to 2-mm, weirs when distilling carbon tetrachloride-benzene at 0.35 mole per minute (Table III, B)

Calgor	Table IV.	Number o	of Plates vs. C	ompositi	on			
(Referred to 5 mole %)								
	Ca: [α =	bon tetrac = $1 + 0.0$	chloride-Benzei 0238 (91.8 -	1e x)]				
%	n	%	n	%	n			
6 7 8 9 10	$1.0 \\ 1.9 \\ 2.7 \\ 3.4 \\ 4.1$	31 32 33 34 35	$12.9 \\ 13.2 \\ 13.6 \\ 13.9 \\ 14.3$	56 57 58 59 60	22.623.123.724.224.8			
11 12 13 14 15	$\begin{array}{r} 4.7 \\ 5.2 \\ 5.8 \\ 6.3 \\ 6.7 \end{array}$	36 37 38 39 40	14.615.015.315.716.0	61 62 63 64 65	25.426.026.627.328.0			
16 17 18 19 20	7.27.68.18.58.9	41 42 43 44 45	$16.4 \\ 16.8 \\ 17.1 \\ 17.5 \\ 17.9$	66 67 68 69 70	$28.7 \\ 29.5 \\ 30.3 \\ 31.2 \\ 32.1$			
21 22 23 24 25	9.39.710.010.410.8	46 47 48 49 50	$18.3 \\ 18.7 \\ 19.1 \\ 19.5 \\ 19.9$	71 72 73 74 75	$33.0 \\ 34.1 \\ 35.2 \\ 36.4 \\ 37.7$			
26 27 28 29 30	$ \begin{array}{c} 11.1\\ 11.5\\ 11.8\\ 12.2\\ 12.5 \end{array} $	51 52 53 54 55	$20.3 \\ 20.8 \\ 21.2 \\ 21.7 \\ 22.2$	76 77 78 79 80	$39.1 \\ 40.7 \\ 42.4 \\ 44.3 \\ 46.5$			

heptane-methyl cyclohexane, average values of α were employed. In the case of carbon tetrachloride-benzene, where α varies with composition, the theoretical plates for any composition referred to 5 mole % liquid leaving the first plate were calculated (Table IV). The theoretical plates for any run are the difference in values corresponding to the top and bottom sample compositions.

Benzene-ethylene dichloride was arbitrarily assumed to have a relative volatility of 1.08 over the range of compositions used in the tests (55 to 65 mole % benzene), so as to make the results comparable to those for carbon tetrachloride-benzene. The value of 1.083, recommended by Griswold (4), was used for the relative volatility of *n*-heptane-methyl cyclohexane. For the system, carbon tetrachloride-benzene, the relative volatility was taken to be:

$\alpha = 1 + 0.00238 (91.8 - x)$

where x = mole % carbon tetrachloride. The average deviation of log α calculated from the above relationship is 6% from the logs of the ob-served values of Rosanoff and Easley (8) over the range of compositions, 10 to 70 mole % carbon tetrachloride.

PLATE EFFICIENCIES

Plates with 1- (column 1a) and 5-mm. weirs (column 2a) were found to have plate efficiencies of 55 and 65% (Table I), respectively, when tested in a fourplate column with benzene-ethylene dichloride (relative volatility assumed to be 1.08). Weirs of 12 (column 3a) and 20 mm. (column 4a) gave the same result, having efficiencies varying from 85 to 70% with distillation rates of 0.1 to 0.7 mole per minute. The use of baffles permitting liquid flow around both ends (columns 2b, 2c, and 3b) had little effect in the case of the 1- and 5-mm. weirs, and decreased the efficiency 15 to 5% in the case of the 12-mm. weirs. However, around-the-end baffles (column 3d) increased the efficiency of the latter 5 to 15% over most of the distillation range, the efficiency falling off 5% near the flood point.

Column 3a was checked in a 15-plate, spaced 50 mm., column (Table II) and columns 2a and 1a in a 48-plate, spaced 26 mm., column (Table III) with carbon tetrachloride-benzene and n-heptane-methyl cyclohexane. The results with carbon tetrachloride-benzene were approximately 10% higher than those with n-heptane-methyl cyclohexane. This may be due to inaccuracies in the liquid-vapor equilibrium values used, though it was observed that the plate action was slightly frothier for the latter system. It appears that there is no appreciable liquid entrainment in the vapor stream, since 50- and 25-mm. plate spacings gave the same efficiencies.

It may be that the increase of efficiency with increased weir height is primarily a result of the better mixing of the liquid due to its longer detention time on the plate. Oldershaw (7) obtained efficiencies comparable to column 3d with a liquid holdup similar to column 1a. The method of construction employed by him would be expected to give very even plate action and complete mixing of the liquid, independent of the holdup. The inserted plates, which are not perfectly horizontal and perhaps with slightly irregular perforations, were observed to be only partly active at low distillation rates. (At speeds less than 0.2 mole per minute some of the plates employing 1-mm. wiers would run dry.) This should cause preferential liquid flow and "shorting out" of part of the plate. The effect is most pronounced in the case of the weirs permitting flow around both ends (cf. columns 3a and 3c).

A comparison with Oldershaw's column 4 (7) shows that the same efficiencies were obtained with column 3d. His liquid holdup is much better, being 0.57 to 2.23 ml. per theoretical plate com-

pared to 2.7 to 4.5. The smaller holdup used in his column enables him to use a plate spacing of 25 mm. whereas column 3d requires a minimum spacing of 30 mm. Column 1a (Table III, B) has a similar holdup but an H.E.T.P. approximately 50% greater. This could be decreased by the use of around-the-end baffles.

It is estimated that approximately 16 man-hours are required by the authors to construct a complete 48-plate column (Table III, B), exclusive of the time necessary for making the die and setting up the equipment used. Since this latter factor may be a major handicap to their use, the G. Frederick Smith Chemical Co., Columbus, Ohio, has offered to make these columns available to those interested.

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A New Mercury Manometer

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THE simplest and most generally used type of manometer for organic work is the closed-end U-type mercury manometer. However, it is somewhat difficult to fill (4), and an even worse drawback is the fact that it must be cleaned and refilled or boiled out periodically because of the accumulation of air bubbles in the closed end (5).

Rechenberg (3) has devised a more intricate manometer of this type which overcomes these difficulties to a large extent, and Zimmerli (5, 6) has improved and modified it to make it more practical. This latter manometer is, however, much larger than the original U-type, and consequently unwieldy. In addition, excessive quantities of mercury are needed for its operation. When desired for use in a barostat assembly, it cannot be readily mounted on a small control panel, and when once mounted, it must be removed regularly for tilting in order to remove air bubbles.



It was therefore considered desirable to design a mercury manometer that would be as simple and compact as the closed-end U-type and at the same time could be rid of air bubbles without emptying or dismantling from a stationary setup. After numerous experiments with different modifications of Zimmerli's design (5, 6) a suitable model was arrived at. Its construction is shown in the accompanying figure.

The manometer is ca. 200 mm. in height and 45 mm. wide. The arms are constructed of 17-mm. Pyrex tubing and placed 6 mm. apart for easy reading on an etched-glass sliding scale mounted centrally behind them. The bottom is made from 2mm. bore capillary tubing. Height to the bottom is mate from 2 standard taper. The cup is 18 mm. high and of 13-mm. tubing. For the upper connection, 8-mm. tubing is used. The outlet is made from 2-mm, bore capillary tubing. The top of arm A is uniformly tapered down under the cock to

prevent bubbles from collecting anywhere other than at the very The plug of stopcock B is scored slightly on opposite ends to top.

prevent a mercury hammer upon opening. A small amount of Dow Corning Silicone grease is used to lu-bricate the stopcocks. In order to fill the manometer, the requisite amount of pure and dry mercury is added to the unmounted manometer through the cup, with both stopcocks open. The cup is sealed by a stopper, and the manometer evacuated by means of a good pump. By warming gently, or tilting to the horizontal and tapping, the air bubbles are removed. Stopcock A is closed and a slow stream of air allowed to bleed into side B_{\star} The manometer is now ready for use.

