PROCEEDINGS

FIFTH ANNUAL SYMPOSIUM

OF THE

AMERICAN SCIENTIFIC GLASSBLOWERS SOCIETY

JUNE 16-20, 1960 • PENN-SHERATON HOTEL • PITTSBURGH, PENNA.

The American Scientific Glassblowers Society
309 Georgetown Avenue
Gwinhurst
Wilmington 3, Delaware

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SYMPOSIUM PAPERS

AMERICAN
SCIENTIFIC
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OFFICIAL PROGRAM

American Scientific Glassblowers Society

FIFTH ANNUAL SYMPOSIUM

THURSDAY - JUNE 16

9:30 A. M.

INTRODUCTION—J. Allen Alexander, President, American Scientific Glassblowers Society

WELCOME—Dr. Blaine B. Wescott, Vice President, and Director of Research, Gulf Research & Development Company

Session 1

Chairman: Dr. John Glaser, Uni-Science, Inc.
Assistant Chairman: Carl Hepler, Gulf Research & Development Company

Granite and Glass

Dr. Frank Preston, Preston Laboratories, Butler, Pa.

The process by which Nature prepares the raw materials of the glass industry from an unmanageable natural melt.

Vacuum Fusion Analysis—Equipment and Technique

Dr. William F. Harris, Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

The presence of oxygen, nitrogen, and hydrogen in metals greatly affects the physical properties of the metal. It is important therefore that accurate quantitative determinations of these elements be made. Vacuum Fusion Analysis is usually used for the determination of the interstitial elements in metals. The design, construction, and operation of vacuum fusion systems ranges from complex equipment for the determination of all three gases in refractory metals to a simple system for the determination of oxygen in copper.

Marking Scientific Glass Apparatus

Ray Andrews, B. F. Drakenfeld & Co., Inc., Glass Colors Div., Washington, Pennsylvania

Covers silk screening, direct rubber stamp, rubber stamp and dust-on, decalcomania transfers and application of color with an ordinary writing pen. It will also take up briefly the subject of coefficient of thermal expansion and amber stains.

10:30 A. M. Session 2

Chairman: Howard M. Nutt, Linde Company
Assistant Chairman: Dana E. Sampson, University of North Carolina

Gas Adsorption on Solid Surfaces

Dr. Donald S. MacIver, Gulf Research & Development Company, Pittsburgh

The techniques used to measure gas adsorption on solid surfaces; also describes the experimental apparatus employed. The advantages and limitations of the several methods are discussed and examples given of the necessary glassware.

Fiber Glass—Today

Dr. George E. Eilerman, Pittsburgh Plate Glass Research Laboratories, Pittsburgh

Presently fiber glass is experiencing a remarkable growth. Special properties of this man-made fiber have permitted the production of new products and have encouraged the evolution of new technologies. The future of fiber glass looks equally bright. A further realization of the properties of fiber glass together with new and improved manufacturing facilities should add to an even broader interest in the use of this material.

Coffee Break during the morning session

1:15 P. M. Session 3

Chairman: Leigh B. Howell, University of California
Assistant Chairman: Clair E. Campbell, Battelle Memorial Institute

Assembly and Operation of High Efficiency Glass Laboratory Distilling Columns

Ned C. Krouskop, Carnegie Institute of Technology, Chemical and Petroleum Laboratory, Pittsburgh

Review of the assembly and operation of the laboratory distilling columns used by the American Petroleum Research Laboratory at the Carnegie Institute of Technology. Discusses construction and operation of 14 high efficiency packed distilling columns and a low pressure distilling column. Details of the pot, rectifying section, jacket, head, reflux regulator, receiving assembly, electrical heating system, thermometric systems and controlled pressure systems are described.

The Philosophy of Glassblowing for the College Graduate

Dr. T. J. Gray, Alfred University, Alfred, New York

6:30 P. M. Cocktail Party, Penn-Sheraton Ball Room

Limited to American Scientific Glassblowers Society members and their wives, as guests of the Kimble Glass Company.

7:30 P. M. Annual Banquet, Penn-Sheraton Ball Room

Guest Speaker: Dr. Jerome Strauss, Consulting Engineer
Subject: "Technique and Style in Glass"

FRIDAY - JUNE 17

9:00 A. M. Session 4

Chairman: Karl Walther, Brookhaven National Laboratory
Assistant Chairman: Kurt Wurster, K. W. Thermometer Company

Sealing Glass Developments

Dr. Robert H. Dalton, Corning Glass Works, Corning, New York

Basic principles of making a fused seal between different glasses and between glasses and other materials such as metals will be reviewed. Effect of seal geometry, a factor often overlooked, will be considered. Technique of sealing by means of "solder glass" will be discussed with special emphasis on the newly developed thermal setting glasses. Some new glasses and techniques, including the copper matching glass, will be described.

Glasses for Metal Sealing

Dr. F. L. Bishop, Kimble Glass Company, Toledo, Ohio

Brief discussion of the specific properties of some Kimble glasses which are available for sealing to some of the more standard metals. Such properties are resistivity and gas permeability.

The History of Glassmaking

Paul N. Perrot, Corning Museum of Glass, Corning, New York

Fascinating and romantic history of the world-wide glass industry, with special attention to the development of glass forming equipment that has brought so much progress and technological improvement.

10:30 A. M. Session 5

Chairman: M. Howe Smith, Fischer & Porter Company
Assistant Chairman: James F. Morris, Northwestern University

Development of High-Temperature Electronic Glass

Earl D. Dietz, Owens-Illinois Glass Co., General Research Div., Toledo, Ohio

Development of a new glass from the compilation of the desired glass properties until the necessary melts have been made and tested to prove that the glass can be made commercially. Will be illustrated by specific development of Kimble EE-2, Aluminosilicate glass.

Glass as an Engineering Material

John R. Blizard, Corning Glass Works, Technical Products Div., Corning, New York

Illustrated discussion of the pertinent applications of glass in pipelines, for heat exchangers, valves, fractionating columns, rayon spinning wheels, thread guides, sight glasses, and many other miscellaneous industrial equipment. Discussion of field flanging of pipeline and drainline should be of particular interest to ASGS members.

Coffee Break during the morning session.

1:15 P. M. Session 6

Chairman: Helmut E. Drechsel, National Scientific Company
Assistant Chairman: John A. Glover, Sinclair Research Laboratories

Large Scale Laboratory Equipment for Separation of the Organic Fraction of Recent Sediments and Ancient Rock Samples for Study of the Genesis of Petroleum

Dr. J. Gordon Erdman, Mellon Institute of Industrial Research

Carl F. Hepler, Gulf Research & Development Company

Ultra High Vacuum Techniques

Dr. William J. Lange, Westinghouse Research Laboratories, Pittsburgh

Attainment, measurement and application of Ultra High Vacuum.

8:00 P. M. Annual Member Meeting, Penn-Sheraton Ball Room

SATURDAY, JUNE 18

9:00 A. M. Session 7

Chairman: Jules Benbenek, R. C. A. Laboratories
Assistant Chairman: Robert Schipman, Food Machinery & Chemical Corporation

Reboil Testing

George B. Brookover, Assistant Chief Psysicist, Kimble Glass Company, Toledo, Ohio

A test has been developed for producing reboil in glass under controlled conditions. The standard conditions include preparation and cleaning of sample, careful control of burner variables and heating rate. The volume of reboil produced during the test is calculated. Glasses may be compared for reboil on this volume basis. Test data obtained have correlated very well with production experience.

A Plate Type Glass Laboratory Fractionating Column and Low Hold-Up Reflux Condenser

J. Allen Alexander, Atlantic Refining Company, Research and Development Department, Philadelphia

Author has designed a practical and sturdy glass Fractionating Column Reflux Condenser, in which volatile liquids can be distilled at a relatively fast rate to produce, in a normal working day, sufficient material for laboratory personnel to work with and which more nearly simulates the degree of separation produced in plant operation. The column and reflux condenser are relatively easy to construct and the author has gone to sufficient detail through drawings, illustrations and adequate description to aid the glassblower materially in its fabrication.

10:30 A. M. Session 8

Chairman: William Wilt, Wilt Laboratory Glassblowing, Inc.
Assistant Chairman: Walter P. Copeland, Gulf Refining Company

The Place of the Glassblower in Radiochemical Laboratories

Henry L. Christie, Atomic Energy of Canada, Ltd., Ottawa, Canada

The last twenty years have been marked by the entry of radioactive chemicals into laboratories all over the world. The glassblower must observe established procedures when working on equipment in which these radiochemicals are processed. Also, protective garments, and especially designed processing equipment are used. Every glassblower working with radioactive materials should know the measures required to permit him to work safely.

Laboratory Distillation Apparatus

Joseph Baum, Sterling-Winthrop Institute, Rensselaer, New York

In laboratory distillation apparatus, there are several basic designs of columns commonly used. Improvements on these designs have been noted in scientific papers. Review of some of those improvements and of some designs made in the author's glassblowing laboratory.

Purifying Instrument Mercury

James B. Lawrence, Bethlehem Apparatus Co., Inc., Hellertown, Pennsylvania

Many instrumentation men are unaware of the purity requirements of mercury for use in instruments. Some apparently believe there are no requirements! Are you one of those who thinks "Our mercury is just used in flowmeters, so it doesn't have to be clean?"

1:15 P. M. Session 9

Chairman: William H. Tozer, Allied Chemical & Dye Company
Assistant Chairman: James N. Christopher, Research Glass, Inc.

Plastic Coating for Glassware

Charles M. De Woody, Ace Glass, Inc., Vineland, New Jersey

Glassware has been coated with plastics for a number of reasons, the paramount ones being: (A) A protective coating against chemical corrosion by alkalies and fluorides (B) Mechanical buffering against abrasion and impact (C) Reenforcement for increased mechanical strength (D) Safety-protection against personal injury, (1) from physical contact with jagged particles (2) from toxic materials contained within, (E) Decorative. The applications and characteristics of films of Teflon, Kel-F, Epoxy Resins, Polyvinyl-chloride, and others will be discussed.

Glass to Metal Sealing

Jules E. Benbenek, R. C. A. Research Laboratories, Princeton, New Jersey

Electro-Conductive Glasses

Dr. John Glaser, Uni-Science, Inc., Pittsburgh

Outline of the technical development and its practical applications in research and industry.

WELCOMING ADDRESS

Blaine B. Wescott
Vice President and Director
Gulf Research & Development Company

Mr. Alexander, members and guests of the American Scientific Glassblowers Society, it is both a privilege and a pleasure to welcome you to Pittsburgh for the Fifth Annual Symposium and the First Exhibit of your Society. When the chairman of your Program Committee, Bill Barr, asked me to say a few words of welcome to you, I accepted gladly and without hesitation for a number of very good reasons.

Those of us who belong to the scientific segment of our community are honored that you selected Pittsburgh for your meeting. We think this was an appropriate selection because the Pittsburgh area is one of most important research centers in this country or, for that matter, in the world. There are, in this area, some 55 industrial research laboratories which employ more than 8,000 people and spend more than $100 million annually in carrying out their programs of industrial research. The diversity of the industries represented can be illustrated by mentioning the names of a few of the companies which support this gigantic technological effort such as Alcoa, U.S. Steel, Westinghouse, Jones & Laughlin, Koppers, Pittsburgh Plate Glass, Allegheny Ludlum, H.J. Heinz, Pittsburgh Consolidation Coal, Pittsburgh Coke & Chemical, Mine Safety Appliances, Harbison-Walker, Mobay, and my own company, Gulf Oil.

Many of these research organizations grew out of Fellowships at Mellon Institute of Industrial Research which was founded here in Pittsburgh in 1910 by A.W. and R.B. Mellon. While DuPont, General Electric, Alcoa, and possibly a few other companies, had small research groups prior to that time, it is generally recognized that our modern concept of organized industrial research originated with Mellon Institute. Just as it pioneered in sponsored industrial research with such effectiveness that it achieved world-wide recognition, it is today a pioneer among non-profit research organizations in directing its programs toward fundamental research.

The institutions of higher education in and around Pittsburgh have contributed their full share to the recognition of this city as an outstanding research center by their fundamental research in the fields of the physical sciences, engineering, public health, medicine, and business administration, to mention just a few.

Now, while I have taken quite a few words to give you a brief picture of the nature, importance, and magnitude of the contribution that the Pittsburgh area is making to the technological progress of this country because I thought it was closely related to the interests of your Society, I also had another purpose in mind. We who are engaged in the conduct of research or the management of research, whether it be industrial, applied, or basic, are fully conscious of the vital importance of the scientific glassblower to our research programs and, on behalf of all of us I wish to acknowlege our indebtedness to you for your ingenuity in devising and skill in constructing the complicated apparatus and equipment so essential to research.

Modern industrial research in this country began just after the first world war. At about the same time it became apparent that if rapid progress were to be made, we must be independent of Germany for scientific glassware and apparatus. This gave the necessary impetus to this new profession. But, for many years scientific glassblowing was an art which evolved gradually into techniques and skills that were jealously guarded secrets. This trade could be learned only by spending many years an an apprentice in the same manner that trades had been taught in Europe for centuries. To some extent this is still true today.

However, just as scientists found out they could benefit mutually and progress faster by free exchange of knowledge and ideas so have the scientific glassblowers arrived at the same conclusion. Realization of this fact undoubtedly had much to do in motivating the people who gathered as the "Glassblowers Discussion Group" at Wilmington, Delaware on March 14, 1952. There were 31 people at this meeting. This led to the incorporation of the American Scientific Glassblowers Society on March 17, 1954. The first meeting of the Pittsburgh Section took place at Mellon Institute on November 8, 1955. The first symposium was held at the famous glass center, Corning, New York on June 8, 1956. Now it is fitting that the first Exhibit of your Society should be held in a city which was the center of the glassblowing industry in the United States in 1820.

In these few years your membership has grown to nearly 700 and your Committee expects a registration of more than 1000, about half of which will be chemists, physicists and other scientists dependent on your ability to provide them with their research tools. It is indeed gratifying to all research workers to see the healthy growth of your society and the provision for free exchange of the knowledge of your profession through meetings and publications.

Your program designates this meeting as a Symposium. Webster defines a symposium as "a drinking together, usually following the banquet proper, with music, singing, and conversation; hence, a banquet or social gathering at which there is a free interchange of ideas". The Program Committee apparently has satisfied all of Webster's criteria for a symposium and I do not intend to delay progress any longer than is necessary to say once again— "Welcome to Pittsburgh, we are honored to have you here and we hope that your stay here will be so profitable and so enjoyable that you will come back again soon for another annual symposium."

ULTRAHIGH VACUUM TECHNIQUES

W. J. LANGE
Westinghouse Research Laboratories

Interest in ultrahigh vacuum has expanded at an extremely rapid pace during the past ten years. Originally a technology employed solely by a few researchers studying thermionic emission, it is now being utilized in many fields of physics and chemistry. By ultrahigh vacuum we arbitrarily mean pressures less than 10^{-8} mm Hg. That is, pressures of the order of a millionth of a millionth of standard atmospheric pressure. Such pressures had been obtained many years ago, however no direct method of measurement was available and ultrahigh vacuum could only be inferred from indirect evidence. As ultrahigh vacuum gauges came into being, in particular the Bayard-Alpert gauge,(1) which were capable of measuring pressures of 10^{-9}, 10^{-10}, 10^{-11} mm Hg, ultrahigh vacuum interest soared and attainment of such pressures spread from a few isolated individuals' laboratories to most scientific institutions. Application of ultrahigh vacuum techniques became obvious to researchers in every field of surface properties and gas discharges. Although all work done in these fields is not utilizing such techniques even now, the advantages of cleanliness and purity are well recognized.

As you know, pressure is the result of collisions of molecules with surfaces. Some collisions result in molecules sticking or adsorbing on the surface. Hence, at equilibrium a certain coverage will result such that under the particular conditions of gas, surface, temperature, and pressure as many adsorbed molecules re-evaporate as incident molecules stick. With as much as one monolayer, that is, the surface covered completely but only one molecule deep (one hundredth of a millionth of one inch) surface properties can change radically. To study clean surfaces one must find a means of first cleaning the surface and then keeping it clean long enough for measurements to be made. One way to accomplish this is to heat the surface to a temperature at which the adsorbed layer is evaporated and can be removed by pumping. Then, if the pressure attained upon cooling is low enough, it will take longer for readsorption to occur than the time required for measurements. Lower pressures result in proportionally longer times, so that, while a monolayer typically forms in 1 second at 10^{-6} mm Hg, it takes several hours at a pressure of 10^{-10} mm Hg.

Systems for obtaining ultrahigh vacuum typically consist of vapor diffusion pumps, backed by mechanical pumps, traps for removal of backstreaming diffusion pump vapors, gauges for pressure measurements, and valves for isolation of one part of the system from another. For many years typical diffusion pumps were mercury filled diffusion pumps with liquid nitrogen cooled traps. Mercury backstreaming from the pumps was trapped by condensation on the walls of the trap. Later, oil filled diffusion pumps came into vogue, again with liquid nitrogen cooled traps. Subsequently, it was found that copper foil at room temperature was capable of adsorbing oil vapors and could keep the pressure in an oil pumped system in the 10^{-10} mm Hg region for many days. Recently, another more effective, unrefrigerated trap has been reported(2) and is now a standard component on systems in our Laboratory. A design for a laboratory size system is shown in Figure 1. Activated alumina or artificial zeolite pellets are employed and have proven to be capable of holding the pressures in the system open to the oil diffusion pumps in the 10^{-10} mm Hg region for more than one hundred days without any cooling.

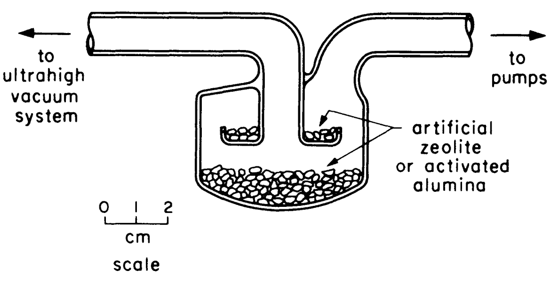

Fig.1- Unrefrigerated trap

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(1) R. Bayard and D. Alpert, Rev. Sci. Instr. 21, 571 (1950).

(2) M. A. Biondi, Rev. Sci. Instr. 30, 831 (1959).

Several types of gauges have been reported and are supplied by manufacturers. The most popular is the Bayard-Alpert gauge which is capable of directly measuring pressures of 10^{-10} mm Hg. The low pressure limit of that gauge is approximately 5×10^{-11} mm Hg and is the result of photoelectrons leaving the ion collector, giving a current of the same sign as positive ions arriving. Measurement of the positive ion current is an accurate measure of the pressure. However, as the pressure is lowered and the positive ion current becomes comparable to the steady photoelectric current, pressure determination becomes inaccurate and eventually impossible. The steady photoelectric current is caused by photons or radiation, produced when electrons strike the electron collector, which strike the ion collector and eject electrons.

A difficulty encountered with ion gauges employing hot filaments is that certain gases interact with the hot filament. This may occur as dissociation i.e., a molecule such as hydrogen when it contacts a hot surface separates into atoms. The atoms, being chemically very active, will cling to the next surface they contact, thus removing them from the volume and decreasing the pressure. It is apparent that ordinarily one does not want the pressure measuring device to change the pressure. In particular, for certain easily dissociated or chemically active gases it would be advantageous to have a gauge which had a cold source of electrons. The schematic drawing of Figure 2 shows such a gauge employing an electron multiplier as the electron source.(3) Ultraviolet light is caused to be incident on the first electrode, or dynode, where it releases photoelectrons. By applying proper voltages and constructing the dynodes of the proper material the few photoelectrons from the first dynode are accelerated to the second dynode where they release more electrons by impact. This process is repeated at succeeding dynodes, thus multiplying the original small photoelectric current until a useful number emerge from the last dynode. As in other ionization gauges, the electrons then are accelerated to an electron collector and in transit collide with and ionize gas atoms. The ions are collected and the ion current or number of ions created measured. Clearly the number of ions created for a constant number of electrons will depend on the density of of gas molecules in the vicinity. Since the density is proportional to the pressure, the ion current is a measure of the pressure. The photomultiplier gauge shown here is useful over the same pressure region as the Bayard-Alpert gauge, i.e., 10^{-4} to 10^{-10} mm Hg.

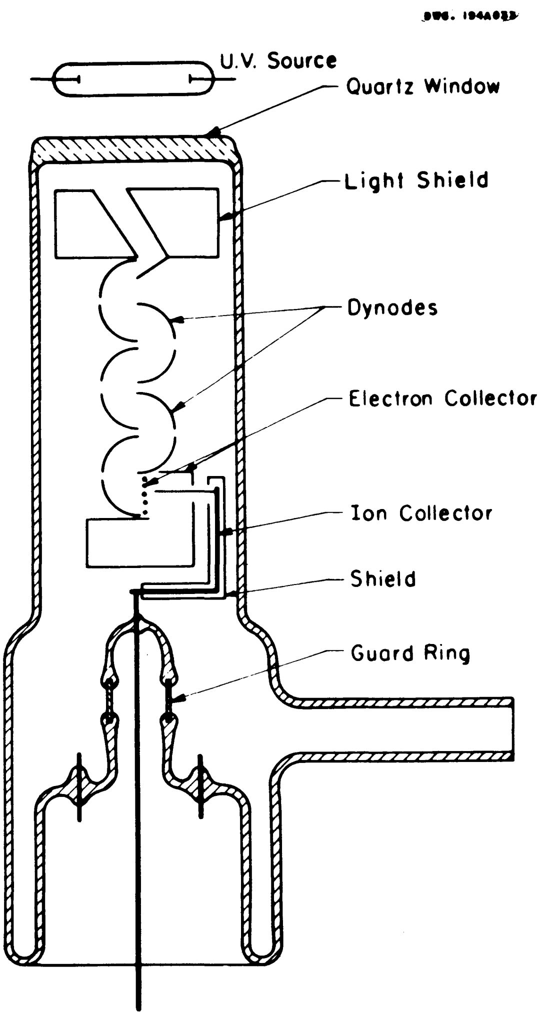

Fig.2 - Photomultiplier ionization gage

Another important mechanism occurring in ion gauges is that of ionic pumping. By ionic pumping is meant the removal of gas by ionizing gas molecules and accelerating the ions to a surface where they are embedded and removed from the volume. Also known as electronic pumping, this process is employed in commercial, so-called, electronic vacuum pumps. The mechanism of ion pumping has

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(3) H. Riemersma, R. E. Fox, W. J. Lange (to be published.)

been the subject of study over several years at our Laboratory, in particular, by Varnerin, Carmichael, and Trendelenburg. It has been found that the embedded ions are not necessarily permanently removed but are slowly released, presumably by thermal means. Alternatively, release is effected by additional ions striking the surface, knocking out or replacing previously embedded ions. Thus, in ionic or electronic pumps we have an effective backstreaming analogous to backstreaming from vapor diffusion pumps. However, in the case of diffusion pumps the backstreaming products can be relatively easily trapped while the backstreaming products from ion pumps are dependent on the history and gases pumped.

For completeness, we should also mention the use of cryogenic pumping. In effect, this method is a brute force means of obtaining vacua not by complete removal of gas from the system, but rather by freezing it out on cold surfaces. Since vapor pressures decrease rapidly with decreasing temperatures, low pressures are obtained by providing a very low temperature trap where all substances have low vapor pressures.

Let us next ask, having the necessary pumps, traps, and gauges, for measuring very low pressures, what is the present typical ultrahigh vacuum attainable and what are the factors preventing still lower pressures from being attained. At the present time vacua of 10^{-10} mm Hg are not at all uncommon. These vacua are relatively easily achieved by using predominantly glass or stainless steel walled systems which can be baked to temperatures of approximately 400°C for several hours. Presumably one could pump for extremely long times and achieve the same vacuum without bakeout. However, the bake serves a purpose analogous to the application of heat for drying clothes. Eventually, the clothes dry at room temperature, but by raising the temperature the water evaporates more rapidly. Similarly, gauges are outgassed by raising the temperature for relatively short times above normal operating temperatures.

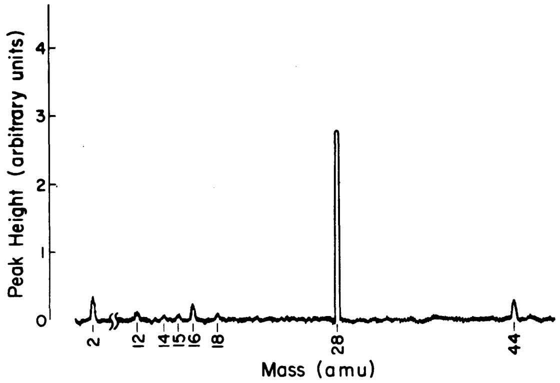


Fig. 3 - Peak height vs $\frac{M}{e}$

Following bakeout and outgassing pressures of approximately 1 x 10^{-10} mm Hg are obtained. Lower pressures customarily are not obtained because of leaks, either real or virtual. Assuming the system has no real leaks the ever present virtual leaks impose a limit on the ultimate attainable vacuum. One of the leaks has been studied thoroughly and is the permeation of helium from the atmosphere, where it is present to only four ppm, through glass walls of the system.

Figure 3 shows a typical mass spectrum obtained at ultrahigh vacuum. Clearly the residual gases are not those one would expect to remain when exhausting from normal atmosphere. Current evidence is that both the carbon monoxide and hydrogen components are closely related to and may be produced by the operation of hot filaments in ion gauges or mass spectrometers.

Recently we have studied another source of gas at very low pressures and have referred to it as photodesorption. By photodesorption we mean the direct release of adsorbed gas by incident radiation, as distinguished from thermal release by the radiation heating the surface on which gas is adsorbed. Figure 4 shows a schematic of the experimental tube and system on which photodesorption was studied. With light incident on the tube the shutter

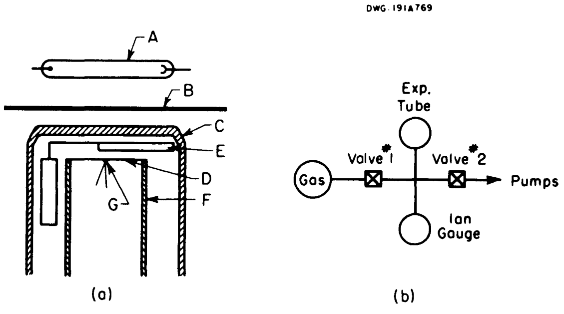


Fig.4-Experimental Arrangement

A. Light Source B. Shutter C. Quartz Window
D. Sample E. Movable Cover F. Current Leads
G. Thermocouple

could be rotated by an external magnet exposing a sample previously loaded with adsorbed gas.

Although the probability of photo-release of a gas molecule was found to be very small, 10^{-8} to 10^{-9} molecules released per incident ultraviolet photon, it nevertheless can be very important in the current experimental studies of controlled thermonuclear power reactors. The reason is that in the process of obtaining a very hot plasma or gas for such reactors, large amounts of radiation, emitted by the excited gas molecules or atoms, are incident on the envelope walls. Photodesorption at the walls results in an effective leak, whereby room temperature or relatively cold gas enters the plasma. This cold gas acts as an impedance since it must also be heated in the process of heating the plasma and, moreover, is in general not the desired fuel gas. For reasons such as this, part of our work is supported by the Controlled Thermonuclear Research Division of the Atomic Energy Commission.

VACUUM FUSION ANALYSIS - EQUIPMENT AND TECHNIQUE

by

William F. Harris
WESTINGHOUSE RESEARCH LABORATORIES
Beulah Road, Churchill Borough
Pittsburgh 35, Pennsylvania

Interactions of gases with metals occur in more processes than is generally realized. Gases may be adsorbed on and desorbed from a metal surface, diffused into the metal or decompose on the metal surface. Reactions of this type occur on tungsten filaments in light bulbs, on satellites in outer space, and in electronic tubes, where metal films absorb impurity gases.

Because the presence of hydrogen, oxygen, and nitrogen in metals can adversely affect the physical properties of the metal, it is essential that a method be available for the accurate determination of these gases. The method used in the majority of cases is vacuum fusion analysis. This consists of melting the metal sample in a vacuum and analyzing the liberated gases.

Oxygen, nitrogen and hydrogen exist in metals not in the elemental form but as ions dissolved in the metal. When the amount of gas present is greater than the solubility of the gas in the metal, then oxides, nitrides and hydrides form. The reactions which take place in the furnace section of the vacuum fusion apparatus where the gases are extracted from the metal are shown in Figure 1. The fusion of the metal is done in a graphite crucible at temperatures ranging from 1200°C to 2000°C depending on the particular metal being analyzed. At these temperatures carbon from the graphite crucible is soluble in the melt. The carbon reacts with the metal oxides and the oxygen in solution and carbon monoxide is formed. The nitrides and hydrides are thermally decomposed and these elements are liberated in the elemental form. Hydrides are decomposed very easily and hydrogen can be extracted from many metals at temperatures well below the melting point of the metal. In most instances however, the decomposition of nitrides is not quantitative so the number of metals analyzed for nitrogen by vacuum fusion is limited.

A flow diagram of the reactions undergone by the gases after extraction from the metal is shown in Figure 2. The gases liberated in the furnace, carbon monoxide, hydrogen and nitrogen, are passed over hot copper oxide to oxidize the carbon monoxide to carbon dioxide and the hydrogen to water. The nitrogen remains

Oxygen

$$M_xO + C \longrightarrow xM + CO$$

Nitrogen

$$2M_xN \xrightarrow{\Delta} 2xM + N_2$$

Hydrogen

$$2M_xH \xrightarrow{\Delta} 2xM + H_2$$

Fig. 1 Reactions in the furnace

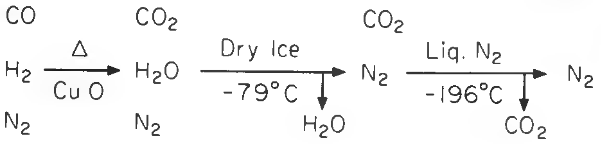


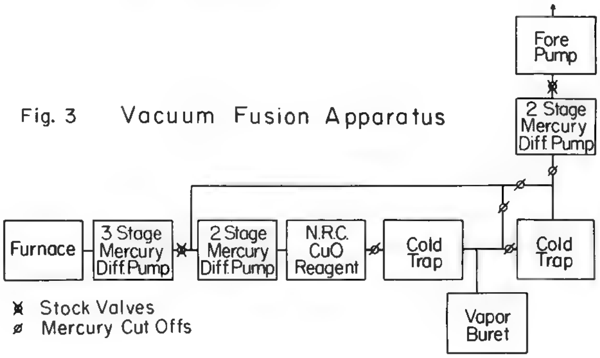
Fig.2 Vacuum fusion flow diagram

unchanged. The gases then pass through a trap cooled with a dry ice slurry at about -79°C where the water is frozen out. The nitrogen and carbon dioxide then pass through a trap cooled with liquid nitrogen at about -196°C where the carbon dioxide is frozen out. The gases are now separated and several schemes are available for the determination of each component. Some vacuum fusion systems contain solid absorbents in the system which absorb the desired gases and so separate them.

A schematic diagram of a system for accomplishing the extraction and separation of the gases as described is shown on Figure 3. The gases liberated in the furnace are pumped into the analytical section by a 3 stage mercury diffusion pump. The gases are circulated through the analytical system by a 2 stage diffusion pump. The gases pass over the hot copper oxide where the carbon monoxide and hydrogen are oxidized and the resulting water and carbon dioxide are frozen out in the appropriate traps. In this system the carbon dioxide is transferred to a vapor buret for measurement. The entire system uses a 2 stage mercury diffusion pump backed by a mechanical pump for evacuation. The vacuum generally obtained is between 10^{-5} and 10^{-6}mm. of mercury.

A photograph of the system is shown in Figure 4. The furnace is located in the front with the 3 stage pump behind. The apparatus to the right of the pump is the analytical section in which the gases are separated and measured. Mercury cut-offs are used instead of valves or stopcocks because of their reliability and maintenance free nature. The thermocouple gauges are used to roughly estimate the pressure in the various sections of the system and not for actual pressure measurements since the pressure observed is dependent upon the composition of the gas present.