Should an air bubble develop at the top of side A, the manom-eter is attached to a vacuum pump with both stopcocks closed. When a good vacuum is obtained, stopcock A is slowly opened A small amount of merclockwise and then counterclockwise. A small amount of mer-cury will be pulled through, and all the entrapped gas removed. In normal use, stopcock A is always kept closed. When enough mercury has accumulated above stopcock A, it is allowed to dropinto side B after releasing the vacuum above the cocks. When under atmospheric pressure, the height of the mercury in side B should be about 20 mm. above the bend. Normal precautions (1, 2) should be taken for high-vacuum work.

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Qualitative Spot Tests for Rubber Polymers

ANECYTICAL IN 1919

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A new color reaction is described which serves to characterize natural rubber, GR-S, and Perbunan. Confirmatory tests included in the same operation distinguish between the remaining commercially important types. For routine assortment of scrap, spot tests are proposed, which are carried out by holding impregnated filter paper strips in the smoke emitted when the sample is branded with a metal rod heated to redness. Color changes indicate the nature of the polymer. Laboratory methods of value in the examination of special samples are also discussed.

TO ELIMINATE processing difficulties and ensure the production of standard natural and synthetic rubber reclaims, the scrap used as the raw material must be carefully segregated. When mold markings are lost, or large consignments of miscellaneous scrap are received, methods for distinguishing between the basic polymers are necessary.

This paper describes a new color reaction which will serve to characterize natural rubber, GR-S, and Perbunan. Confirmatory tests included in the same operation distinguish between the remaining commercially important types. The procedure is sufficiently rapid to be practical in the testing of representative samples from carload shipments, or for establishing the identity of materials on which indecisive results are obtained by less specific methods.

For the routine assortment of scrap, spot tests are proposed which are carried out by holding impregnated filter paper strips in the smoke emitted when the sample is branded with a metal rod heated to redness. Color changes take place which indicate the nature of the polymer. One test distinguishes between natural rubber and GR-S, a second is specific for Butyl, while a third differentiates Neoprene GN, Neoprene ILS, and Perbunan from one another and from the hydrocarbon rubbers. The spot reactions can be carried out very rapidly, and are particularly useful when large numbers of samples must be examined.

Several laboratory methods for the identification of the components of mixtures are discussed. While they require too much time for routine testing, they are of value in the examination of special samples.

In a previous publication (1) a procedure for the identification of natural and synthetic rubbers was described. The test depends primarily on an approximate determination of the pH and specific gravity of the products obtained by destructive distillation of the sample. Although the method is adequate in many applications, the inclusion of color tests to distinguish the hydrocarbon rubbers is desirable. The difference in specific gravity between the pyrolyzates obtained from natural rubber and GR-S is small, and to reproduce the test requires carefully controlled experimental conditions, and occasionally a preliminary extraction to remove organic compounding ingredients.

As reactions can be carried out more conveniently on the pyrolyzates than on the original materials, these were first investigated in order to obtain sufficiently rapid tests for plant control work. Although GR-S contains aromatic nuclei, and natural rubber is purely aliphatic, this distinction does not apply to their pyrolyzates, for while the primary decomposition products of rubber are isoprene and dipentene, a number of aromatics are produced through secondary reactions (7). A more rapid and definite distinction can be made by reacting the pyrolyzates with materials capable of condensing with compounds containing labile hydrogen atoms. Of the reagents investigated, *p*-dimethylaminobenzaldehyde was found to be the most effective, and yields colored condensation products with the distillates from a number of polymers, which are sufficiently characteristic to serve as criteria of identity.

The reaction is carried out by distilling the pyrolyzate from a rubber sample into a dilute alcoholic hydrochloric acid solution of the aldehyde. An initial color is produced which is intensified and altered by diluting the reaction mixture with methanol and heating on a water bath. The distillate from natural rubber produces an intense violet-blue, and that from GR-S a green. Perbunan yields a red product, neoprene a yellow-green, and Butyl a blue-green of comparatively low intensity.

The pyrolysis test previously described (1) has been rearranged to include the aldehyde reaction. The indicator and buffer systems are completely revised, but accomplish essentially the same purpose as those described in the earlier paper. The alkalinity test for Perbunan and the drop test for natural rubber are omitted, as the aldehyde reaction is more specific.

Solution I contains *p*-dimethylaminobenzaldehyde in dilute alcoholic hydrochloric acid to which hydroquinone is added as a stabilizer. The specific gravity is adjusted to 0.851 with ethylene glycol, so that Butyl rubber can be distinguished from the other polymers by the low density of its pyrolysis product. Solution II contains Metanil yellow and bromocresol green in a citrate buffer. The initial color is green, which changes to yellow in the presence of acetic acid and to red in the presence of hydrochloric acid. These color changes are used for distinguishing polymers which yield organic acids and those which contain chlorine, from one another, and from materials which give neutral or alkaline products on decomposition.

In place of the previously specified heating element and quartz tubes, 10×75 mm, soft glass test tubes heated with a microburner are employed. This is made possible by the fact that the color tests do not vary as widely with respect to experimental conditions as the drop tests. The tubes are inexpensive and can be discarded after one use. In addition to the added speed and con-





I. Natural rubber. II. 50-50 rubber-GR-S mixture. III, GR-S

venience of making the tests, a smaller sample is required, which is often of importance in the analysis of surface coatings or other materials which are available only in small quantities and must be laboriously removed from the supporting fabric.

Table I describes the reactions which occur when the decomposition products from the compounded polymers are distilled into the test solutions. In the case of the aldehyde reaction, both the initial color and that obtained after dilution and heating are listed. The table includes the types in most common use, and two simple mixtures, in which both components are present in considerable amounts.

REAGENTS

SOLUTION I. Dissolve 1.0 gram of *p*-dimethylaminobenzaldehyde and 0.01 gram of hydroquinone in 100 ml. of absolute methanol. Add 5 ml. of concentrated hydrochloric acid and 10 ml. of ethylene glycol. Adjust the specific gravity to 0.851 at $25^{\circ}/4^{\circ}$ C. by the addition of a calculated amount of solvent. The reagent is stable over a period of several months when stored in a brown bottle.

SOLUTION II. Dissolve 2.00 grams of sodium citrate, 0.20 gram of citric acid, 0.03 gram of bromocresol green, and 0.03 gram of Metanil yellow in 500 ml. of distilled water.

PROCEDURE

Place approximately 0.5 gram of the sample in a 10×75 mm. test tube and attach a 4-mm. outside diameter side arm by means of a cork. Suspend the tube by a wire from a ring stand and heat with a microburner until the sample begins to decompose. Avoid localized overheating to prevent softening of the glass.

When vapors appear at the mouth of the side arm, immerse the end beneath the surface of 1.5 ml. of solution II contained in a 10 \times 75 mm. tube. After it is evident whether a color change will take place or not, remove the tube and continue the distillation into 1.5 ml. of solution I. Permit the tubes to cool for a minute or two and shake. Note the position of the droplet in solution I and the color changes which take place. Transfer solution I to a 16 \times 150 mm. test tube and add 5 ml. of absolute methanol. Heat on a water bath at 100° C. for 3 minutes and note the color which develops. A description of the reactions obtained is given in Table I.

If the absence of other interfering polymers has been established by the above test and the principal interest lies in the detection of natural rubber and GR-S, repeat the experiment on a 0.2to 0.3-gram chloroform-extracted sample. Collect the total distillate under 1.5 ml. of solution I and note the color of the solution before and after heating. If a blue-green to green-blue color is obtained, it is probable that the sample is a rubber-GR-S mixture or a natural rubber reclaim. Test for the presence of crude rubber by the Weber method (1), and if necessary confirm the presence of GR-S by the coupling procedure (8).