Fig. 3 Vacuum Fusion Apparatus



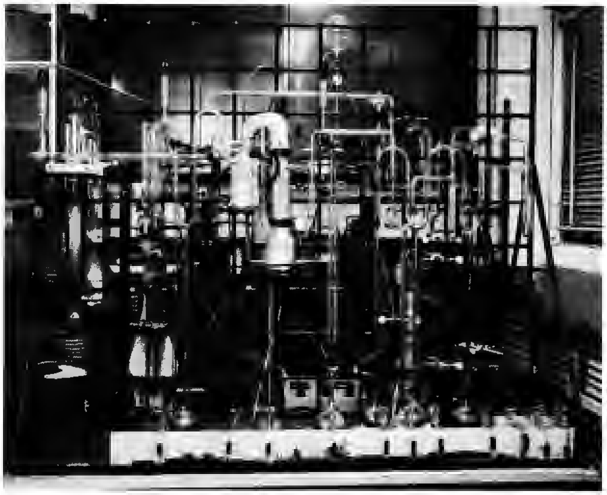


Fig. 4

Figure 5 is a close up of the furnace section. The furnace tube is made from quartz and joined to the rest of the apparatus through a 40/50 joint. The upper portion of the tube is 1-1/4" in diameter and the lower

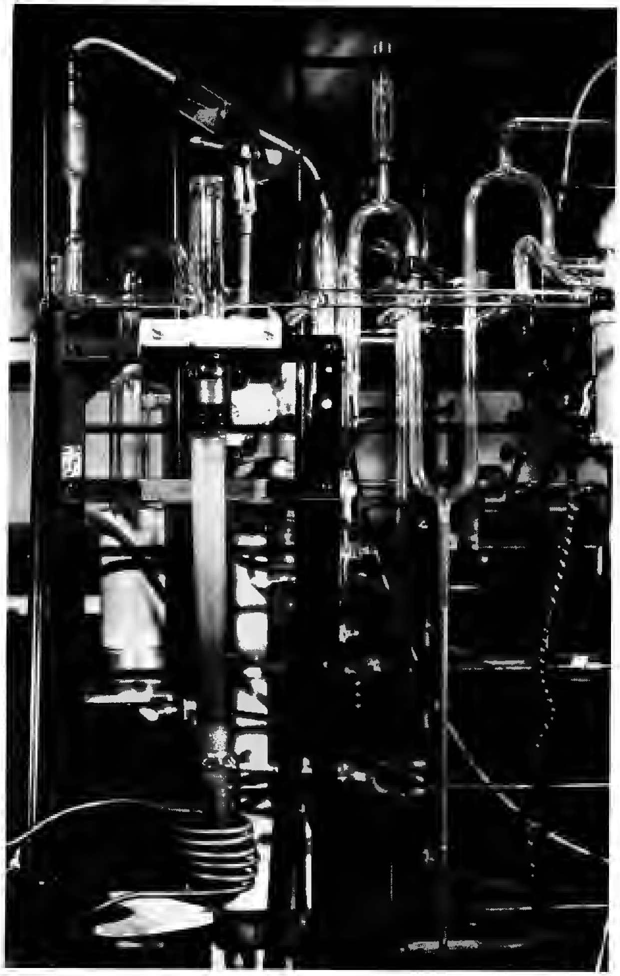


Fig. 5

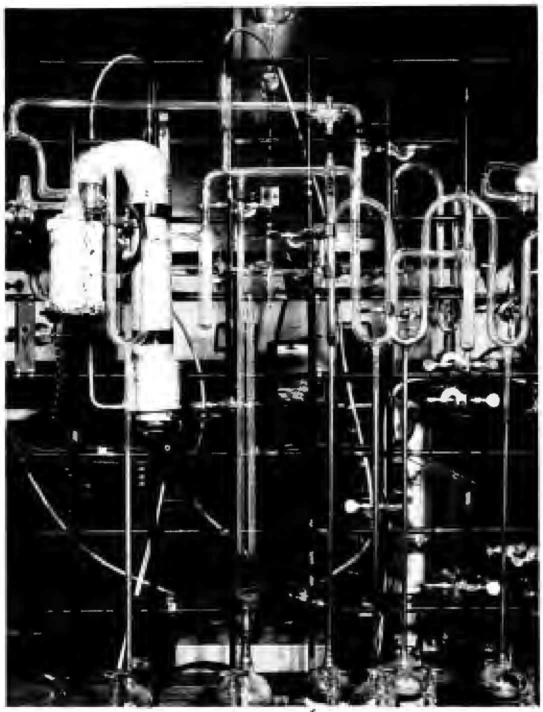


Fig. 6

portion is 2". The graphite crucible assembly can be seen in position inside the induction heating coils which supply the heat to the crucible. At the degassing temperature of 2300°C the temperature of the furnace tube is 450 to 500°C with normal convection cooling. The samples are stored in a loading arm extending from the right side of the top of the furnace assembly before being dropped into the crucible. The temperature is measured by sighting an optical pyrometer into the crucible by means of a mirror. An optical flat is sealed into the top of the furnace section to aid in this measurement. Temperatures above 2400°C are rarely used because the vapor pressure of the graphite parts becomes appreciable at this temperature.

A close up of the analytical section is shown in Figure 6. The diffusion pump circulates the gas liberated in the furnace over the hot copper oxide and through the traps where the water and carbon dioxide are frozen out. The main tubing is 14 mm pyrex and the risers for the mercury cutoffs are 6 mm pyrex.

The vapor buret which is used to measure the quantity of carbon dioxide is constructed from two precision bore volumetric burets with the markings of both precisely aligned. The right leg has a calibrated capillary tip which gives a large surface area for freezing out the gas while having a small volume. Using volumetric burets instead of regular tubing enables us to make pressure-volume measurements quickly and easily without raising the mercury level to certain exact calibration points. With this buret quantities of carbon dioxide equivalent to 0.25 γ of oxygen can be measured. By adjusting the sample weight, oxygen contents as low as 0.00002% can be measured with this apparatus.

The system just described is capable of handling all analyses of gases in metals which are necessary at the present time. However, for certain special jobs this equipment would not be fast enough or rugged enough for plant control operations. Since the time from sampling to analysis can be 6 hours, for the determination of oxygen in copper a simplified vacuum fusion system has been designed and built. The apparatus shown in Figure 7 is essentially a standard volume equipped with a mercury manometer. The 9 inch quartz furnace tube is joined to the manometer section through a 40/50 joint sealed with high vacuum wax. The rest of the system is made from 8 mm borosilicate glass tubing. The 12/30 joint is used for attaching the apparatus to a mechanical vacuum pump for evacuation.

The method consists of melting the copper contained in a graphite boat in the evacuated system and measuring the pressure of carbon monoxide liberated. It has been found that more than 99.5 wt. % of the gas liberated from tough pitch copper is carbon monoxide, therefore it is not necessary to make a separation of the gas. With this apparatus an analysis can be made within 15 minutes from the time of sampling the melt. This apparatus is limited to oxygen contents of at least 0.005% and only metals containing oxygen as the only gaseous impurity can be analysed.

Both of these systems were built in the Westinghouse Research Laboratories glassblowing shop by the group headed by Mr. C. J. Cassidy. Both are excellent examples of the importance of scientific glassblowers in industrial research.

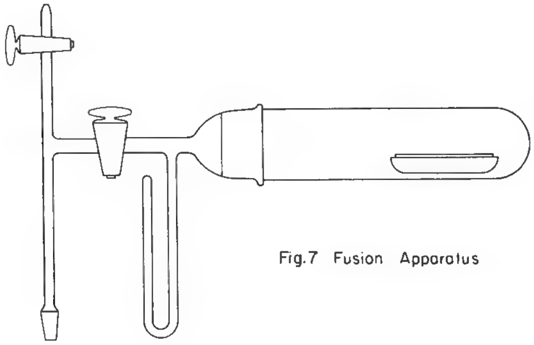


Fig.7 Fusion Apparatus

ASSEMBLY AND OPERATION OF HIGH EFFICIENCY GLASS LABORATORY DISTILLING COLUMNS

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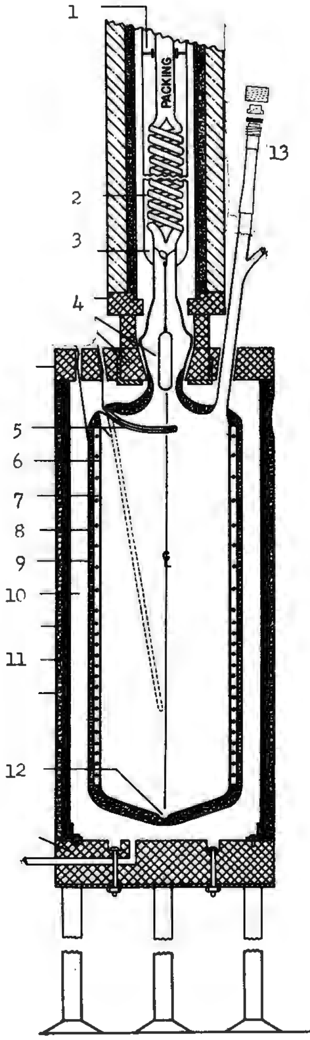
The basic assignment of the American Petroleum Institute Research Project 6 at the Carnegie Institute of Technology is to learn what petroleum consists of in terms of its individual hydrocarbon compounds or groups of related compounds. To do this job, the Project develops and operates fractionating processes to a degree of separating power much greater than is necessary in ordinary research operations. These fractionating processes have made possible the isolation from petroleum of hitherto unknown and unseparable compounds. About 50 percent of the representative petroleum crude selected in 1928 for study has been accounted for in terms of the 175 individual hydrocarbons so far isolated. In the program for the purification of API Standard and API Research Hydrocarbons we have about 275 hydrocarbons with purity above 99.85 mole percent.

Some years ago the Project completed the assembly of a battery of laboratory distilling columns of high separating power ranging from 150-200 theoretical plates for operation on a routine basis, 24 hours per day, 7 days per week. (1) To house the 20-foot columns the laboratory consists of two floor levels. All the thermometric measuring equipment and electrical controls are in an adjacent control room on the top level of the distillation laboratory.

The construction and operation of these distilling columns are unique. Figure 1 shows a schematic drawing of the lower portion of the distilling column assembly. All the distillations performed in the laboratory are batch distillations with the charge to be distilled charged into the pot of the column by means of a charging tube at the shoulder of the pot. Since the heat from the pot caused the flow of the grease used to seal the glass cap on the pot closure, a commercial metal closure with teflon "O" ring was installed through the aid of a metal-to-glass 14/35 standard taper soldered with 50-50 solder. The distilling column is a single glass unit with the rectifying section sealed to the neck of the pot and the glass distilling head sealed to the top of the rectifying section. Three types of packing are being used in our laboratory - Heligrid, 3/32" stainless steel helices and Helipack.



1 - Support for rectifying tube
2 - Double helix expansion coil
3 - **Throat to direct liquid**
4 - Drop counter
5 - Thermocouple well
6 - "Pyrex" glass pot
7 - Special "Glascol" heater
8 - Asbestos insulation
9 - Aluminum foil
10 - air gap
11 - Glass cylinder, asbestos paper and aluminum foil
12 - Well for residue removal
13 - Metal pot closure

FIGURE 1 Lower portion of distilling column assembly

The rectifying section has a silvered vacuum jacket surrounding it to minimize any heat transfer. To compensate for any heat loss through the vacuum jacket, the outside of the column is heated with electric heaters. The rectifying section has a double helical coil on the inside of the vacuum jacket to compensate for the expansion between the inside and the outside of the rectifying section. Columns with convolutions on the outside jacket to take care of expansion have given unsatisfactory service because all the strain is concentrated at one point.

The head assembly shown in Figure 2 is an off-set vertical condenser that allows all of the condensate to flow over a ground glass plug at the base of the condenser. The glass plug is attached through a tungsten rod going up the center of the condenser to a brass regulator that allows micrometer adjustment. There is a metal bellows on the inside of the regulator to keep the system closed from the atmosphere. The taper of the glass plug is 1 in 5. The connection of the regulator to the glass condenser is made with a 12/20 standard taper soldered with 50/50 solder. There is an apron at the base of the head assembly to direct the liquid from the condenser to the thermometer well. The thermometer well is located inside the vacuum-jacketed rectifying system to give a good liquid-vapor equilibrium temperature. The 20-foot columns expand about 3/8" to 5/8" when taken up to temperatures of 200°C. They are therefore supported by the neck of the pot which is tapered to fit a transite block. This transite block supports the weight of the pot and its contents as well as the 50-to-60 pound glass rectifying section. There is no other support for the column except for a transite collar at the top to keep the rectifying section in a vertical position so the reflux will not run to one side and thus reduce the efficiency of the column.

After the distillate is removed at a reflux ratio of 200 to 1, it enters the receiving assembly, shown in Figure 3. The distillate passes through a water condenser on into a graduated receiver. A spiral condenser connecting the controlled pressure to the column makes certain that no material enters the pressure system. The through-put of the column is controlled by the pressure difference between the head of the column and the pot of the column. This is maintained by a mercury manometer that is preset for a certain pressure differential. This manometer operates a relay that controls the heat input to the pot. With such a long length of tubing coming from the pot to the manometer vapor from the pot can condense in the arm. When this is detected, the operator displaces the volume of gass in the arm by introducing a measured quantity of N_2 gas.

Glass stopcocks were used to isolate the receiver from the distilling column, using triethylene glycol citrate or tetraethylene glycol as stopcock grease. These greases are insoluble in hydrocarbons but readily soluble in polar compounds. As the work of the laboratory required more and more azeotropic distillations with polar compounds we were forced to replace all the stopcocks with stainless steel diaphragm valves. (2) The seat of the lever-operated diaphragm valve was modified so there would be no liquid hold-up when the valve was installed in the distillate line. The stainless steel diaphragm is sealed with a teflon gasket.

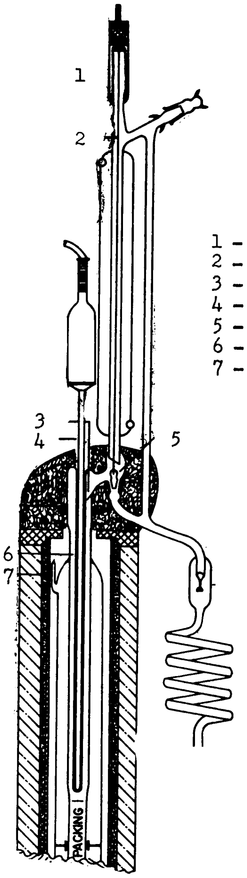
The graduated receiver is constructed of Pyrex glass with a capacity of 100 ml with 1 ml divisions. It has a water-jacketed condenser around the receiver and a vacuum jacket surrounding the whole thing to stop condensation and sweating. The receivers are made so they are interchangeable and are sealed to the valves by the use of the metal-to-glass solder joints.

The thermometric system consists of a platinum resistance thermometer that measures the liquid vapor equilibrium temperature at the head and is connected to a resistance bridge through a selector switch that allows us to select any of 20 platinum resistance thermometers and read the resistance to the nearest 0.01°C. The temperature of the column heaters and temperature of the liquid in the pot are determined by the use of single-junction copper-constantan thermocouples.

The heating of the column is done through the use of electric heating mantles - one for the upper third, one for the middle third and one for the lower third of the column. The pot is heated by two electrical heaters. The heater for the lower half of the pot is on all the time but is not hot enough to raise the pressure in the pot to the preset value on the mercury manometer. The heater for the upper half of the pot is set so as to furnish more heat than is needed to raise the pressure in the pot to the preset value on the mercury manometer which controls a relay circuit that regulates the upper heater.

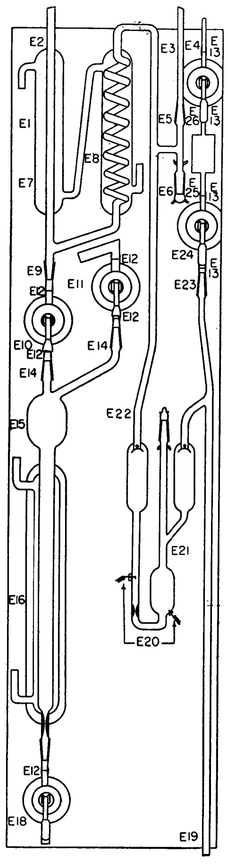
Each of the 14 distillation columns may be operated on any of three controlled pressure systems - 30 mm, 214 mm or 760.0 mm Hg. There is a manifold at each column to allow the pressure system to be connected to the column. Indicator lights installed in the operating area, and connected in series with the solenoid valves, permit the functioning of the pressure system to be closely observed and abnormal operation to be promptly recognized. The mercury manometers used in keeping the pressures constant are encased in an air thermostat. The air thermostat is provided with an electric space heater, a rotary air circulator driven by a motor mounted outside the thermostat, a mercury thermoregulator, and appropriate relays. A constant temperature inside the air thermostat is maintained at ±0.1°C. The three pressure systems contain dynamic rather than static pressures and the values of the controlled pressures are obtained from observations of the boiling point of pure p-xylene, using a special boiler. From these observations and from hourly observations of temperature made over long periods of time during many distillations of highly purified hydrocarbons at a controlled pressure of 760 mm Hg, it is found that the immediate variations in pressure at the head of the column during the operation of the solenoid valve, as well as the long-time changes in the controlled pressure normally do not exceed about ± 0.05 mm Hg.

The experience of our laboratory has indicated that prolonged stay at temperatures above 200°C. will cause significant decomposition of hydrocarbons. To avoid such decomposition of hydrocarbons, the regular distillation of hydrocarbons normally boiling above 200°C. must be performed at pressures below 1 atmosphere. This is easily accomplished in the regular distilling operation because each column is equipped with a manifold connected to several different controlled pressures down to 30 mm Hg. At this pressure, hydrocarbons normally boiling near 300°C. will boil at 135°C. With the increase in molecular weight and normal boiling point occurring as one



1 - Metal regulator with bellows
2 - Tungsten rod, No. 12 AWG
3 - Apron
4 - Platinum resistance thermometer
5 - Ground - glass valve
6 - Thermometer well
7 - Seal-off for evacuated jacket

FIGURE 2 Upper portion of distilling column assembly



*E*1. Transite supporting board
*E*2. Product line from head
*E*3. Copper line to controlled pressure system
*E*4. Copper line to source of inert gas
*E*5. Copper-to-glass standard-taper joint (soldered)
*E*6. Outlet to atmosphere, standard ground joint 12/30
*E*7. Condenser for cooling product line, near 10° C.
*E*8. Spiral condenser between receiver and controlled pressure system, near 10° C.
*E*9, *E*14, *E*17, *E*23. Monel-to-glass standard-taper joints (soldered)
*E*10. *E*11, *E*18, *E*24, *E*26. Lever-operated diaphragm valves of Monel
*E*12, *E*13. Connections of Monel (soldered)
*E*15. Overflow portion of receiver
*E*16. Receiver, graduated, water-jacketed
*E*19. Connection to manometer from pot
*E*20. Tungsten contacts
*E*21. Manometer (mercury, with tungsten contacts)
*E*22. Connection from manometer to head through spiral condenser
*E*25. Reservoir for introducing inert gas to pot

FIGURE 3 Receiving assembly for distilling column

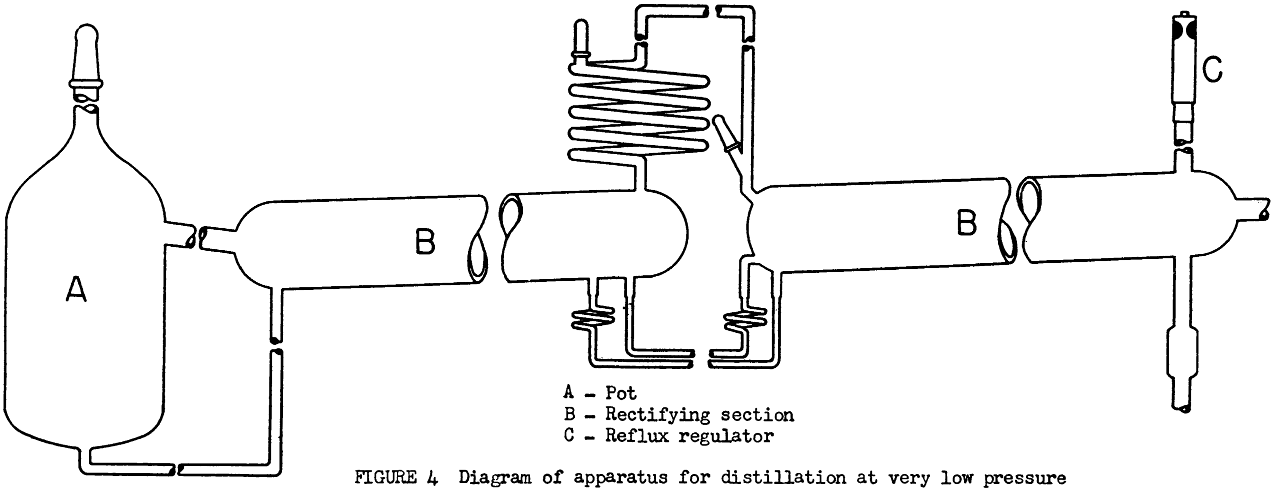


FIGURE 4 Diagram of apparatus for distillation at very low pressure

proceeds into the higher fractions of petroleum (from the gas-oil into the lubricating oil range), the pressures at which the hydrocarbon material will boil become smaller and smaller. A hydrocarbon of 25 carbon atoms per molecule will have a vapor pressure of the order of 1 mm Hg at 200°C. When the pressure is lowered still further, the concentration of the molecule in the vapor phase is so small that true thermodynamic equilibrium between liquid and vapor no long exists. We then go from regular distillation to a type of distillation involving the rate of escape of the different molecule species. This type of distillation has been called molecular distillation, evaporative distillation, unobstructed path distillation and high vacuum distillation. In our laboratory, when the liquid phase has a vapor pressure below 0.1 mm Hg, we refer to it as distillation at very low pressures.

We have a multi-stage apparatus for distillation at very low pressures, shown in Figure 4, involving counter-current movement of the material being fractionated. The material is added to the glass pot and the whole column is evacuated and the material degassed to an operating pressure of less than 0.01 microns. The material (20-35 carbon atoms per molecule) is heated and passed up the rectifying section to the regulator where the material is removed at a reflux ratio of about 38 to 1.

The cylindrical pot is made of Pyrex glass and contains an annular ring for collecting the distillate which condenses on the upper portion of the walls. The pot is connected to the rectifying section at two points. The upper connection is for the passage of distillate from the collecting annulus to the rectifying section. The lower connection permits liquid reflux to return from the rectifying section to the bottom of the pot. The rectifying section consists of a gently sloping glass tube with internal stainless steel fittings arranged in such a manner as to constitute a succession of plates. The outer containing tube is of Pyrex glass with the lower side flattened. Inside this tube is a stainless steel sheet, curved to fit the walls and bent to form troughs. Successive plates are separated from each other by liquid-tight seals in the troughs and by vapor barriers as well as by ridges. The small drip tubes are installed at the back of the troughs and pass the distillate upward through the column.

In practice, the bottom of the rectifying section is heated to vaporize a portion of the liquid. The vapor condenses on the cooler upper walls and the condensate flows to the trough and is delivered through the stainless steel tubes to the next higher plate. In this way the distillate passes upward through the rectifying section to the top plate where a portion is returned as reflux. The reflux returns to the bottom of the rectifying section by passing over the ridges in the lower flattened side of the glass tube. The ridges serve to maintain a small amount of liquid in each plate. Excellent separations are being performed by this column.

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LARGE-SCALE LABORATORY EQUIPMENT FOR SEPARATION OF THE ORGANIC FRACTION OF RECENT SEDIMENTS AND ANCIENT ROCK SAMPLES FOR STUDY OF THE GENESIS OF PETROLEUM

by

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The Geochemical Section of the Gulf Fellowship at Mellon Institute is engaged in a long range fundamental study of the chemical aspects of the genesis of petroleum in the earth. Briefly, the objective is the investigation of the chemical composition of plant and animal remains being deposited or buried in aquatic sediments and the chemical transformations that take place through the subsequent ages.

Plant and animal detritus deposited in the earth is rapidly destroyed by bacteria wherever oxygen is present. Thus, such material can survive only when deposited in undisturbed sediments, such as swamps, brackish coastal marshes, sounds or lagoons, flat areas or depressions in the continental shelves and in the basins of the deep ocean. The ecology, i.e., the assembly of plants and animals, differs from one of these typical environments to another and, consequently, the chemical composition of their remains which pass into the sediments. After deposition, other factors such as bacterial flora, acidity or alkalinity, temperature, etc., each varying with the environment, come into play. Thus, it is believed that certain environments will lead to the genesis of crude oils, while others will favor the genesis of other natural bitumens such as coals.

To comprehend the complex chemistry involved in the genesis of these substances, it is necessary to follow the steps of the transformations taking place in each environment. Naturally, it is impossible to observe a single sample through a span of millions of years. Instead a series of samples typifying each initial environment, but deposited at various times ranging from the near recent back into the geologic past, many millions of years ago, are selected.

In such a study it is necessary to follow the transformations taking place in all types of organic materials. However, since the principal interest is in the genesis of petroleum, emphasis is given to the gaseous, oily, and waxy hydrocarbons and similar material likely to be converted to petroleum. The concentrations of these materials in most aquatic sediments is not high. In the case of the low molecular weight aliphatic and aromatic hydrocarbons which make up natural gas and the lightest fractions of crude oil, analytical methods must be capable of detecting parts per million or even parts per billion. Even the heavy oily and waxy fractions usually represent only tenths and in rare instances, a per cent or two of the total sample. The data in Table 1 are typical. For example, one kilogram of the last sample on a dry weight basis contains only 9 milligrams of the low molecular weight aromatic hydrocarbons and approximately 220 mg. of total oily and waxy material. Further, it should be exphasized that these samples originally contain anywhere from 30% to 80% water which must be removed prior to extraction with organic solvents.

Before proceeding with the discussion of the mechanics and apparatus for the separation of the organic material a few

TABLE I

Typical Concentrations of Volatile and Heavy Oily or Waxy Material in Aquatic or Marine Sediment or Rock Samples

		Concentration of	
Initial Environment	Age in Years	low molecular weight aromatic hydrocarbons, ppm.	oily and waxy material*, per cent
subtropical swamp	4,475±120**	none	9.00
brackish marsh	2,200±200**	none	0.248
sound	1,400±100**	none	0.548
shallow marine	3,480±140**	none	0.0202
swamp (probably subtropical)	Pennsylvanian (~ 420 million)	4.5	0.10
fresh or brackish marsh or lake	Eocene (~ 45 million)	56.4	1.75
shallow marine	Oligocene (~ 27 million)	9.2	0.0223

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* Hydrocarbons, fatty acids and alcohols, sterols, etc.

** Determined by radiocarbon dating.

Operations Involved in the Isolation of Organic Matter from Recent Sediments and Ancient Rock Samples

Fig. 1

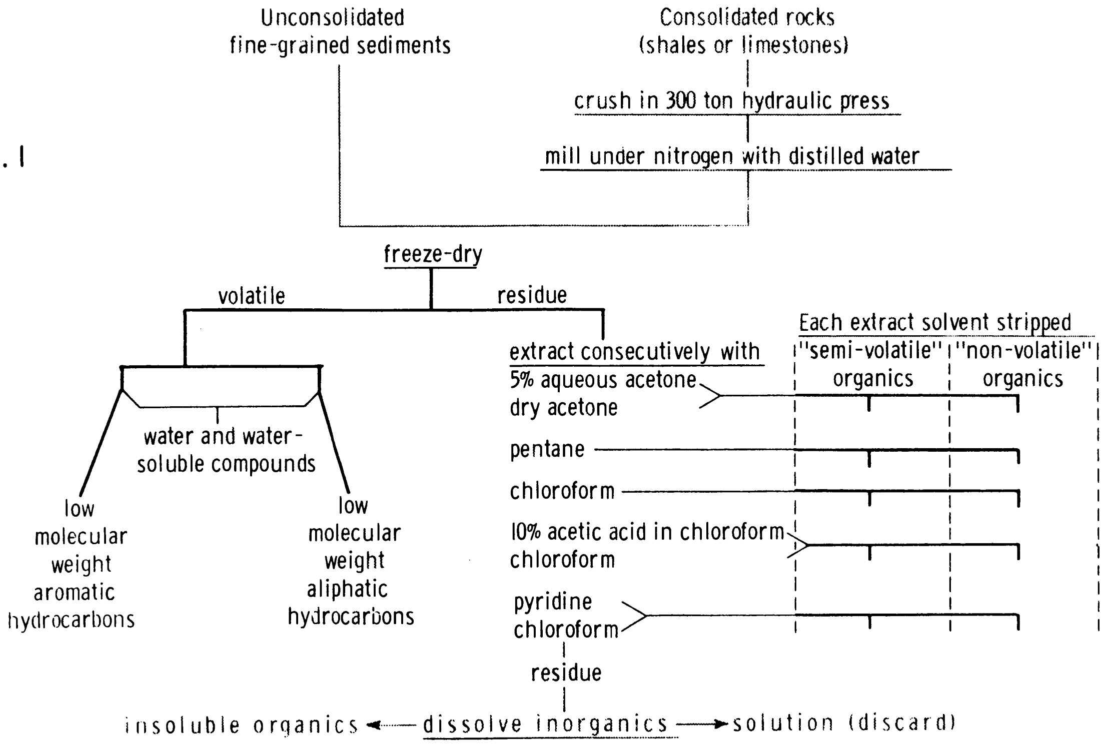
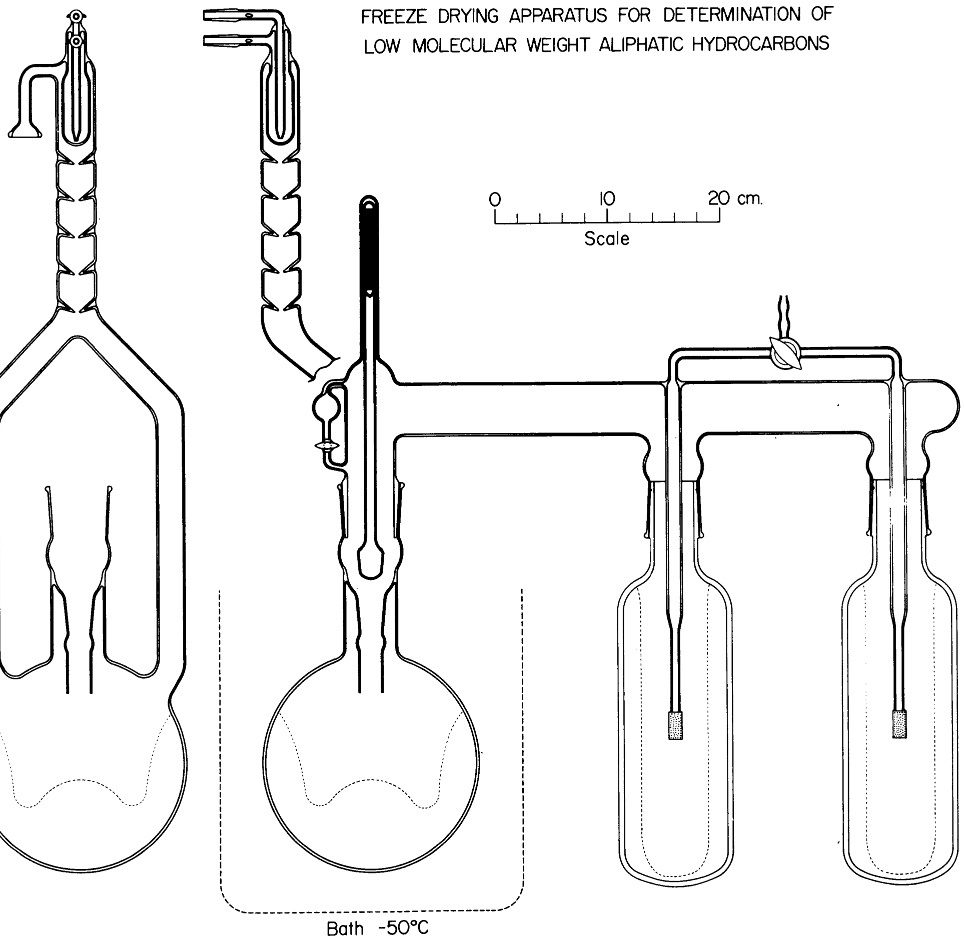


Fig. 2



FREEZE DRYING APPARATUS FOR DETERMINATION OF LOW MOLECULAR WEIGHT ALIPHATIC HYDROCARBONS words must be said concerning the chemical stability of these substances and the precautions which must be taken in handling them. Despite the fact that they have been entombed in the earth for hundreds, thousands or even millions of years, they are reactive substances. Their environment in the earth is oxygen free, the temperatures are low (in the deep ocean, only a few degrees above freezing) and there is no light. To prevent post-sampling alteration, therefore, it is essential that the entire processing be carried out with rigid exclusion of atmospheric oxygen, with the avoidance of prolonged exposure to elevated temperatures, and without exposure to strong light.

A flow sheet of the operations involved in the isolation of organic matter from recent sediment and ancient rock samples is shown in Figure 1. In this discussion, emphasis will be placed upon apparatus and procedures for performing the steps shown in heavy line and type. The first of these is the freeze-drying step which separates the water and volatile organic material. One experimental variation permits determination of low molecular weight aliphatic hydrocarbons, while another permits determination of low molecular weight aromatic hydrocarbons. The second step involves sequential solvent extraction of the residue, yielding two series of fractions which we will arbitrarily designate as semi-volatile organics and non-volatile organics.

Let it be assumed that the sample is in the form of a slurry, ready for separation of the water and volatile organic material. If the drying operation were carried out in a vacuum oven, the material would be converted to lumps, brick-like in consistency, hard on the outside, wet on the inside. To dry the center, would require prolonged heating which would lead to loss of volatile organic material and chemical alteration of the non-volatiles. For extraction, the hard lumps would have to be broken up by a dry milling operation; a step difficult to perform with the exclusion of oxygen.