Table I. Pyrolysis Tests							
strength and show the	Solution	n I	Solution II,				
Material	Initial color	Color after heating	Color				
Blank Polyvinyl chloride Neoprene GN	Pale yellow Yellow Yellow	Pale yellow Yellow Pale yellow green	Green Red Red				
neoprene ILS,							
bunan mixtures Perbunan	Orange red Orange red	Red Red	Yellow to red Green				
GR-S	Yellow green	Green	Green				
50 GR-S-50 rubber	Olive green	Green blue	Green				
Natural rubber	Brown	Violet blue	Green				
Butyl Polyvinyl acetate	Yellow (droplet floats) Yellow	Pale yellow green	Yellow				

p-Dimethylaminobenzaldehyde has been used for the colorimetric estimation of pyrrole (4), indole (9), menthol (6), and a number of biological materials. The reaction with pyrrole depends upon the formation of a pyrrolenine compound which gives a deep red color in hydrochloric acid solution (3, 10). No attempt has been made to isolate those compounds in the pyrolyzates of the elastomers which give rise to the colored products. However, it is evident that the reaction depends upon the production of compounds containing labile hydrogen atoms which react with the aldehyde with the elimination of water to form colored salts of the type



On the addition of alkali the solutions become yellow, but on acidification the initial colors reappear. On prolonged standing fading takes place. This is particularly noticeable in the case of natural rubber where the solution changes from violet-blue to violet during the course of a few hours.



Figure 2. Absorption Spectra of p-Dimethylaminobenzaldehyde Reaction Products with Polymer Pyrolyzates

Perbunan. II. Neoprene

Absorption curves of the reaction products of the pyrolyzates obtained from vulcanized chloroform-extracted samples are shown in Figures 1 and 2. The optical measurements were made with a Beckman spectrophotometer, and the specific extinction coefficients calculated from the weights of the distillates and the dilutions employed. The curve for natural rubber exhibits a maximum at 550 m μ , and that for GR-S a maximum of approximately one-half the intensity at 620 m μ . Composite curves are obtained on mixtures of the two polymers, the shape of the curve depending upon the percentage composition. The reaction product obtained from Perbunan has an intense band at 540 mµ, while that from neoprene absorbs weakly at 540 and $635 \text{ m}\mu$. The curves are not quantitatively reproducible, but the differences in absorption between the products obtained from the various polymers are sufficient to allow for accurate identification over a wide range of compounding.

The wave lengths at which maximum absorption takes place are independent of the state of cure, although in general more intense colors are obtained from vulcanizates than from crude polymers. A series of natural rubber samples in which the sulfur content was varied from 1.5 to 12 parts produced colors differing only in intensity from that obtained from pale crepe.

By making absorption measurements at 550 and 620 m μ on the qualitative test solutions obtained in the analysis of natural rubber, GR-S, and Perbunan, density ratio values characteristic of

Table II. Density Ratio	Values of Qualitativ	e Test Solutions
Composition	R (Extracted)	R (Unextracted)
Crude Perbunan Compounded Perbunan Reclaimed Perbunan Pale crepe	3.18 2.56	3.21 2.83 2.04 1.46
Grade F camelback 50 rubber-50 GR-S Grade C camelback	1.42 1.23 1.11 1.14 0.90	1.43 1.30 1.10 1.10 0.89
Compounded GR-S Grade A camelback GR-S reclaim	0.74 0.73 0.82	0.74 0.72 0.73 0.75

the polymers can be obtained. These serve as numerical indexes of the reproducibility of the test and can be used in the evaluation of interfering substances. If the measurements are made on solutions of the same concentration at both wave lengths, the ratio of the optical densities will be independent of absolute concentration if the validity of the Beer-Lambert law is assumed.

$$= \frac{\left(\log\frac{I_0}{I}\right)550}{\left(\log\frac{I_0}{I}\right)620}$$

R

Measurements made on a series of diluted test solutions with a Lumetron colorimeter using monochromatic filters of $30 \, \text{m}\mu$ band width indicate that the density ratio varies from 0.7 to 0.8 for GR-S, from 1.3 to 1.6 for natural rubber, and from 2.8 to 3.3 for Perbunan. Intermediate values are obtained on mixtures and reclaims.

Typical ratios obtained on extracted and unextracted samples are shown in Table II. Each value represents the average of four independent determinations on the same sample. The standard deviations are 0.11 for Perbunan, 0.04 for natural rubber, and 0.02 for GR-S. While chloroform extraction may result in a change in ratio, the change is usually not great enough to alter the color of the solution.

It can be shown that the density ratio of the solution obtained from a binary mixture can be calculated from the percentage composition and the relative extinctions of the components, providing it is assumed that the reactive constituents are produced in the same proportions in which the polymers occur in the sample. Where K_{λ} and L_{λ} are the relative specific extinction coefficients of natural rubber and GR-S, and P is the per cent GR-S, this equation takes the following form:

$$R = \frac{100 K_{550} + P (L_{550} - K_{550})}{100 K_{620} + P (L_{620} - K_{620})}$$

If a value of unity is arbitrarily assigned to K_{550} , the remaining constants can be evaluated from the density ratios of solutions prepared from the pure materials and a mixture of known composition. While the reproducibility of the test does not justify an exact method of calculation, the relationship is useful in establishing the range of applicability of the color reaction. If a density ratio difference of 0.2 is the smallest which can be visually observed, it can be calculated that the limit of detection of GR-S in the presence of natural rubber is about 35%, while the limit of detection of natural rubber in the presence of GR-S is about 20%.

SPOT TESTS

When time is not an important factor, the pyrolysis procedure described above is recommended. However, when large numbers of samples must be tested, the use of spot methods has been found convenient. The general procedure is to dip a prepared indicator paper into a wetting solution and hold it in the smoke which is emitted when the sample is branded with a metal rod heated to redness. A characteristic color reaction is obtained in 4 to 6 seconds.

For the detection of neoprene and Perbunan, the papers are impregnated with Metanil yellow and cupric acetate and dipped in an alcoholic solution of benzidine dihydrochloride prior to use. If the polymer contains chlorine, a red color is produced by the action of the liberated hydrochloric acid on the acid-base indicator. This will ordinarily serve as a test for neoprene or poly-vinyl chloride, although other chlorine-containing polymers give similar results. If the sample is Perbunan or a polymer containing nitrile nitrogen, a green color appears due to the pres-This ence of cyanide radicals in the decomposition products. This reaction, which takes place in the presence of benzidine and copper acetate, has been widely used for the detection of hydrocyanic acid in air (5). The color is normally blue but is modified to a green by the color of the acid-base indicator. If substantial amounts of both chlorine and nitrile nitrogen are present as in Neoprene ILS, and neoprene-Perbunan mixtures, both colors appear in bands on the filter paper strip, the green color appearing on the wet zone, and the red color most prominently on the dry portion of the paper. In the presence of the hydrocarbon rubbers no color changes are observed, although the paper may darken on drying. The presence of GR-S or natural rubber in admixture with either of these types does not alter the results obtained by the test, but the appearance of the colors may be delayed by dilution of the active constituents.

Butyl rubber is distinguished from natural rubber and GR-S by the use of blank filter paper strips which are immersed in a solution of mercuric sulfate in dilute sulfuric acid prior to making the tests. The pyrolyzate obtained from Butyl yields a brilliant yellow color, while rubber and GR-S produce dull browns. The test depends on the presence of isobutylene in the decomposition products, which reacts with mercuric sulfate to form a complex with empirical formula corresponding to $C_4H_8(HgSO_4,HgO)_3$ (2).