The freeze-drying procedure overcomes these limitations. The design of one of the units is shown in Figure 2 and will serve to illustrate the process. As is indicated by the dashed lines, the slurry is frozen on the walls of the heavy-walled cylindrical glass bulbs. At a controlled vacuum of 1 mm. of mercury the ice and any volatile organic material evaporates or sublimes directly from the solid state. As the water is withdrawn the residue assumes a sponge-like texture, the apparent density of which is dependent upon the initial concentration. In the case of sediment samples comprised of fine grained clay particles, the product is fluffy and talc-like in consistency. Since the operation takes place at sub-freezing temperatures, no chemical alteration occurs. Further, since the dehydration progresses backward from the face of the frozen mass, the water vapor, expanded to great volume by the high vacuum, sweeps through the already dehydrated cake, removing any organic material possessing a finite vapor pressure.

This particular unit is designed for the determination of the volatile aliphatic hydrocarbons as well as for dehydration. The vapors are jetted against the bottom of the spherical bulb where the water condenses to ice. The cobalt glass tipped nozzle absorbs enough heat from above to prevent condensation of water vapor and clogging with ice. In this apparatus no attempt is made to trap the most volatile hydrocarbons by condensation; instead they are allowed to escape from the apparatus through the side arms into a train where they are given a rough fractionation and then compressed into ampoules for gas chromatographic or mass spectral analysis. The heavier or less volatile hydrocarbons condense in the large bulb along with the water. After the drying operation is complete, the magnetically controlled valve is closed and sealed with mercury from the small side reservoir. The cold bath is then removed and the sublimate allowed to melt and boil under the vacuum which now has been decreased to approximately 1 cm. by introduction of purified helium through the tubes capped with sintered glass. The remaining hydrocarbons thus effectively steam distill out of the pot, and are collected for analysis.

Another style of freeze-drying unit is shown in isometric projection in Figure 3. This assembly is used for the determination of volatile aromatic hydrocarbons, such as benzene, as well as for dehydration. It will be noted that four sample bulbs have been used to double the capacity and that two small

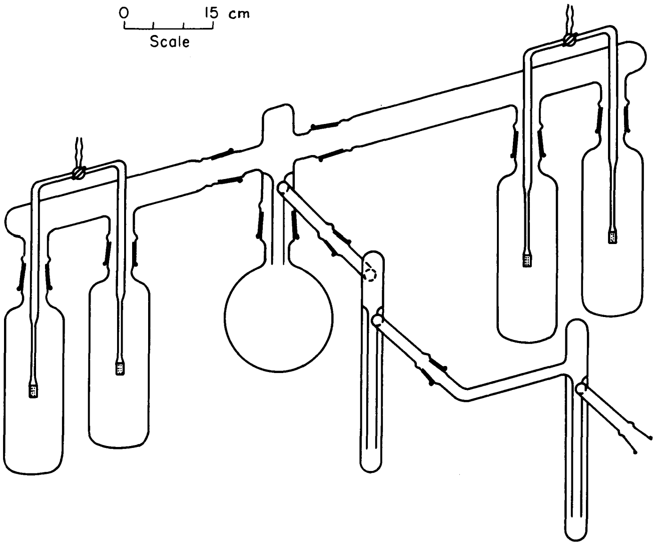


Fig. 3

ARRANGEMENT OF FREEZE DRYING EQUIPMENT FOR DETERMINATION OF AROMATIC HYDROCARBONS finger condensers have been put in series following the main condenser which is maintained at -50°C. The two small traps are cooled by means of liquid nitrogen. As each sample bulb is attached to the apparatus, a small amount of isooctane is added. This paraffinic and spectrally transparent hydrocarbon distills or vaporizes with the water and aromatic hydrocarbons, and upon condensing in the traps absorbs or extracts the aromatic hydrocarbons out of the water layer. At the completion of a run, the isooctane is separated, scanned spectrally in the ultraviolet for detection and determination of the aromatic hydrocarbons.

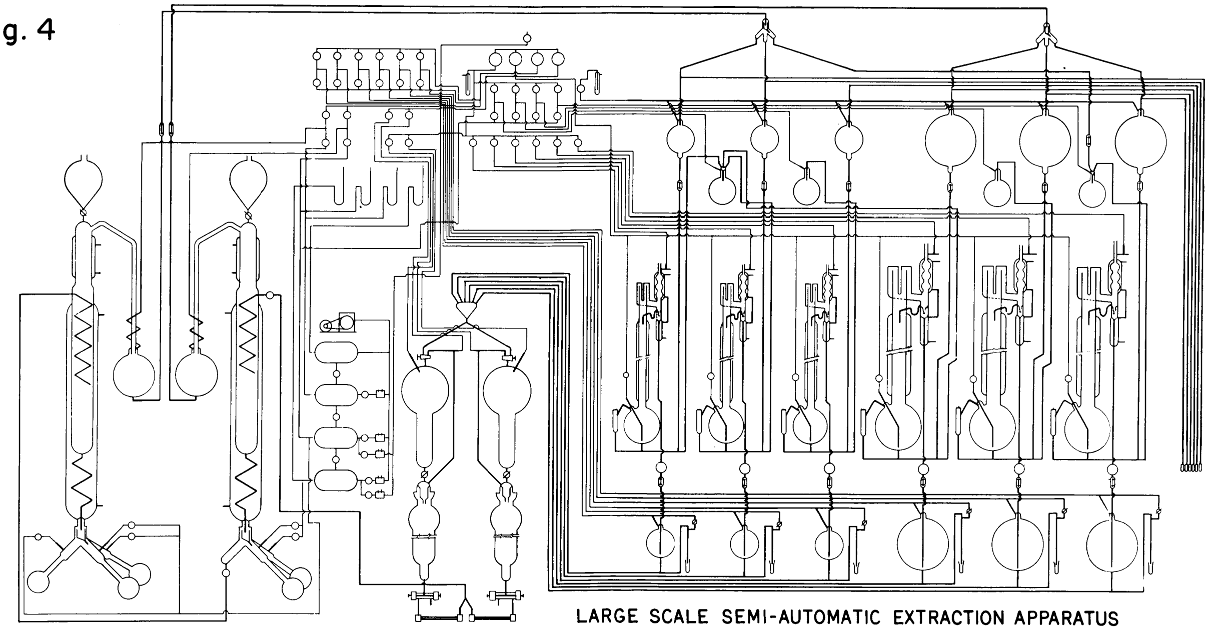
If operation of the unit has been satisfactory, about 99.8% of the water and the higher molecular weight, less volatile aromatic hydrocarbons are condensed in the large trap. A few grams of water and the most volatile of the hydrocarbons pass over and are caught in the first finger condenser. The second finger condenser acts as a guard trap and should remain empty. If spectral examination indicates the presence of any material in this trap the run is discarded owing to the danger either of loss of aromatics from the apparatus or contamination by back diffusion from the pumps and vacuum control system. As a further precaution, the pumps are charged with methyl silicone which is spectrally distinct from hydrocarbons.

Since a freeze-dry operation requires approximately eight hours and since it is often desirable to operate during the night, automatic replenishment of the liquid nitrogen from reservoir flasks is provided. The level of liquid nitrogen around the finger condensers is monitored by oxygen thermometers which actuate a dispenser relay controlling two solenoid valves, one of which opens and introduces air pressure to drive over liquid nitrogen, and the other to release the pressure when sufficient liquid has been dispensed.

When the three units, maintained in this laboratory, are operating at full capacity, 9 kg. or about 18 lbs. of a slurry containing 70% water can be dehydrated every twenty-four hours. At the termination of the freeze-dry runs, the sample bulbs are flooded with purified nitrogen through the tubes tipped with sintered glass discs protruding down into each sample bulb. As the bulb is removed a cap equipped with a similar tube is brought over the mouth of the bulb. The capped containers finally are introduced into a nitrogen-filled chamber for transfer to the apparatus for solvent extraction.

The extraction of the dehydrated sediment samples also represents a major operation requiring rather elaborate equipment. After dehydration the organic material is tightly adsorbed on the surface of the mineral particles and must be displaced by a small amount of a highly polar substance such as water. The amount of water added for this purpose must be carefully controlled to prevent swelling of the clays. Secondly, certain of the organic fractions, such as the chlorophyll pigments, must be extracted by a fairly polar organic solvent containing no alcohol or halogen. Waxy material, on the other hand, is best extracted by a paraffin hydrocarbon, such as pentane, and aromatic and non-hydrocarbon organic material by such solvents as chloroform and pyridine. Since some of the organic material is contained in the calcareous tests or skeletons of the organisms or in limestone granules, it is necessary to use acid to break these up. Further, owing to the fact that very large volumes of solvent in proportion to extract have to be used, the solvents must be freed of all traces of non-volatile organic material and maintained so throughout the operation. In like manner, the solvents must be free of molecular oxygen thus air must be excluded from the apparatus throughout the entire extraction

Fig. 4



LARGE SCALE SEMI-AUTOMATIC EXTRACTION APPARATUS procedure. A semi-schematic layout of the apparatus designed for this step is shown in Figure 4.

Solvent purification is accomplished in the bank of stills to the right. The first still is charged with acetone, the second with pentane, the third with chloroform, the fourth with acetic acid, the fifth with pyridine, and the sixth with water. Prior to charging the entire apparatus is purged with purified nitrogen. The raw solvents are charged to the series of solvent feed reservoirs shown above the stills where they flow through solenoid valves down into the pots, the check valves being controlled by level sensing devices attached to each pot. The still columns are packed with glass helices and equipped with take-off regulators at the top. Reflux conditions are such that about ten plates of fractionating efficiency are achieved. The purified solvents collect in the bank of reservoirs shown below the stills. After the solvents have been distilled, the pots are thoroughly rinsed with solvent which is vented, the ejection being accomplished by applying nitrogen pressure to each still pot.

It is well at this time to point out that grease lubricants must not come in contact with the solvents or extracts, for even small amounts would represent considerable contamination. Wherever possible, stopcocks have been replaced by all-glass solenoid valves, by rotating glass funnels, by Teflon diaphragm valves, and by strategic application of pressure to parts of the system. In a few instances where stopcocks and joints could not be avoided, lubrication was effected by means of a mixture of sorbitol, manitol, glycerine, carboxymethylcellulose, and water. This mixture is water-soluble, virtually insoluble in organic solvents, and spectrally transparent in the visible and ultraviolet regions of the spectrum.

To begin an extraction, the two columns, lower center, which operate in parallel, are filled with dehydrated sediment. Two columns are used rather than one larger column in order to maintain a favorable length-to-width ratio and to avoid a weight difficult to handle. The columns, as shown, hold approximately 5 to 7 kilograms, depending on the density of the sample.

For the first extraction, 50 ml. of purified water is forced from the collection reservoir of Still 6 into the mixing heads, located above the columns, followed by 950 ml. of acetone from the collection reservoir of Still 1. The volume is determined by calibrations on the mixing heads. The pressure on the top of the heads now is decreased, while the pressure below the heads and at the top of the columns is increased. By cracking the stopcocks, nitrogen bubbles up through the liquid in the head, mixing the water and the acetone. After thorough mixing is obtained, the pressures are equilibrated, whereupon the liquid runs down through the stopcock into the column. Low pressure applied at the bottom of the column allows the liquid to seep through the sediment, extracting the organic material. After all the aqueous acetone has been transferred from the mixing head to the column, dry acetone is transferred to the head and thence to the column immediately following the acetone water. In turn, pentane is transferred and fed to the column followed by chloroform. While the chloroform is passing into the column, acetic acid and chloroform are mixed in the head and then fed to the column, followed by pure chloroform, then pyridine, and finally more chloroform. The extracts leaving the bottom of the columns pass up through rotameters (not shown) to determine flow rate and are then combined and passed to the solvent stripping stills.

A requirement of the study is that the extract removed by each solvent be collected separately. It is necessary, therefore, to be able to detect when one solvent has passed completely through a column and to interrupt the flow until the second column catches up. Monitoring of the solvent systems passing through the columns is accomplished electrically by observing changes in capacitance. The columns of the solvent stripping stills then are washed down, the receivers at the base of the columns changed, and the solvent condensers emptied. The next solvent then is allowed to flow out of the extraction columns.

Approximately 15 liters of solvent must be stripped during the extraction of the sediment contained in the columns. This step is effectively accomplished by means of the two stripping stills assembled in series. The principle of operation of a stripping still is that the solution is allowed to flow as a thin film down the inside wall of a heated container, countercurrent to the flow of a gas. The liquid should not boil, and the rate of evaporation of the solvent depends upon the partial pressure which is maintained over the film. Low partial pressure of solvent relative to temperature of the film can be maintained by increasing the flow rate of the gas or by decreasing pressure. Too slow a flow of gas causes the liquid to boil, too high a flow results in disruption of the film and overloading of the pumps. The advantage of the solvent stripping still over pot stills or rotating film evaporators is that any one particle of the residue is not exposed to jacket temperature for more than the time necessary for it to pass from the top to the bottom of the still column, usually less than a minute.

In the solvent stripping stills jacket temperature is maintained at 80°C. A control pressure system, shown between the extraction columns and the stripping stills, allows the selection of stabilized pressures of 40, 20, and 10 cm. of mercury for the still to the right, and 16, 8, 4, 2, and 1 cm. for the still to the left. To stabilize the flow of gas into the systems, the pressure gradient across the control valves is kept low. For example, when the first still is operating at 40 cm. pressure nitrogen is bled from a reservoir maintained at 60 cm., or when the still is maintained at 10 cm., nitrogen is bled from an equivalent reservoir held at 20 cm. In each still the nitrogen stream flowing countercurrent to the liquid passes out of the top of the column and into a condenser and collection bulb shown between the still columns. During operation, the condenser and bulb are contained in a cold bath maintained at about -40°C. Most of the solvent is condensed from the gas stream, the rest being lost with the nitrogen out of the apparatus. At the bottom of the first stripping still is a three-legged pants with a glass funnel enclosed which can be rotated to direct the concentrated extract into any of the three legs. Concentrated extract is here emphasized because the stripping column must be operated under such conditions as to allow at least a small amount of solvent to remain in the residue. Otherwise, the viscosity would be too high to permit it to drain out of the column and through the directing funnel. Two of the legs of the glass pants, attached to the first still, are equipped with collection ampoules. The third leg of the pants consists of a throttling valve and tube leading to the inlet of the second stripping still. Thus, a concentrate from the first column can be passed into the second. At the bottom of the second stripping still is another three-legged pants and directing funnel. All three legs here, however, are equipped with collecting ampoules. Nitrogen inlet jets are directed into each of the collection ampoules.

The stripping stills are used in the following manner. It will be remembered that the first solvent system contains acetone and water. Acetone is much more volatile than water, boiling at approximately 57°C. while water boils at 100°C. By operating the first stripping still at a pressure of 20 cm., and adjusting the flow of solvent to about 7-10 cc. a minute, virtually all the acetone can be flashed off in the column without appreciable removal of water. The emulsion of oil and water is directed through the throttling valve into the second stripping still where the pressure is maintained at 1 cm. At the lower pressure and slower flow rate, most of the water is stripped off and the viscous emulsion drains into one of the collection ampoules, where the last of the water is evaporated by the impinging nitrogen stream.

The next solvent system is pentane. This solvent boils at 36°C. To avoid bubbling in the first stripping column, it is necessary to increase the operating pressure to 40 cm. Since the solvent system consists of one component, only the first stripping still is needed, and the concentrated residue is directed into one of the collection ampoules at its base.

The third solvent system is chloroform with a boiling point of 61°C. By decreasing the pressure in the first stripping still to 10 cm., this solvent can be stripped and the extract passed into the second collection ampoule.

The fourth solvent is a two-component system containing acetic acid boiling at 118°C. and chloroform boiling at 61°C. A pressure of 10 cm. in the first stripping still causes most of the chloroform to evaporate, but very little of the acetic acid. The acetic acid concentrate is passed through the throttling valve into the second stripping still where the acetic acid is evaporated and the concentrate collected in another collection ampoule.

The last solvent also is a two-component system consisting of pyridine and chloroform. The former boils at 115°C., and the latter at 61°C. Again, chloroform is stripped in the first still and the pyridine concentrate passed into the second still where the pyridine is removed.

A certain amount of extract sticks on the walls of the stripping still columns during each operation. To prevent these residues becoming mixed with the subsequent extracts, it is necessary to wash down the walls of the still. This is accomplished as a reflux operation. Circulation of hot water through the upper condenser above the inlet is stopped and replaced by ice water. A small amount of purified chloroform is drawn from the reservoir of Still 3 and introduced into the stripping column through the dropping funnel at the top. The chloroform runs down through the chilled upper condenser but boils in the lower heated portion of the column. The vapor does not escape, however, because it condenses in the chilled upper portion, running back down into the lower heated portion. Thus, a reflux is established between the lower section of the column and the region above the inlet for the extract. The streaming liquid washes the section between the two jackets. Now, the flow of hot water through the main column jacket is interrupted and slowly replaced from the top by hexane, chilled to about -10°C. Since hexane is lighter than water, even when cold, it forms a layer on top of the water. The chloroform now condenses in the portion of the column cooled by the hexane, streams down, evaporates in the section where the water is hot, condenses in the upper portion, and flows back again. By slowly dropping the hot water-cold hexane interface, the zone of reflux can be made to move from the top to the bottom of the column, progressively washing down the walls until at last the chloroform passes out of the bottom of the column, through the funnel and into the collection ampoule. At this point, the hexane is returned through a proper valving system to the refrigerated reservoir and the jacket washed with isopropyl alcohol. Circulation of hot water through both the upper and lower jackets is then resumed, and the flow of nitrogen directed into the ampoule. When the last of the solvent has evaporated, the bulb of the collection ampoule is chilled in dry ice and the constriction in its neck sealed off without contact with air.

Thus far, nothing has been said concerning the disposition of the solvents condensed from the nitrogen streams leaving the stripping columns. Owing to the very large solvent-to-extract ratio, a small amount of higher boiling material is carried over. To avoid loss of this important intermediate fraction, as well as to economize on solvents, provision has been made for recycle of the solvents as long as batches of the same sediment sample are being processed. For example, for a 100 kg. sample, the extraction would have to be carried out in twelve to fifteen batches.

Extract carried over with the solvent, owing to its higher boiling point will collect in the still pots. After all the batches of a sample are extracted, the level controls are inactivated, the liquid in each still pot reduced to a small volume, and bled off into containers for work-up. The used solvent is then withdrawn from the system and fresh solvent introduced for the processing of the next sample.

Construction drawings of the components are shown in the following figures. In Figure 5 is shown the design of the stills. The columns are vacuum jacketed and packed with glass helices. Two types of level controllers are used and are shown. The one to the left operates on the principle of make and break of two electric circuits and is applicable in those cases where the solvents conduct an electric current, i.e., water, acetic acid, and pyridine. For the non-conducting liquids, i.e., acetone, pentane, and chloroform, the controller shown on the left is used.

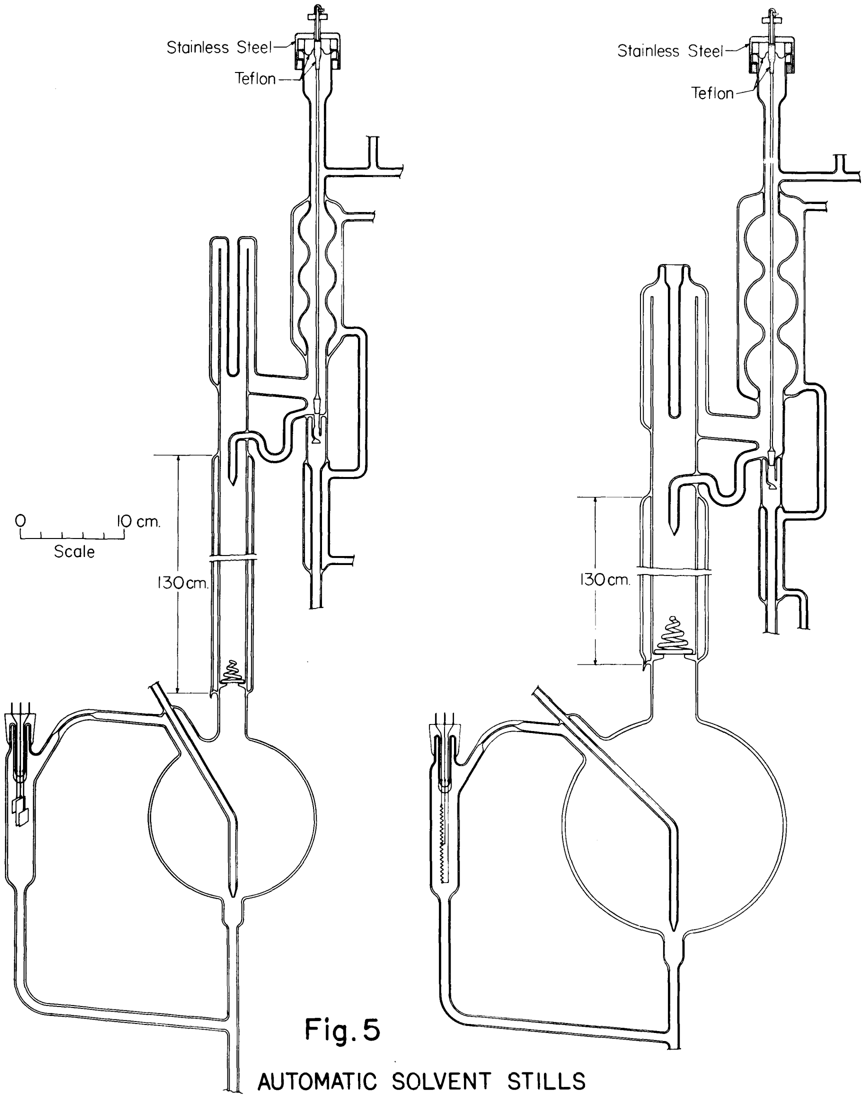
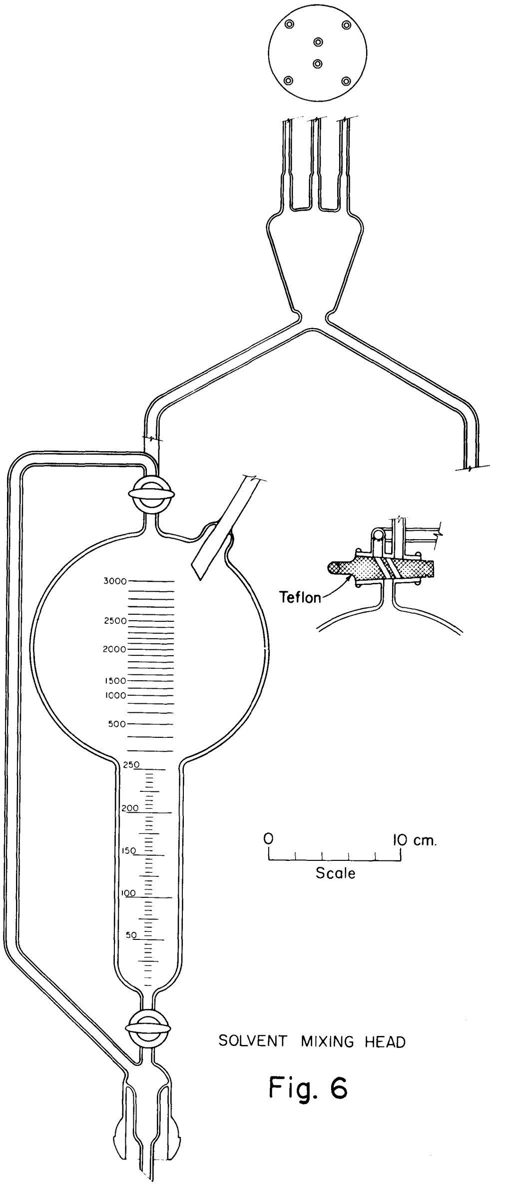


Fig. 5

AUTOMATIC SOLVENT STILLS



SOLVENT MIXING HEAD

Fig. 6

This controller consists of two coils heated slightly by the passage of an electric current. The temperatures of the coils when submerged in the liquid is somewhat less than when in the vapor. Changes in resistance in relation to temperature provide the necessary signal. All the metal touching the solvents is of platinum.

Take-off regulators turned out to be a particular problem. The first regulators consisted of a stainless steel bellows attached to the head of the still through a Kovar seal, the bellows providing stroke to a stainless steel shaft and taper. Upon putting the system into operation, severe corrosion of these regulators took place. Replacement with corrosion resistant type M stainless steel did not improve the situation. Plating of the components with rhodium gave only temporary relief. The unsatisfactory performance probably was due to the oxygen-free atmosphere wherein the stainless steel could not build up a protective oxide film. It finally proved necessary to replace the regulators with the Teflon devices shown. Here the stroke is accomplished by the motion of a rippled diaphragm rather than a bellows.

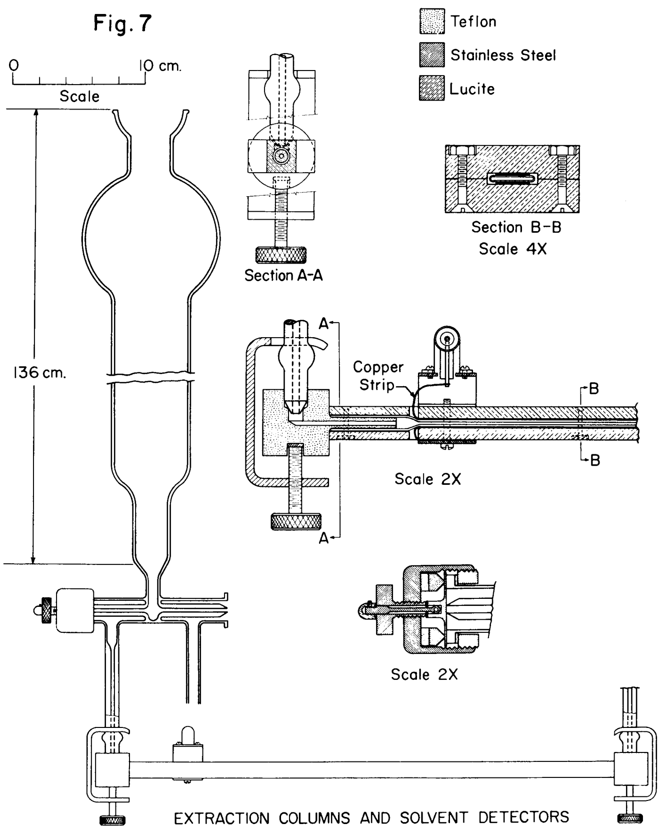
Construction of the solvent mixing heads is shown in Figure 6. The manifolding device for the solvents was developed out of a Erlenmeyer flask. The six tubes were attached in the design shown. The cyclindrical portion of the chamber permits accurate measurement of small volumes, i.e. of water, acetic acid, and pyridine. The spherical portion provides capacity for measuring the large volumes of acetone, pentane, and chloroform without making the apparatus excessively long.

The columns which hold the sediment for extraction and which are attached through the ball joints to the solvent mixing heads are shown in Figure 7. The joints here are not too objectionable because the nitrogen pressure at the head of the column is always above atmospheric, thus any leakage would be outward.

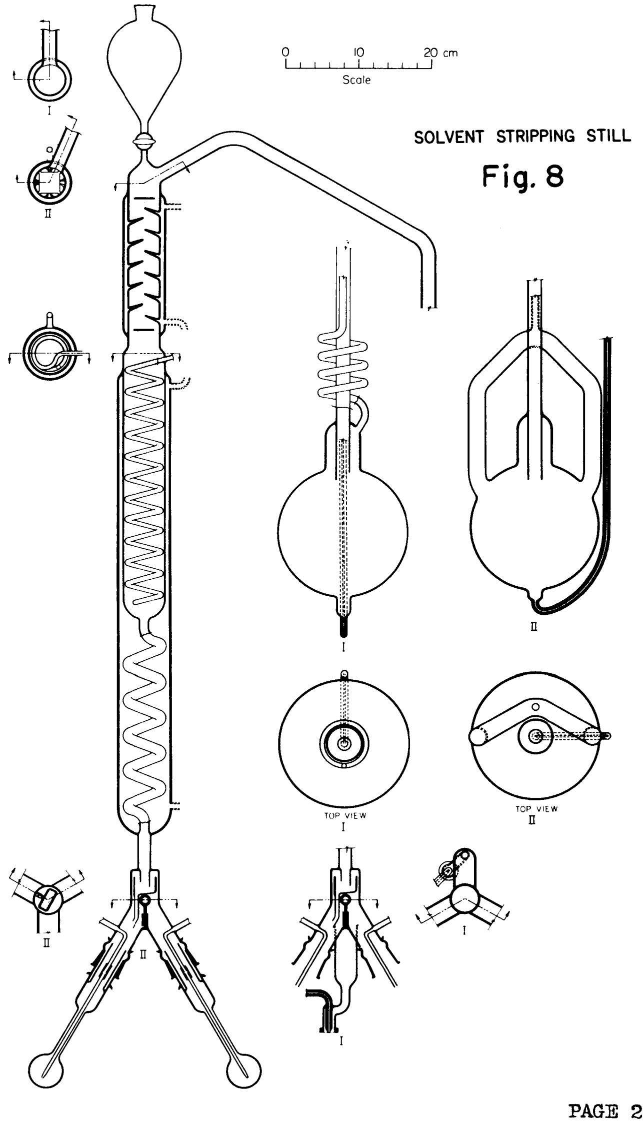
The design of the diaphragm valves and solvent detectors also are shown in detail. The valve consists of a Teflon disc which is pressed against or pulled away from a capillary tube ground in the shape of a cone. A flange seal is effected between the Teflon disc and the outer glass barrel, thus the liquid never touches metal. The solvent detector consists of a thin Teflon tube flattened between two copper electrodes which act as the plates of a condenser. The capacitance of the condenser depends on the dielectric properties of the liquid contained in the tube between the plates. The Teflon blocks and clamps provide a method for attachment to the glass column.

The construction drawing of the solvent stripping stills is shown in Figure 8. The upper jacketed portion is of

Fig. 7



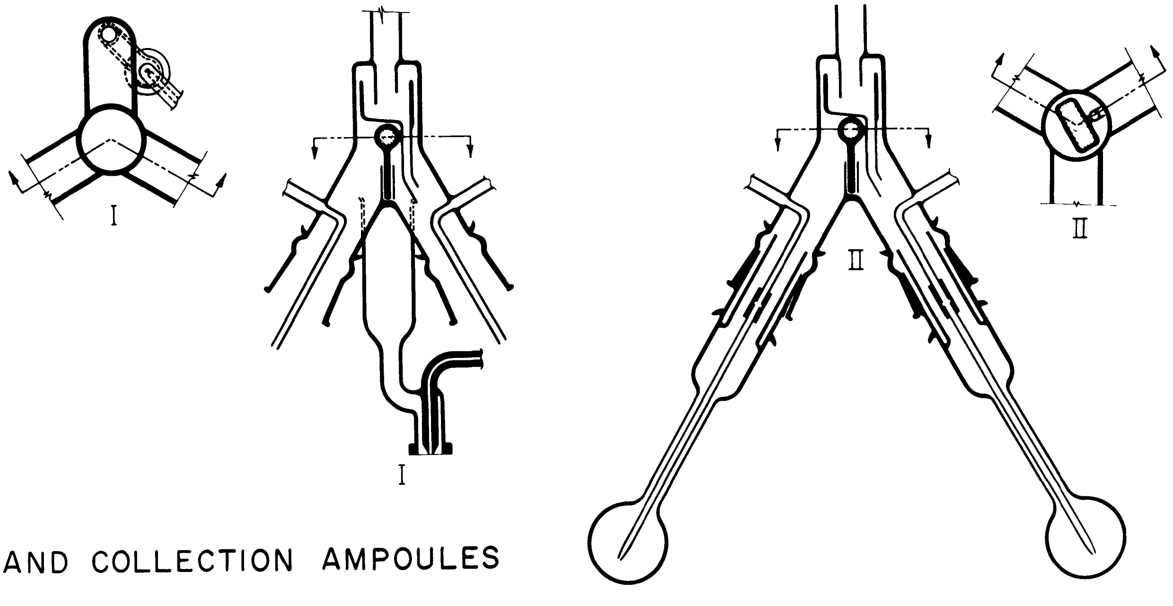
EXTRACTION COLUMNS AND SOLVENT DETECTORS



SOLVENT STRIPPING STILL

Fig. 8

Fig. 9



GLASS PANTS AND COLLECTION AMPOULES

punch column design to minimize spray carryover. A baffle placed below this section intercepts larger droplets. The main evaporation chamber is cylindrical at the top and spiral at the bottom. In the cylindrical section, the solution enters through a tube which makes one complete turn inside the chamber. Perforations along this tube allow the liquid to stream down the walls as a film. After one revolution, the tube becomes a solid rod which makes four more turns. The rod and tubing fit the walls of the evaporator snugly but not tightly, and serve to respread the falling curtain of solution over the walls providing maximum area for absorption of heat and for evaporation. Most of the evaporation is accomplished in the cylindrical portion. The coil at the bottom acts mainly as a spring to relieve strain caused by the sharp temperature changes incurred in shifting from hot water to refrigerated hexane.