The most useful test in the series is that which distinguishes natural rubber from GR-S. The materials required are prepared indicator paper strips impregnated with p-dimethylaminobenzaldehyde, and a 30% solution of trichloroacetic acid in isopropanol. A strip of indicator paper is dipped in the acid solution and held in the smoke emitted when a hot rod is held against the surface of the polymer. Rubber produces an intense blue coloration and GR-S a green. Mixtures containing equal parts of the two substances test as GR-S, although the green may be modified to a blue-green. Samples containing 25 parts and less of GR-S test as natural rubber. The principal difficulty is caused by indecision in the classification of mixtures. The test is of value only for distinguishing GR-S from natural rubber, as the other polymers also give color reactions. While by careful observation, it is possible to distinguish some of the other types, more specific tests are preferred. Butyl produces a blackish coloration which fades to a pale lavender on standing 3 to 4 minutes. Perbunan produces a green color, but if the paper is held close to the heating unit until dry, a reddish brown spot appears. Neoprene gives a reaction almost indistinguishable from that of GR-S. Although the reaction is not specific, it may be used without supporting tests in many instances where it is only necessary to distinguish between natural rubber and GR-S.

A summary of the reactions obtainable by use of the spot tests is shown in Table III. If the origin and most probably composition of the sample are unknown, the pyrolysis procedure is recommended. However, if a distinction must be made between a limited number of possibilities, the spot tests offer definite advantages with regard to economy of time and ease of manipulation.

APPARATUS

The tests can be conveniently carried out by use of a triangular file heated to redness in a Bunsen flame. When large numbers of samples are to be tested or where the presence of an open flame is undesirable, an electrically heated nickel-chromium knife can be employed. Units adaptable to the purpose are available from the Sta-Warm Electric Company, Ravenna, Ohio. The blade should be curved so that it can be easily applied to the surface of the rubber and the end filed to a width of about 1 cm. to decrease the heating area and increase the temperature. When operated at a dull red heat, a test can be obtained in 4 to 6 seconds. The organic residue burns off between applications, and the inorganic deposit which slowly accumulates can be scraped off with a file.

INDICATOR PAPERS AND REAGENTS

NEOPRENE-PERBUNAN TEST. Dissolve 2.0 grams of cupric acetate and 0.25 gram of Metanil yellow in 500 ml. of methanol. Impregnate filter paper squares with the solution, dry, and cut into strips. Dissolve 2.5 grams of benzidine dihydrochloride in a mixture of 500 ml. of methanol and 500 ml. of water. Add 10 ml. of a 0.1% aqueous solution of hydroquinone. Store in a brown bottle. A precipitate forms on standing, but if the solution is protected from light and air. it can be used for several months.

bottle. A precipitate forms on standing, but if the solution is protected from light and air, it can be used for several months. BUTYL TEST. Use blank filter paper strips. To prepare the wetting solution, add 5.0 grams of yellow mercuric oxide to a mixture of 15 ml. of concentrated sulfuric acid and 80 ml. of water. Bring to a boil and continue heating until the oxide dissolves. Cool and make the volume up to 100 ml. with water.

RUBBER-GR-S TEST. Impregnate filter paper squares with a solution of 3 grams of p-dimethylaminobenzaldehyde and 0.05 gram of hydroquinone in 100 ml. of ethyl ether. Dry and cut into strips. Papers stored in brown glass bottles show no discoloration and retain their activity after several weeks' storage. On prolonged storage under adverse conditions, the aldehyde oxidizes and the tests become progressively less distinct. To prepare the wetting solution, dissolve 30 grams of trichloroacetic acid in isopropanol and make the volume up to 100 ml. This solution must be used with care, and contact with the skin should be avoided.

Table III. Spot Tests							
	Neoprene- Perbunan Test	Butyl Test	Rubber– GR-S Test				
Neoprene GN Perbunan Neoprene ILS	Red Green		1111				
neoprene-Perbunan mixtures Butyl Natural rubber GR-S	Red/green Blank Blank Blank	Yellow Brown Brown	Blue Green				

PROCEDURE

Wet a 1-cm. section of the test paper with the corresponding impregnating solution and hold it in a parallel position about 5 mm. from the surface of the heating element which is pressed against the rubber sample. If the evolution of vapor is sufficiently rapid, an adequate test is obtained in 4 to 6 seconds. In testing for natural rubber and GR-S, it is desirable to continue the test until the color which is formed can be seen through the back of the paper. The hue should be judged from the appearance of the paper facing the heating element. Charring the paper and overdeveloping the color should be avoided.

The reactions which are obtained from the various polymers, using the three types of indicator papers, are summarized in Table III.

DETECTION OF MIXTURES

A general procedure for the detection of mixtures requires more specific and detailed methods than those described. However, by careful observation of the results obtained by the pyrolysis procedure, it is frequently possible to detect deviations from normal behavior which will indicate the need for a more complete analysis.

Compounds containing natural rubber and GR-S present in approximately equal amounts yield green-blue reaction products which are readily distinguishable from those of the pure materials. The test is not applicable to compounds in which the minor constituent comprises less than 25 to 35% of the total polymer, as the colors are difficult to match and may be simulated by the presence of other materials. Natural rubber reclaims produce greenblue to blue colors which differ in appearance from those obtained on compounds based on crude rubber and may suggest the presence of GR-S as the minor constituents of a mixture. In such cases more specific tests must be applied to make identification certain. Experiments on samples of known composition indicate that the Weber test (1) can be used to detect natural rubber in the presence of GR-S, neoprene, and Perbunan. Positive reactions are obtained from natural rubber (Hevea), guayule, and balata. A violet color of low intensity is obtained on testing polyvinyl acetate. Natural rubber reclaim gives a red-violet color which is distinguishable from the opaque blue-violet obtained on testing samples containing crude rubber.

A qualitative test for GR-S in the presence of natural rubber is described in a recent publication (8). The extracted sample is nitrated, reduced, and diazotized. The formation of a crimson azo dyestuff on coupling with β -naphthol indicates the presence of GR-S, or more generally, the presence of a polymer containing aromatic groups. The method is of value whenever a laboratory procedure can be used and will serve to establish the presence of GR-S in small amounts.

Perbunan is readily detected in the presence of neoprene by the reaction with p-dimethylaminobenzaldehyde, as the intense red color masks the yellow-green of the neoprene (Figure 2). On testing Neoprene ILS which contains both nitrile nitrogen and chlorine, positive tests for both groups are obtained in the initial pyrolysis procedure. The acid-base indicator confirms the presence of an acidic material in the decomposition products, while the aldehyde reaction indicates the presence of a nitrogenous polymer. Perbunan can also be satisfactorily detected in mixtures by the copper acetate-benzidine reaction or by the Prussian blue test (1).

The presence of neoprene as a minor constituent in mixtures is established by use of the Beilstein test when the low concentration and the presence of alkaline compounding ingredients obscure the normal acid reaction.

A copper wire is heated to redness and touched to the sample. If, on reheating, a brilliant green color is imparted to the flame, a compound containing chlorine is present. Polyvinyl chloride and other nonvulcanizable polymers can be distinguished from neoprene by extracting the sample with acetone and examining the residue obtained on evaporating the solvent for the presence of a resinous material of high chlorine content. Neoprene is not removed from vulcanized compounds by acetone extraction. This procedure is of general value for distinguishing curing from noncuring polymers when present in mixtures. The choice of the solvent and the method of isolating the extractible polymer from the residue must be decided in each case from a knowledge of the properties of both constituents.

DISCUSSION

The pyrolysis procedure has been applied to compounds prepared in the laboratory, and to a large number of commercial samples, including most of the standard reclaims. The color reactions give more consistent results than the specific gravity tests (1) on unextracted samples, and vary less widely with experimental conditions. When circumstances permit, it is preferable to make the tests on extracted samples, but in many cases this step is unnecessary. The density ratio values (Table II) illustrate the normal variations between extracted and unextracted samples. In most cases the differences are too small to be detected visually, and are less than those obtained on testing extracted samples containing the same polymer taken from different compounds.

The best evidence for the reliability of the test is provided by the successful testing of reclaimed rubbers, for they may be regarded as composite samples of the different types of compounds used within a commodity group. In addition, they are subjected to a devulcanizing process in which considerable amounts of softening agents are added, and which is accompanied by partial degradation of the original polymer.