Two condenser and reservoir designs are shown. Type 1 is attached to the first stripping still and serves to condense the more volatile solvents which remain liquid at bath temperature. Type 2, attached to the second still is designed for collection of those solvents which condense as solids. The capillary tubes leading from the extreme bottom of the bulbs serve for return of the solvent to the solvent still feed reservoirs.

The two styles of three-legged pants are shown at the bottom of Figure 8 and enlarged in Figure 9. The design to the right shows one leg fitted with a diaphragm valve which throttles the flow of liquid to the second still. The other legs of this pants and all three legs of the pants attached to the second still, and shown to the left, are adapted for attachment of collection ampoules. Since lubricated joints must be used here, grease channels and a trap are provided to prevent lubricant from getting into the receiver. An important feature for cleaning is that the female portion of the pivot for the funnel be vented as shown. The glass enclosed magnet is Alnico and is rotated by means of a slightly curved bar magnet held against the outside wall by means of a spring.

The glass pants used for directing the condensed solvents to the proper still feed reservoirs are of similar design but without the joints.

When the extraction apparatus is in full operation, the working period is five days, twenty-four hours a day without interruption. In this five day interval, the team leader and a technician work the day shift, with lone technicians operating the two alternate shifts. Under favorable conditions, three to four complete extraction cycles can be performed in the week, the freeze-drying units being adequate to provide the necessary amount of dehydrated sediment. The final step, which is not a part of the extraction procedure proper, represents the pooling of the equivalent extracts from consecutive extractions of the same sample. At the same time, any last traces of solvent are removed and the weight is accurately determined. Again, to avoid contact with air, the ampoules are introduced into an inert atmosphere chamber for handling through an air lock.

The equipment described in this paper is believed to be the most complete and rigorously designed apparatus for the extraction of recent unconsolidated sediments and ancient rock samples for geochemical study which has ever been devised.

Acknowledgment

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ELECTROCONDUCTIVE GLASSES

by John H. Glaser
Uni-Science, Inc.

ELECTRIC CONDUCTION IN GLASS

Historically, glass has served as an electric insulator. The electronics industry uses it today largely for this purpose.

However, early researchers studying the value of electric insulation found that at higher temperatures glass becomes a conductor, and that its electrical conductivity varies with the composition, physical state, and thermal history of the glass. It was further discovered that volume conductivity and surface conduction could be separated.

This paper describes recent research directed towards the study of both volume and surface conduction of various glasses.

VOLUME CONDUCTIVITY

Electrical conductivity in glass is ionic; that is, the electric current is carried by migrating ions as in the case of electrolytes. Highly mobile alkali ions such as sodium, potassium, and lithium are responsible for much ionic conduction phenomena, and conductivity increases as the alkali ion content increases.

We can visualize the structure of glass as a network comparable to a fishing net, where the size of the mesh, the strength of the twine, and the bond of the knot determine the number, strength, and size of the fish which it can retain. Using this fish-net analogy for glass, we can assume that the alkali ions, being tied to the silicon-oxygen network, are able to move freely through the holes of the net when electrolysis or thermal mobility is present. The mobility of the alkali ion can be restricted by adding glass modifiers such as the oxides of calcium, magnesium, or aluminum to the composition of the glass, resulting in glasses which are stable over a wide range of temperature and moisture conditions, and increasing the electrical resistivity of soda silicate glasses.

Conductivity and electrolysis increase rapidly with a rise in temperature. The volume resistivity of a number of glasses has been measured, using direct current as a function of temperature. It was found that a linear relationship exists between the logarithm of resistivity and the reciprocal of the absolute temperature. At melting temperature the resistivity will be of the order of 50Ω/cm, which means that the glass has become a conductor.

SURFACE CONDUCTIVITY

Surface conductivity of glasses is caused by the absorption of moisture and the condensation of a conductive film into the surface of the glass. A moist atmosphere leaches the alkali ions to the surface, creating a layer of glass which is relatively high in alkali content and therefore a good conductor. Smoke particles containing metallic or alkaline vapor and carbon residues will produce conductive paths on the surface of most glasses.

At the beginning of the nineteenth century, fish bowls were given an iridescent film by coating them with a composition of tin, copper, and antimony chlorides. A mixture of these salts was vaporized in an iron spoon placed in a muffle furnace (called a "glory hole") and the metal vapors were condensed onto the red hot glass. This iridescent coating was later found to be electrically conductive. A new technique using controlled temperature and vapor deposition was then developed, and is now the basis of commercially available electroconductive films on and in glass such as Corning's E Glass and P.P.G. Nesa films.

These films are extremely thin (a few millionths of an inch), transparent, and fairly hard, but they are also subject to abrasion, chemical influence, and diffusion into the glass, resulting in hot spots and an irregular resistance pattern over the surface.

Coatings of gold, platinum, iridium, rhodium, silver, aluminum, indium, and many alloy combinations of these metals have been evaporated and condensed onto glass by a high-vacuum technique or an electro-sputtering process. The application of metal resins (that is, metal salts in combination with oils and solvents) dates back to antiquity, and was used primarily for decorative purposes. By controlling temperature, time, and atmosphere, we have learned to produce good coherent coatings on most substrates, suitable for the severe requirements of the electronic and optical industries.

A metallic film can also be formed by reducing and depositing metal ions from aqueous or organic solution. An extensive literature and numerous patents cover this field.

Vapor reduction of the metallic constituents in glass by means of hydrogen or carbon monoxide gas forms a metallic surface film which has been used for certain electronic requirements. Lead, antimony, cadmium, copper, vanadium, and niobium glasses are frequently used with good results.

VOLUME CONDUCTIVITY

To obtain electronic conduction from metallic particle to metallic particle in a glass, a conductor was required which would resist oxidation, could be finely dispersed in very small particles, would uniformly wet-out within a glassy matrix, and which would be chemically and physically stable over a wide temperature range.

The noble metal group was first evaluated, beginning with silver, gold, platinum, rhodium, rhenium, osmium, iridium, and palladium. Considering the electron configurations of these metals, palladium appeared to have the most inert and balanced configuration, with 2 electrons in the K shell, 8 electrons in the L shell, 18 electrons in the M shell, and 18 electrons in the N shell. The behaviour of palladium has fully met our expectations.

When silver is present with palladium in a glass, electrical resistance is reduced by several magnitudes. The silver becomes partly ionized and enters the network structure by replacing the sodium ion. It therefore acts as a bridging element for the palladium. However, silver is soluble in H_2O and is therefore subject to migration and polarization. This might lead to a cat-ion accumulation at the anode and change the characteristics of the matrix.

Gold, silver, and platinum, with a single electron in the outer shell, are relatively active and must be partly oxidized to be bonded into the glass structure.

Tungsten, tantalum, rhenium, lanthanum, osmium, and iridium, with paired electrons in the outer shell, produce conductive media of higher stability.

The process of film forming on conductive glass is illustrated by the attached microphotographs and tables. An 80/20 palladium-silver glaze was printed on an alumina substrate to form a film 25 microns thick. After suitable drying in air, the film was fired in an electric muffle furnace to form a smooth glass after five minutes at 760°C. After this first step, Microphoto #1 shows an agglomeration of distinct particles on the glass: the glass is not yet electrically conductive. The remainder of this demonstration is summarized in Table I. Tables II and III show the results obtained by varying the composition of the glass.

APPLICATIONS

These new families of conductive glasses can be used as conductors, resistor elements, heaters, potentiometer elements, and capacitor constituents in printed circuits; in high-temperature control equipment such as atomic reactors; and as heating elements for such applications as room heating, windshield heating, and defrosting and defogging of aircraft.

Considerable development work is still required to produce glasses with low temperature and voltage coefficients, high thermal shock resistance, and overload stability.

1960 may well be remembered as the year when glass became an electrical conductor after having been an electrical insulator for centuries.

TABLE I

80/20 Pd/Ag Glass
Magnification: 560X

Microphoto	Temperature (C)	Time in Minutes	Glass Characteristics	Resistivity per cm	Relative Electrical Conductivity
1	760°	5	Agglomeration of distinct particles		Not conductive
2	800°	5	Agglomeration of particles in distinct clusters with bridge-forming		Not conductive
3	820°	4-1/2	Sintering of cluster into conductive network		Partly conductive
4	825°	5	Conductive network with large pinholes	9.6 MΩ	Conductive
5	830°	5	Conductive network with small pinholes	2.1 MΩ	Conductive
6	835°	5	Conductive network with very few imperfections	0.5 MΩ	Conductive


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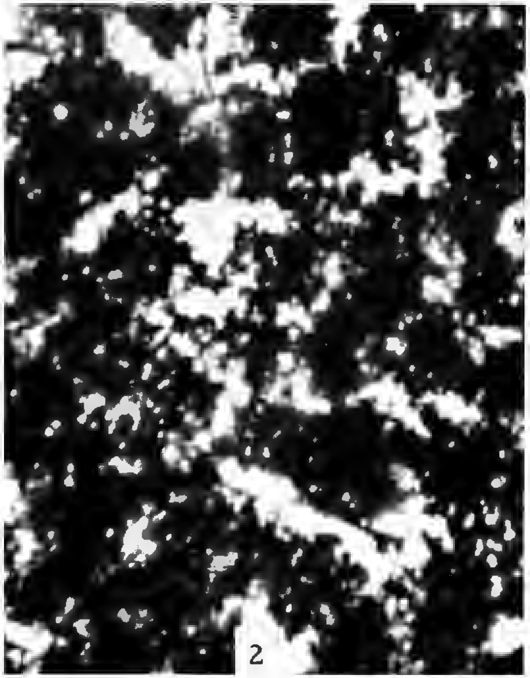
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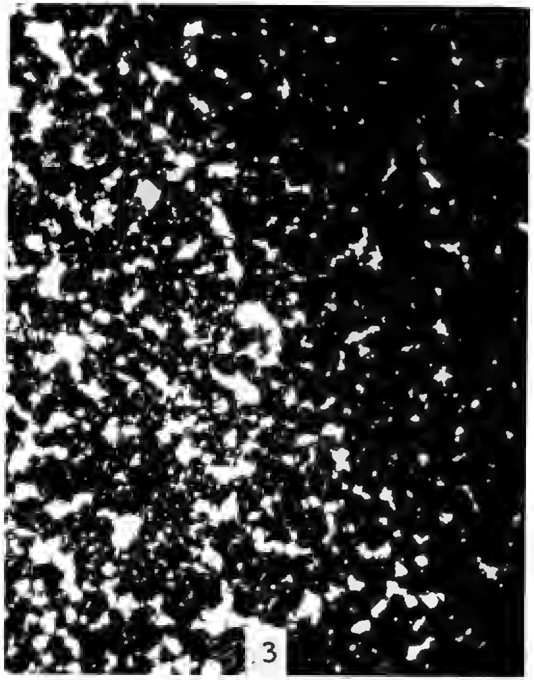
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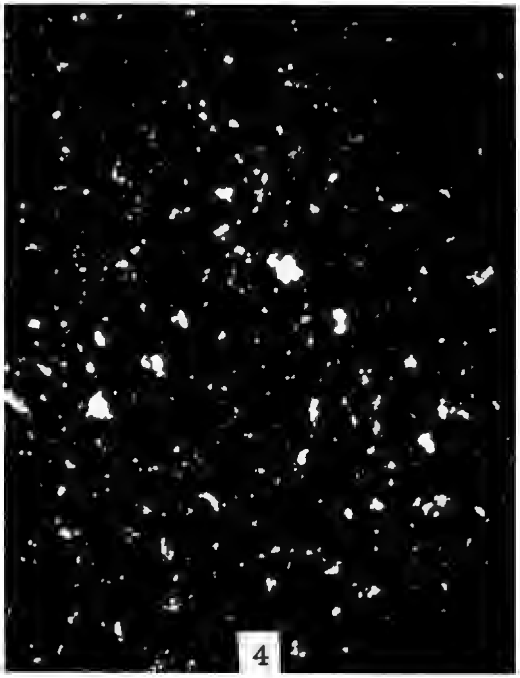
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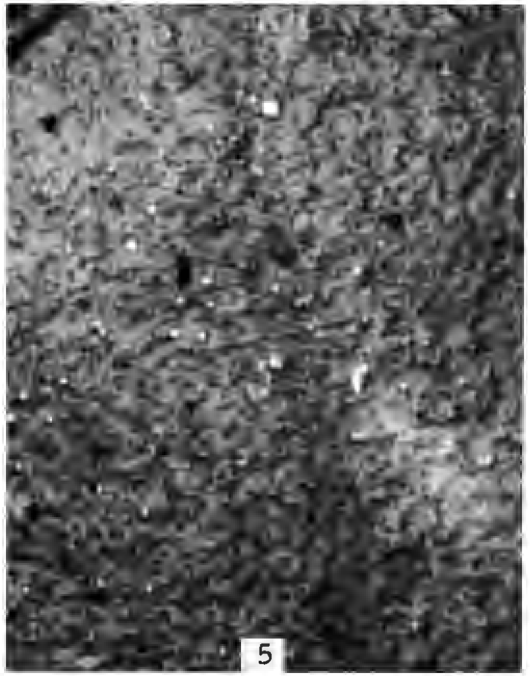
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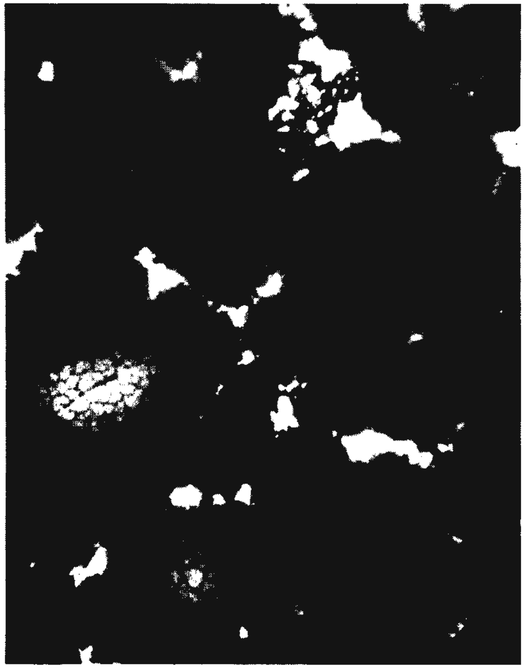

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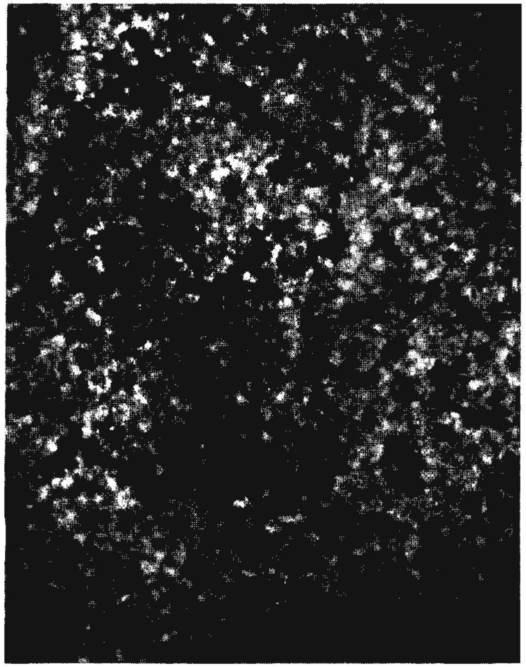
TABLE II

Temperature: 800°C
Time: 5 min.
Magnification: 560X

Microphoto	Glass Composition % Pd	% Ag_2O	Glass Characteristics	Resistivity per cm	Relative Electrical Conductivity
7	5		Individual agglomeration		Not conductive
8	1	4	Network forming	10 MΩ	Conductive
9	2	3	Branch forming	1 MΩ	Conductive
10	4	1	Film forming	100 KΩ	Conductive



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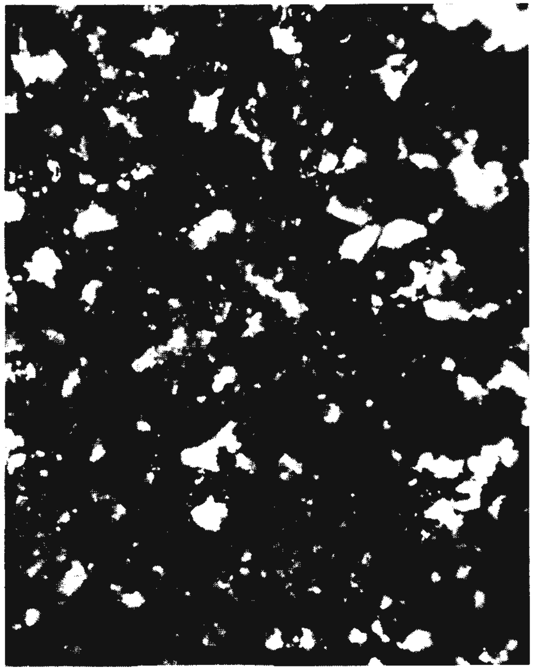