A number of materials which are commonly found in rubber products yield pyrolyzates which react with *p*-dimethylaminobenzaldehyde (Table IV). While color reactions are obtained on many of them, in general the intensities are of the same order





or less than those obtained from the polymers, and as in the case of natural rubber-GR-S mixtures, a considerable amount of the minor constituent must be present before a noticeable alteration in hue is obtained.

The pyrolysis procedure is preferred for general testing purposes. However, the spot reactions are more convenient when it is necessary to test a large number of samples to confirm the presence of a particular polymer type, such as in the segregation of mixed natural rubber-GR-S consignments, or in the separation of Perbunan and Neoprene ILS scrap from neoprene prior to reclaiming. In some cases it is convenient to use the spot tests for Butyl and neoprene in conjunction with the pyrolysis procedure, and eliminate the pH tests made with solution II. The spot test for natural rubber and GR-S gives well defined results on compounds prepared from pure gum stocks, and can be used in most applications. When the sample is based on a mixture of the two polymers, the intermediate color which is obtained is more easily distinguished when the reaction is carried out in solution. However,

if the sample contains a large amount of cellulose which cannot be separated mechanically before making the test, the spot reaction should be used, as the aqueous products which are formed on decomposition of the cellulose retard the development of the color in alcohol solution.

The tests described provide a rapid, accurate method for the identification of the principal polymer types likely to be present in commercial rubber samples. When mixtures containing considerable amounts of both components are encountered, tests intermediate between those of the pure materials are usually obtained. In some instances a positive identification can be made on the basis of these tests alone; in others, more detailed methods of analysis must be employed.

In the foregoing discussion the reactions of the polymers have been classified under specific types which represent the most commonly used members of groups of closely related materials-for instance, the reactions which serve to classify compounds based on pale crepe are equally applicable to guayule and balata. Most of these reactions, while useful for distinguishing polymers and groups of polymers from one another, provide insufficient evidence for a fundamental proof of structure.

It is possible that the pyrolysis technique can be used for the evaluation of polymers by the application of quantitative methods to the analysis of the distillates. The radicals formed on thermal decomposition should give rise to compounds, the nature of which are predetermined by the structure and composition of the original materials. An application is illustrated in Figure 3. in which the ultraviolet absorption spectra of the pyrolyzates from uncompounded natural rubber and GR-S are shown. The appearance of the absorption bands clearly reflects a difference in composition between the two substances. As the products formed in pyrolytic reactions usually vary with experimental conditions, it is evident that these factors must be carefully controlled before useful data can be obtained. While the optical and chemical properties of the pyrolysis products are of potential analytical interest, the application of quantitative methods is beyond the scope of this discussion.

ACKNOWLEDGMENT

The author wishes to express his thanks to W. J. S. Naunton for permission to describe the qualitative test for GR-S contained in Users' Memorandum U.9 on the "Identification and Estimation of Natural and Synthetic Rubbers".

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Sintered-Glass Valves

Application to Spectrometer Calibration and to Preparation of Known Mixtures

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A method which utilizes sintered disk valves is presented for both the storage and use of liquid and gaseous calibrating compounds and mixtures. A technique also involving a sintered-disk valve is presented for preparing small quantities of liquid mixtures having accurately known compositions. These methods should find considerable application in the calibration and testing in infrared and mass spectrometers, particularly where calibrating compounds are available only in very small quantities.

THE recent application of mass and infrared spectrometers to the analysis of complex hydrocarbon mixtures necessitates the repeated use of large numbers of highly purified compounds for calibrating and testing purposes. At present the methods in use for handling such compounds, which in many cases are available only in small quantities, are only partially adequate and often excessively time-consuming. There appears to be a need for methods of storing and using these calibrating compounds, and for preparing, storing, and using known mixtures of them which would be more rapid than existing methods, would handle liquids as well as gases in a uniform manner, would be free from the disadvantages common to the use of stopcocks, and would tend to conserve the limited supplies of pure hydrocarbons available.

PRINCIPLE OF METHOD. The usefulness of the sintered-glass disk valve for introducing calibrating compounds into a mass spectrometer was originally proposed and successfully demonstrated by Hunter (3). The extension and development of this technique have proved highly successful, and it is felt that the principle may be applied equally well to infrared spectrometers. The control of gas flow by means of such sintered-glass disks has been proposed several times, particularly by Pyrtz (2), Stock (6, 7), and Prausnitz (5). The disks used are porous to gases and liquids in general, but nonporous to mercury. Material may be transferred simply by touching together two sintered disks, thereby displacing the mercury seal covering them and allowing flow to take place through the disks.

APPARATUS AND PROCEDURE

INTRODUCTION SYSTEM AND STORAGE VESSELS. The apparatus shown in Figure 1 consists of three types of storage vessels, A, B, and C, and two alternate types of introduction systems, D and E. A may be used to store both liquids and gases for mass spectrometer calibration, where the amount of material needed is relatively small. For infrared calibration, larger vessels such as B or C may be more suitable for storing gaseous compounds or mixtures. Commercial 10-mm. sintered disks of "F" porosity are used in all these vessels. The disks are covered with mercury to a depth of about 10 mm. to prevent the entrance of air into the vessels. Either D or E may be used in conjunction with the storage vessels for introducing material into the spectrometer inlet system.

Inlet system D consists of a small sintered disk, a, scaled into tubing of 3-mm. outside diameter. The end of a is scaled from the atmosphere by mercury contained in the removable cup, b. Handle c is provided for moving b after the storage vessel is in place around a. A piece of spring wire, d, wound in a helix keeps c fixed firmly in place. Guides e make for easy manipulation of b, when immersed in the mercury scal, and cover f protects the assembly when not in use. This system allows advantage to be taken of the simpler construction of gas vessel B, but suffers the disadvantage of requiring somewhat careful manipulation. System E is considerably more simple in construction and use than D, and is preferred on that account.

The method of introducing calibrating compounds and known gaseous mixtures into the spectrometer with the apparatus described consists of the following steps:

With system D either A or B is brought to inlet device D and held so that the mercury seal of the storage vessel covers b. bis lowered by means of c until its top clears a, and is then swung to one side and raised so that the bottom of b is somewhat above a. A or B is then raised until the two sintered disks touch. When sufficient material has been transferred contact between the disks is broken, b replaced around a, and the storage vessel removed.

With system E, A is completely immersed, except for the handle in the mercury seal of E, and then brought upward until the two sintered disks touch. C is immersed to the point where its mercury seal clears the inlet sintered disk. It is then moved over and upward, thus contacting the two disks and transferring material.

By this procedure no air can enter the spectrometer inlet system; consequently pumping out air between additions of calibrating compounds is not necessary. Compounds having vapor pressures as low as 1 mm. of mercury readily pass through the disks, while flow from tubes filled with gas at 1 atmosphere is easily controlled. Table I shows the approximate rate of flow of gases into an evacuated system through a sintered-glass valve similar to the ones described.



Table I. Approximate Rate of Flow through Sintered Glass Valve into Evacuated System

Pressure in Vessel Mm. of mercury	Flow Rate Cc./mm./minute
$760 \\ 320 \\ 150 \\ 106 \\ 48 \\ 30 \\ 12$	6400 2300 1400 540 440 130 47

A, B, and C are originally filled by distillation through the inlet tubes with the mercury seals in place, following thorough evacua-tion. The tubes are sealed off after freezing the liquid or gas with liquid nitrogen placed around the bottom of A, or the cooling tubes of B and C. When dealing with mixtures mild thermal When dealing with mixtures mild thermal convection should be resorted to in order to assure a completely homogeneous phase. Filling may also be accomplished directly through the disk except when the use of rubber tubing is objectionable and complete evacuation is necessary. With the mer-cury seal in place the vessel is attached to the vacuum system with a short piece of rubber tubing slipped over the sintered disk. The vessel is tilted until the disk is uncovered and then evacuated through the disk. With a pressure on the pump side of 20 to 50 microns the pressure in the vessel can be reduced to approximately 100 microns after 5 to 6 minutes' pumping. Gas samples may then be expanded into the vessel, and the seal replaced by allowing the mercury to cover the disk once more. Liquid samples may be pipetted into a vessel evacuated in this manner, as described under Mixture Apparatus, after removal from the vacuum system. Gas samples which should not be in contact with rubber tubing may be introduced after evacuation as above through a second sintered disk immersed in the mercury seal of the storage vessel. Pumping out may also be accomplished without rubber tubing by using this second sintered disk, but it has been found considerably more time-consuming and for this reason is not recommended.

Figure 2 illustrates a microburet, A, made from selected thermometer tubing. One end is ground to a cone around the capillary, so that contact with the sintered disk, B, is assured. The disk shown is a commercial 10-mm. immersion filter of "F" porosity, covered with a mercury seal to exclude air from the spectrometer inlet system. Thermometer tubing may be obtained to deliver as little as 1.5×10^{-4} ml. per cm. length, and which will experimentally reproduce the volume delivered to within $\pm 0.7 \times 10^{-6}$ ml.

Liquids are introduced by means of the microburet as follows: The top of the buret is fitted with either a rubber medicine dropper bulb or a 1-ml. hypodermic syringe, and an excess of liquid compound over that needed is brought up into the capillary. The buret is taken from the liquid and the bulb or syringe removed. The buret is then inverted momentarily, whereupon liquid will run back from the tip. The conical end is carefully dried and the buret brought slowly back toward the vertical, allowing the liquid to approach the tip. When it just reaches the tip the movement of liquid is stopped by adjusting the angle of the buret and liquid volume is read with the buret tip just above the surface of the mercury seal (Figure 2). The tip is then carefully immersed beneath the mercury surface and the buret brought back to the vertical. The tip of the buret is touched to the sintered disk, whereupon liquid will be transferred from the buret through the disk. Breaking contact between the two stops the flow of liquid, and a final buret reading gives the amount of liquid introduced.

MIXTURE APPARATUS. The apparatus for preparing liquid mixtures is shown in Figure 3.

It consists of a weighing bottle made from a short length of glass tubing of 5-mm. outside diameter fitted at one end with a small sintered disk. Around the disk end of the weighing bottle, and held in place by a rubber ring, is placed a short length of 10-mm. outside diameter glass tubing acting as a cup to hold a mercury seal over the sintered disk. Glass legs attached to this tubing hold the assembly upright on a balance pan.

A pipet, for adding components to the weighing bottle, is made by drawing out a piece of 6-mm. tubing to a fine capillary, and placing a rubber medicine dropper bulb over the large end. The size of the capillary is determined by the amount of each component to be added and the accuracy with which it is desired to approximate the final composition of the mixture. If the capillary pipet is properly drawn out, quantities of each component from 1 to 20 mg. can be estimated, before weighing, within 30%, thus allowing a mixture to be made up to approximately any desired composition.

For the preparation of semimicroquantities of mixture (approximately 10 to 100 mg.) a microbalance should be used and weighings carried out to 0.002 mg. For larger quantities an ordinary analytical balance may be used, with weighings made to 0.1 mg.

To prepare liquid mixtures the weighing bottle must be evacuated before use, in order for liquids to pass through the disk and into the bottle. This is accomplished by connecting the original open end of the sintered disk tube to a vacuum system, placing the mercury seal in position, and evacuating the bottle to several microns' pressure. The tube is then sealed off 2 to 3 cm. from the sintered disk and is ready for use. Any liquids may be used, so long as the sum of the partial pressures in the weighing bottle is sufficiently low to allow the liquids added to pass through the disk. This pressure, for one disk used, was found to be approximately atmospheric. The weighing bottle assembly, which should weigh from 10 to 20 grams, is tared on a microbalance, and a small amount of one of the liquid components to be introduced is drawn up into the capillary pipet. The end of the pipet is carefully wiped dry, immersed in the mercury seal, and touched to the sintered disk, whereupon the liquid is drawn into the weighing bottle. The pipet tip is removed from the disk when sufficient liquid has been transferred. A second weighing the accurately determines the amount of liquid added. This process is repeated until as many components as desired have been added.

The lower portion of the weighing bottle is then immersed in a cooling medium such as liquid nitrogen to condense into the bottle any material still remaining in the sintered disk. The bottle is alternately warmed to room temperature and cooled slightly several times to help mix its contents and is then carefully inverted under mercury, taking care that no air enters through the sintered disk. Gentle shaking will then complete the mixing operation. The original mercury cup is removed under mercury, thereby allowing access to the sintered disk. By thus inverting the tube, the liquid in the weighing bottle comes in contact with the disk and permits a sample of the liquid phase to be withdrawn by touching the disk of the weighing bottle to a second sintered disk placed under the mercury surface and connected to the spectrometer inlet system (Figure 2).

Where the accuracy attainable with a balance is not required, a microburet may be used to introduce the components into the weighing bottle.



Figure 2. Microburet

SOURCES OF ERROR. Certain factors in the method were given consideration because of their potential source of error.

Loss of Mercury from the Seal Due to Sticking on the Pipet. Repeated immersions and withdrawals of the pipet from the mercury seal showed that the amount of mercury adhering to the pipet was in all cases less than 0.005 mg. For a 10-mg. quantity of component this factor would therefore contribute less than 0.05% error to the determination of such component.

Trapping of Liquid in the Mercury Seal. It was anticipated that some error could be introduced should liquid leak from the pipet into the mercury seal during immersion and not be transferred through the sintered disk. This factor was investigated by allowing the end of the pipet to remain wet with a drop of 2,2,4-trimethylpentane before immersion in the mercury seal. Such a condition was always indicated by a rapid drift of the balance pointer when the bottle was weighed. Evaporation of the iso-octane, however, was complete in 10 to 15 minutes and the bottle always attained its original weight to within ± 0.002 mg., indicating that error from this source was negligible or within the limit of precision of the microbalance. Relatively nonvolatile liquids could cause error, but such leakage of liquid into the mercury never inadvertently occurred in over 100 weighings using proper precautions.

Reproducibility of Weighings with Microbalance. Inasmuch as weighings were always made by difference, the principal error, introduced by the balance was the uncertainty of weighings. This was found to be ± 0.002 mg, for the microbalance used in this work, and for a 10-mg, quantity of component would cause an error of $\pm 0.02\%$ in the determination of each component.



Figure 3. Weighing Bottle and Pipet

Change of Composition in Weighing Bottle. Some difference in composition between the liquid and gas phases coexisting in the weighing bottle would be expected because of the difference in relative volatility of the components. This effect was estimated by assuming an equimolal mixture of 2,2,4-trimethylpentane and n-octane to be present in the bottle at room temperature, with a vapor-liquid ratio of 2. From vapor pressure data it was calculated that the equilibrium concentration of iso-octane in the liquid phase under these conditions would be 49.98 mole %. This represents an error of 0.04% based on either component. For mixtures with greater vapor pressure differences this error will increase, but will not exceed 0.5% for the extreme case of a vapor pressure difference of 600 mm. of mercury. The effect can be reduced somewhat by decreasing the vapor-liquid ratio, but it does not seem experimentally feasible to decrease this much below 1.

Holdup in Sintered Disk. Usually the analysis of the first sample withdrawn through the disk will be somewhat in error, probably because of holdup in the sintered disk, which has the effect of trapping a small volume of material with somewhat different composition than the main body of the mixture. The volume trapped in this manner is ordinarily completely withdrawn with the first sample through the disk and by rejecting this sample the disk is sufficiently purged. The volume thus removed and the difference in composition between it and the known composition are both so small that no measurable change in mixture composition results from this procedure. The first sample through the disk must also be rejected when gas mixtures are introduced by means of the inlet systems illustrated in Figure 1.

Change in Composition Caused by Flow through Sintered Disk. Some change in composition of the mixture might be due to flow through the sintered disk. No estimate of this effect was attempted, however, because of the indeterminate flow conditions existing during transfer. Instead, a mixture of *n*-pentane and iso-octane was prepared according to the method described

Table II. Mass Spectrometer Analysis of *n*-Pentane-Iso-octane Mixture

	Mole % Iso-octane
Composition by weight	Through two sintered disks (liquid phase)
33.3	$\begin{array}{c} 30.5^{a} \\ 33.5 \\ 32.2 \\ 32.7 \\ 32.6 \\ 34.1 \\ 34.5 \end{array}$
	Av. of last 6 33.5

^a First sample through disk is usually erroneous, owing to holdup.

Table 111.	Mass Spe	ctrometer M	Analysis	of	Hydrogen-n-Pentane
		(Atmosph	eric pressu	re)	
		Mole %	6 Hydrogen		
	Through stopcock			Ti	hrough two ntered disks
	85.7 84.6 84.4			•	84.8 84.7 85.0
A	v. 84.9				84.8

specifically to test the sintered disk system for mixtures introduced as the liquid phase. Table II shows the results of seven consecutive analyses of the same known mixture. The first analysis shows the usual deviation attributable to holdup in the disk; the next six analyses are considered satisfactory checks of the known composition.

To test further the suitability of the sintered disk system for the introduction of gaseous mixtures a hydrogen-*n*-pentane mixture was prepared. Table III shows six analyses of this mixture sampled at atmospheric pressure from the same storage vessel and taken alternately through a stopcock and a sintered-glass valve. It is apparent that no significant difference exists between the two methods of introduction.

In order to determine at what pressures composition changes would occur due to differential effusion through the disks gaseous mixtures of hydrogen-*n*-pentane, methane-*n*-pentane, and ethane-*n*-pentane were analyzed at several pressures. From the data thus obtained the separation factor α was calculated:

Separation factor, $\alpha = \frac{N/1 - N}{n/1 - n}$

where N = mole fraction of one component in the effusedphase

n = mole fraction of the same component remaining in storage vessel

Table IV shows the variation in separation factor with pressure for the three gas mixtures. It is evident for the hydrogen-*n*pentane mixture that measurable change in composition begins to occur in the region of 500 mm. of mercury. For methane-*n*pentane and ethane-*n*-pentane mixtures this point is closer to

Table IV. Sep	paration Factor, a	, as a Function	of Pressure
		Gas Mixtures	
Pressure, Mm. of Mercury	Hydrogen- n-pentane	Methane- n-pentane	Ethane- n-pentane
760 500 400	1.00 1.02 1.04	1.00 1.00 1.00	1.00 1.00 1.00
300 200 100	$1.19 \\ 1.55 \\ 2.25$	$1.02 \\ 1.05 \\ 1.18$	1.02 1.05 1.09
50 25	3.10	$1.45 \\ 1.93$	$\begin{array}{c}1.26\\1.50\end{array}$

Component	Weight Desired, Mg.	Weight Obtained, Mg.	% by Weight	Weight % by Mass Spectrometer	Predioted Standard Deviation for Mass Spectrometer Analysis
3,3-Dimethylhexane 2,5-Dimethylhexane 2,4-Dimethylhexane 2,3,4-Trimethylpentane	2.0 15.0 15.0 10.0	1.899 18.096 15.729 9.612	3.6 34.6 30.1 18.4	4.4 4.2 33.5 34.5 29.1 29.7 18.9 19.7	0.8 0.4 0.8 0.3
2,2,3-Trimethylpentane 2,2-Dimethylhexane	$5.0 \\ 0.5$	$6.274 \\ 0.667$	$12.0 \\ 1.3$	$\begin{bmatrix} 13.2\\0.9 \end{bmatrix} 11.9$	$1.0 \\ 1.0$

300 mm. of mercury. To guard against error from this source, when using sintered disk valves, it is therefore essential to store mixtures of compounds of widely different molecular weights close to atmospheric pressure.

SINTERED DISKS. The smaller sintered disks illustrated in Figures 1 and 3 are not available commercially and were made in the laboratory. The preparation of similar disks presents no difficulties and has been described several times (1, 4, 8). The following method, however, has been found particularly convenient for the present purpose.





Pieces of Pyrex tubing are thoroughly crushed in a mortar, or by other suitable means, and the portion passing through a 200-but held on a 300-mesh sieve is collected for use. A mold is next prepared by drilling a hole 3 to 4 cm. deep in a small carbon block (Figure 4), so as to provide a close fit for the glass tube. The tube is ground down to a sharp tapered edge as shown and cut to a length of 5 to 6 cm. A small quantity of the powdered glass is placed on a flat surface and the tapered end of the glass tube pressed into the pile. A close-fitting glass rod is inserted into the top of the tube and the powdered glass tamped into the tapered end until a packed layer about 2 mm. deep is formed. The tube is then carefully transferred to the carbon mold, tapered end down, and the powdered glass given a final tamping with the glass rod to form it into the bottom of the mold. The mold containing the tube is placed in a muffle furnace and held at approxi-mately 1800° F. for several minutes, or until the protruding portion of the glass tube sags to an almost horizontal position. The mold is then removed from the furnace and allowed to cool. When the tube is removed from the mold, it will be found that the powdered glass has sintered together but has also shrunk away from the glass tube somewhat. To effect a tight seal between the two, a carbon rod is drilled with a tapered hole (Figure 4) just large enough to allow the sintered end of the glass tube to enter. The glass tube is then cut off at the bend and sealed to a 10-cm. length of larger tubing which acts as a handle.

The end of the carbon rod containing the tapered hole is next heated with a torch to a red heat. The flame is removed and the sintered disk tube quickly pressed into the hole and rapidly rotated. This swages the glass tube around the sintered disk and provides a tight seal between the two. To test the disk for porosity the open end is connected to a vacuum system and the sintered end immersed in mercury. If no mercury leaks through after the tube is completely evacuated, it is satisfactory in this

APPLICATIONS AND ADVANTAGES

SPECTROMETER INLET SYSTEMS. Applied to a mass spectrometer the arrangements shown in Figure 1 have been found convenient for introducing both liquid and gaseous calibrating compounds and known mixtures into the spectrometer inlet system.

An alternate method of introducing liquid compounds involves the use of a microburet such as shown in Figure 2. This method is useful where the presence of dissolved air in the compound is not objectionable, and where a pressure-volume measurement of the compound in the gaseous form is not practicable.

PREPARATION OF MIXTURES. In addition to the calibration of spectrometers with pure compounds, it frequently is desirable to test over-all performance or computational methods by analyzing known mixtures of normally liquid compounds. Ordinary methods of preparation are unsatisfactory when dealing with the small volumes of pure calibrating compounds now available. By means of the semimicromethod described, however, mixtures may be made from as many components as desired and individual components may be weighed in amounts as low as 1 mg. or less with the aid of a microbalance. The method may be readily extended to macroquantities without sacrificing its advantageous features, and these liquid mixtures may be stored and introduced with the same sintered disk tubes used for their preparation (Figure 3). The chief interest in this method for the authors centered around its usefulness in determining the accuracy of mass spectrometer methods applied to certain hydrocarbon analyses, particularly of normally liquid compounds. Table V illustrates the results obtained for a typical known liquid mixture consisting of six octanes. The last column gives the calculated standard deviation to be expected for such a mixture, based on the known mass spectra of the pure components.

ADVANTAGES. The principal advantages of this sintered disk technique are: The material contained in the storage vessels is kept free from air and water; the use of stopcocks, which might cause trouble due to leakage or absorption, and which need periodic regreasing, is eliminated; no pumping out to remove air is necessary before introducing material into the spectrometer; any pure compound or mixture may be introduced with but little manipulation; and liquid mixtures may be prepared rapidly and accurately with either semimicro or macroquantities of material.

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PRESENTED at the Spring Meeting of the Philadelphia Section, June, 1945.

NOTE ON ANALYTICAL PROCEDURES

Improved Distilling Head for Laboratory Fractionating Columns

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ISTILLING heads are generally of two types, the partial vapor condensation and the total vapor condensation head. The partial vapor condensation head first employed by Peter and Baker (6) now has been almost entirely replaced by the total condensation head.

Bruun (1, 2) was among the first to design a satisfactory total vapor condensation head for laboratory columns. His design is generally satisfactory for most purposes, but lacks ease of operation and is not applicable to distillation of immiscible and corrosive liquids. Many other (3-11) different designs, which are generally satisfactory for laboratory distilling columns, are now in use; but each, including the one now proposed, possesses some disadvantage. It is very difficult to design a distilling head which will eliminate all disadvantages, but this paper presents a satisfactory distilling head which has been in operation for more than five years.

All parts are made of glass, and therefore may be used for distilling corrosive liquids, including inorganic acids except hydrofluoric.

2. All stopcocks and joints are precision ground. These require very little, if any, lubricant and work well under high vacuum.

3. It is easy to operate. The nipples of the stopcocks are accurately calibrated and the reflux ratio is determined by counting the drops. Once the reflux ratio is set, the ratio will remain constant for an indefinite period of time.

The temperature of the reflux and the product is easily 4. determined.

Vapor temperature may be accurately determined during 5. fractionation period.

¹ Present address, Morton Chemical Co., Greensboro, N. C.



Figure 1. Side View of Distillation Head



Figure 2. Front View of Distillation Head

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Figure 1 'shows

the side view of

the distillation

head, while Figure

2 shows the front

view. In actual operation, the dis-

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This device requires a degree of skill too great for fabrication by an amateur glass blower. However, it can easily be made by a professional glass blower or purchased at relatively low cost from Otto R. Greiner Company, Newark, N. J. This type of distillation head may be made to fit any size of fractionating column for laboratory or pilot-plant use. The design, as illustrated, has been used with a 1.5-inch inside diameter-48-inch laboratory column for more than 5 years with excellent results.

For ordinary distillations, the thermometer wells for the reflux and distillate may be omitted, thus reducing the cost of the head.

ACKNOWLEDGMENT

The author is indebted to J. E. Hunt of the Engineering Department for the drawings.

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815

CORRESPONDENCE

Thermal Decomposition of Perchlorates and Determination of Sodium and Potassium in Silicates

SIR: Marvin and Woolaver (2) have studied thermal decomposition of seven perchlorates with aid of the thermobalance. Their findings are interesting and important, because most textbooks, having in mind alkali perchlorates, state that "perchlorates upon being strongly heated are converted into chlorides with liberation of oxygen". Marvin and Woolaver find that ferric perchlorate and the perchlorates of magnesium and aluminum are completely changed to oxides, while calcium perchlorate is to some extent changed to oxide.

With respect to the calcium salt, they find that the residue corresponds fairly closely to CaO.20CaCl₂. (It should be pointed out that in the article as published there is a printer's error and capital O appears instead of a zero.) It is a bit unfortunate that this formula was given at all, for it is based on a single weight of residue obtained on heating a sample of perchlorate which was not perfectly anhydrous. I would call attention to the fact that the weight of residue obtained on heating Ca(ClO₄)₂ was only 1.45% low if only CaCl₄ were formed, and with LiClO₄ the error was -3.2%, with NaClO₄ -0.74%, and with KClO₄ -1.45%. It is regrettable, therefore, that the residue obtained with acid in the presence of methyl orange. This would have been better proof of formation of some CaO.

The authors state that with the thermobalance decomposition points were obtained within a few degrees, but the data presented in plots do not show complete decomposition. Thus the curve in Figure 4 for conversion of $Fe(ClO_4)_4$ stops at approximately 235° where loss in weight is only 39 mg., whereas complete conversion of 0.092 gram of anhydrous $Fe(ClO_4)_4$ calls for loss of over 71 mg.

The argument that alkali perchlorates are decomposed into chlorides with loss of oxygen seems sound. On the other hand, assumption that perchlorates of iron, magnesium, and aluminum are simply hydrolyzed into oxide and HCIO, does not appear to be proved. If hydrolysis takes place completely one would expect this within 100° of boiling point of water, when the decomposition takes place in an open dish. But ferric perchlorate does not appear completely changed to oxide when the temperature of 225° is reached, and in the case of magnesium perchlorate only 81% of the expected loss in weight occurs when 425° is reached on the assumption that the perchlorate was anhydrous at the start. Of course, if the sample were MgClO4.6H2O at the start, one would expect considerable hydrolysis to take place, but the plot shows a loss of only 55 mg. and 87 mg. of MgClO₄.6H₂O contain 42 mg. of water of crystallization. Every mole of perchlorate requires 4 of water for its hydrolysis. Does it seem reasonable that 4 moles of water remain for each mole of undecomposed Mg(ClO₄)₂ after a temperature of 425° has been reached? The data given do not prove that conversion of perchlorates of iron, magnesium, and aluminum is entirely the result of hydrolysis.

A method for determining sodium and potassium (1) is based on heating a silicate with HClO4 and HF in platinum and converting perchlorates formed to chlorides and oxides by ignition in glass to 550°. After dissolving in water and precipitating the calcium and magnesium as oxalate and oxinate, respectively, the chlorides were weighed in glass. In the analysis of 6 samples of silicates, 20 to 24 mg. of NaCl + KCl were weighed in "250-ml. tall-form beakers". The results agreed better with the Bureau of Standards results than the results obtained with KClO4 recorded in the previous article (2). We older chemists would never have dared to weigh 20 mg. of residue by difference in a 250-ml. glass beaker. We used to employ platinum dishes and with platinum it is much easier to get constant weights than with glass. Remarkably good agreement was obtained (1) with the Bureau of Standards values, but no analysis was made of actual sodium and potassium contents. One would expect some attack on glass by the rigorous treatment and, in carrying out the J. L. Smith procedure, we always had to make allowance for alkalies picked up from the glass and from reagents. Apparently in the experiments of Marvin and Woolaver, loss in alkali during ignition of perchlorates happened to compensate the gain in weight from glass vessels and from reagents.

Rochester, Mass.

WILLIAM T. HALL

GEORGE G. MARVIN

SIR: Professor Hall suggests that in order to determine the presence of calcium oxide the residue might have been dissolved in water and titrated with acid. This was performed during the course of our experiments and we are sure that calcium oxide is present because of the alkalinity of the resulting solution. A quantitative value on the amount of calcium oxide would undoubtedly be of little significance because it would probably vary from one sample to another. Also I would like to point out that after this suggested formula the statement is made that it "has no particular significance".

Comment is also made on the fact that the curves do not indicate complete decomposition of samples. The purpose of the paper, as illustrated by Figures 1 and 2, is to show a sharp point of inflection indicating that decomposition begins at a definite temperature and will continue, faster and faster, over an indefinite range upwards. The curves for iron, magnesium, and aluminum perchlorates should be viewed in contrast with Figures 2 and 3 rather than in comparison. There was no interest or intent to carry these curves through to complete decomposition. Of course, the ultimate purpose of the paper was to show that a maximum temperature would be required to break down these common perchlorates for analysis for sodium and potassium.

The comment regarding possible mechanism of breakdown of perchlorates is of interest, but we made no effort to prove that it followed a definite mechanism. We simply offered a possible explanation for the decomposition.

On the method for determining sodium and potassium (1), Professor Hall refers to decomposition of perchlorates in glass. This decomposition cannot be performed in platinum because of the serious attack of the platinum dish. Checks were carried out in quartz dishes against the same work in glass vessels, the error being of such small magnitude that it was considered entirely feasible to use Pyrex.

Blank results were carried on throughout this work, and all indications point to the reasonable conclusion that results obtained by this method are accurate. There were numerous side experiments and tests performed in connection with this research that could not be included in the article because of the necessity for conciseness.

Cambridge, Mass.

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