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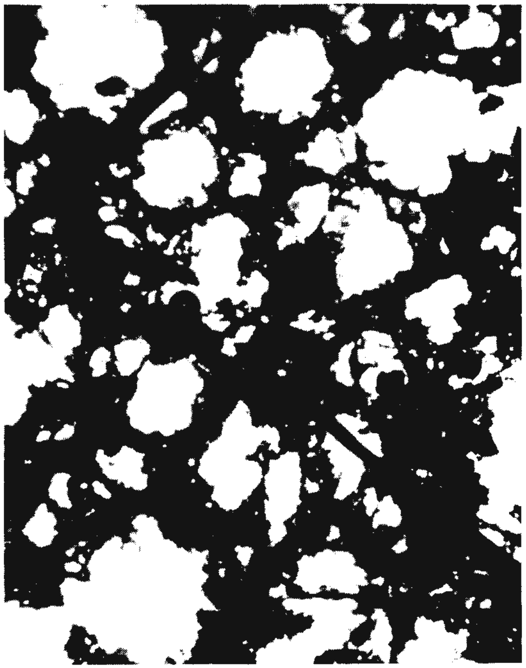

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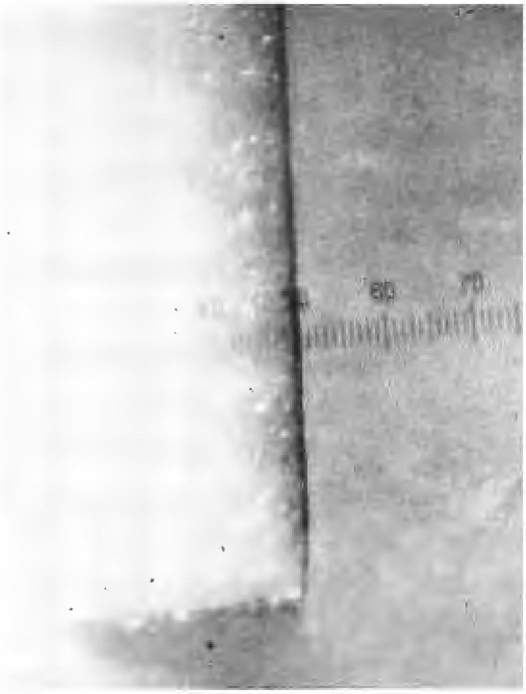
TABLE III

Temperature: 800°C
Time: 5 min.

Microphoto	Composition	Magnification
11	60% Pd, 40% Ag	2200X
12	Glass 5.7 μ thick on alumina substrate	560X

11



12

MARKING SCIENTIFIC GLASS APPARATUS

Ray Andrews
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After scientific glass apparatus is formed, it is frequently necessary or desirable to mark it with a trade mark, graduation, numerals or other identifying symbols. The purpose of this paper is to discuss the various methods of marking which are available today.

Most glass enamels are a two-component system composed of a clear, colorless flux and a coloring oxide or pigment.

Fluxes are made by mixing and melting together lead oxide, boric oxide, and silica, plus lesser amounts of soda, titanium dioxide, zirconium oxide and cadmium oxide. Titanium dioxide helps to improve acid resistance, and zirconium oxide aids alkali resistance.

During the process of manufacture, as the flux is melted, a thin stream is allowed to run into water which breaks it up into a size suitable for grinding. This process is usually referred to as water-cracking or waterquenching. Typical examples of an acid and alkali resisting flux, and a non-resisting flux, are:

	Resistant Flux	Non-Resistant Flux
Lead Oxide	48.6	66.6
Boric Oxide	6.9	18.3
Silicon Dioxide	25.0	14.8
Cadmium Oxide	3.6	
Sodium Oxide	3.2	
Titanium Dioxide	2.4	
Zirconium Dioxide	6.7	
Sodium Silica Fluoride	3.6	

The flux serves as a permanent vehicle for the coloring pigments which are added as a mill addition, and it governs, to a large extent, melting temperature, coefficient of expansion, chemical durability and the stability of the resulting glass enamel.

Coloring pigments are usually made by mixing together and calcining at temperatures ranging between 1600°F. and 2400°F. various metallic oxides--or salts of these oxides which will, on heating, yield the oxide.

The one exception to this is bright red which is made by mixing and calcining, at about 1200°F., cadmium sulphide and selenium. Reds can also be made by a wet-chemical process.

Some typical examples of how coloring pigments are made include:

Bright Blue - By calcining a mixture of cobalt oxide and aluminum oxide.

A very good black - By calcining together a mixture consisting of equal parts of the oxides of cobalt, iron and chromium.

Yellow - From antimony, tin, and lead oxides.

Blue-Green pigments - Usually from calcined mixtures of chromium, cobalt, aluminum, and zinc oxides.

The watercracked flux, along with a suitable quantity of coloring pigment, is charged into a ball mill and waterground until it will pass a 325 mesh screen. This ground and dried product is a finished glass enamel.

Before application to glass these powdered glass enamels must be mixed with a liquid vehicle such as squeegee oil, turpentine or ethylene glycol. After application to the glass the liquid vehicle is burned out during the firing process and the flux is melted, causing the color to adhere firmly to the glass.

SILK SCREEN

By far the most common method used to mark glass apparatus, especially when it is made in large quantities, is direct silk screen application. This method of marking is being used extensively on such items as pipettes, burettes, graduated cylinders, volumetric flasks and even test tubes. This method is best applied where large volumes of ware are to be printed and where the glass surface to be printed is either flat or cylindrical and is designed in such a way that it can be rotated in a chuck.

Silk screen printing is accomplished by mixing the dry color in a vehicle known as a squeegee oil. The color is mixed to a consistency of heavy cream and then is printed onto the glass by forcing it through a silk screen stencil with a rubber blade. After application to the glass, the color is fired by placing it in a suitable oven and raising the temperature to between 1000 and 1150°F., depending on the firing temperature of the color and the softening temperature of the glass onto which it has been applied. The glass is maintained at top temperature for a period of ten to fifteen minutes and then allowed to cool slowly to permit good annealing.

DIRECT RUBBER STAMP

One of the easiest and simplest ways to mark glassware is by means of direct rubber stamp. While this does not usually produce an attractive marking, it does produce a legible marking and if the need is functional rather than artistic, this method can be used. To accomplish this, the color is mixed to a heavy paste with Polyethylene Glycol #400. It is then spread out onto a glass plate in a thin film. A rubber stamp bearing the desired design is pressed against the wet film of color and is them transferred to the glass to be marked. The process is identical to marking paper with ordinary ink and a rubber stamp. After application to the glass the color must be fired to permanently fix it to the glass surface.

RUBBER STAMP AND DUST-ON

This method is a refinement of direct rubber stamp. To accomplish this, a heavy, tacky oil known in the trade as heavy English printing oil is rolled out onto a glass plate to a thin film. This oil is transferred to the glass being marked by means of a rubber stamp. After application of the oil to the glass, powdered color is dusted into the tacky impression with a piece of ordinary absorbent cotton. With some practice this method will give excellent results both from a standpoint of legibility and sharp, clean-cut impressions. Because English printing oil is difficult to burn away, it is important during the firing of the color that it be maintained at a temperature of about 800°F. for a period of ten to fifteen minutes before carrying it on up to firing temperature. This extra pre-heat is necessary so the color will not blister and carbon will not be retained in it after firing.

DECALCOMANIA TRANSFERS

Perhaps the most satisfactory way of all to mark scientific glass apparatus is by the use of decalcomania transfers; and perhaps the most serious objection to them is cost. Decals are simple to use and can be applied on practically any piece of glass in any location. The transfers are made up of a piece of paper coated with a water-soluble size. Color is silk screen printed onto this sized surface and then overprinted with a clear, transparent film which holds the design together during transfer. To use a decal, it is only necessary to dip it in water for about 30 seconds and then slide the colored impression off onto the glass in the proper location. After transfer, the decals should be pressed down or rolled down to remove water and air bubbles from underneath it. A worthwhile precaution in the use of decals is to allow them to dry for a period of twelve to twenty-four hours at room temperature before firing. After careful drying they are fired in the usual manner.

FILL-IN

In days gone by, the most popular method of marking scientific apparatus was by filling etched graduations and numerals with color. This was usually accomplished by mixing the color to an almost dry paste with turpentine and then filling the etched lines by simply rubbing the color over them and wiping off the excess. The color was then fired in the usual manner. Because of the extremely high cost of etching, this method of marking is gradually giving way to direct silk screen application.

WRITING PEN

If the only requirement is a legible mark, perhaps the simplest way to mark glass is with an ordinary writing pen. Powdered color is mixed with ethylene glycol, picked up with a writing pen and applied to the glass just as ink would be applied to paper during writing. A typical formula would be two ounces of dry color mixed with one ounce of ethylene glycol. For best results, the color and ethylene glycol should be milled in a ball mill to insure good dispersion free of lumps. After writing on the glass, it is fired in the usual manner at the desired temperature.

COEFFICIENT OF EXPANSION

When glass which is marked with a vitrifiable glass enamel is heated and cooled, both the glass and the enamel expand and contract. It is extremely important that this expansion and contraction of the glass and enamel be such that no stress will develop which will adversely affect the strength of the glass. Most of you have had the experience of marking a piece of Pyrex glass with a glass enamel and then find that the glass has been weakened very seriously. This is a problem which occurs so frequently some discussion of it seems justified.

As a general rule it can be said that an enamel, to have a good fit to the glass, should have an expansion of not less than 3 x 10^{-7}°C. lower than the expansion of the glass itself. For example, if a glass has a coefficient of expansion of 81 x 10^{-7}°C., then the enamel to be used on the glass should have an expansion of 78 x 10^{-7}°C., or less. If the expansion of the enamel is less than this, an improvement in both the thermal and mechanical strength of the glass will be noted.

On the other hand, when the expansion of the enamel is greater than the expansion of the glass on which it is applied, the strength of the glass will be diminished. If by actual measurement the expansion of the enamel is just equal to the expansion of the glass, there will be a discernible weakening of the glass. When the expansion of the enamel is raised to the place that it is 10 x 10^{-7}°C. higher than the expansion of the glass, spontaneous crazing of the enamel will occur and, in many cases, the glass will break as a result of excessive tension stress in the enamel.

It is a good rule to remember that the enamel functions as the outside surface of the glass so whatever happens to the enamel automatically happens to the glass on which it is applied.

When borosilicate glasses are decorated with ordinary glass enamels the expansion differential between the enamel and the glass is usually great. In many cases it will exceed 40 x 10^{-7}°C. In these cases a very fine type of crazing develops in the enamel and very shortly these crazes join each other immediately under the enamel surface. The stress in the glass is relieved enough so that borosilicate glasses are not as seriously weakened as a soda-lime glass would be if it were decorated with an enamel having an expansion of only 10 x 10^{-7}°C. greater than the glass.

Much time and effort has been expended on the problem of developing enamels which are satisfactory for the low expansion glasses; much progress has been made. Today it is possible to make a good range of glass enamels for borosilicate glasses which have a coefficient of expansion of approximately 45 x 10^{-7}°C. and a firing temperature of about 1160°F.

The problem of decorating the very low expansion borosilicate glasses still remains unsolved. If Pyrex glass must be marked with a vitrifiable enamel the enamel should be applied in as thin a layer as possible and then fired only to a semi-gloss. If the enamel is applied in a heavy layer and fired to a high gloss, it will, after a short period of service, craze off the glass leaving only a clear, etched line.

AMBER STAIN

By far the most satisfactory material to use to mark the low expansion borosilicate glasses is an amber stain. This material is not a vitrifiable enamel at all, but a silver bearing pigment which, when applied to glass and fired will permit silver ions to migrate into the glass surface and produce a stain ranging in color from light yellow to dark, transparent brown. This stain can be used on any type of glass regardless of expansion and since it does not weaken the glass, it is a material to be recommended above everything else for the marking of scientific glass apparatus. Amber stains can be fired at temperatures ranging between 800°F. and 1200°F. depending on the composition of the glass and the color which is desired. As a general rule, the lower the firing temperature, the longer the time the stain should be fired. For example, if a stain is fired at 800°F. it should be allowed to remain in the furnace for a period of 30 to 45 minutes. However, if a stain can be fired at a temperature of 1200°F., then the time interval can be reduced to as little as 5 minutes.

In addition to having no affect on the strength of glass, amber stains also have the added advantage of being as chemically durable as the glass itself so that they are practically unaffected by long exposure to strong acid alkalis, and hot corrosive liquids.

THE PHILOSOPHY OF GLASSBLOWING FOR GRADUATES

by

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Accompanying the present rapid expansion of graduate research programs in the many universities of this country, there exists an ever-increasing demand for highly qualified glass technologists experienced in the design and construction of complex glass research apparatus. While many stock items are directly available from a number of excellent glassblowing organizations, their assembly remains very largely the concern of the staff scientific glassblower in close liaison with the individuals concerned with the research programs. Although this primarily refers to academic institutions, nevertheless the same considerations apply in general to other research laboratories. In the assembling and use of complex research equipment, the glassblower and the research worker have separate but interrelated responsibilities, a better understanding of which could undoubtedly lead both to an improvement of the skill of the individual glassblower and to the progress of the research programs.

While it is never possible to dogmatize, particularly where individual abilities are involved, it is firmly believed that all graduate research personnel should be capable of achieving a certain minimum of glassblowing ability. They should certainly be capable of assembling simple stock items and effecting all minor repairs. To this end, courses in glassblowing by a skilled and experienced staff glassblower should be available to all graduate students. From experience, it has been found that a satisfactory minimum standard of competence at the bench and with the hand blow torch requires not less than six months of training at the rate of three to four hours a week. Although some limited degree of competence can be achieved in a shorter period, this is, in many ways, unsatisfactory and probably results in much unnecessary repair and reconstruction for the staff glassblower. Force of circumstances may dictate classes larger than the desirable maximum of six but the essential demand for individual training will be prejudiced by larger numbers. It should be fully appreciated that this careful individual attention demands a dedication to teaching which is somewhat rare and can only be developed over a period of time and in a suitable environment.

Although the instruction of graduate research personnel in the art of glassblowing is primarily to develop a practical ability, it also serves an equally important purpose in training personnel in the application and limitations of glass equipment. Many graduates at present complete and receive doctorates without any real appreciation of the capabilities and limitations of the glass apparatus which is almost invariably designed and constructed for them. Many applications which might be of profound importance in facilitating their research programs are overlooked. Although excellent texts exist these appear to be read more generally by the glassblowers than by the research personnel and even then to far too limited an extent. A graduate research worker should be able to rely on guidance and expert advice from the staff glassblower which implies that the latter must be fully conversant with the most recent developments, both in general techniques and those specifically related to local research interests.

While the training of graduate research personnel to perform a minimum of glassblowing is imperative for all institutions, it is essential that scientific glassblowers themselves should receive more adequate training and instruction. The majority of qualified and experienced glassblowers have acquired a very broad background of relevant information through their own application to the profession. Much would be gained by the establishment of preferred courses which would acquaint apprentice glassblowers with the many additional facets of their profession so necessary for the better development of their unique abilities. This is particularly the case for those aspiring to become scientific glassblowers at academic institutions, research laboratories or with other organizations concerned with the design and development of new and often highly intricate glass apparatus. In no case is this more important than in the field of vacuum technology. A thorough grounding in physical and inorganic chemistry is essential together with an advanced knowledge of those aspects specifically related to the fundamental characteristics of vacuum practice. Special courses in this important subject should be provided together with courses on such topics as glass-to-metal and glass-to-ceramic sealing, properties of materials and similar topics. Where organic research predominates, an adequate appreciation of distillation principals is imperative. Undoubtedly, many other aspects of fundamental importance to the scientific glassblower should be considered. On the basis of this, it is interesting to explore the possibilities for improving the instruction available to apprentice glassblowers.

One avenue of approach which has much to commend it is the selection of suitable candidates at the start of the sophomore year in schools or departments of ceramics, permitting selected candidates to develop glassblowing skills on a half-time basis while continuing to take special courses more especially relevant to their future profession. For the majority of schools, this would require an additional year before graduation but would be of very considerable advantage to the individual and to the profession at large. Alternately, selected candidates with an aptitude for glassblowing might be encouraged in their senior year to start developing the art and to continue after graduation for a year, taking special courses and training intensively in the practice of glassblowing.

These observations should not be taken to infer that a university degree is essential although the desirability cannot be denied. Suitable candidates, whether apprenticed in industry or trained in some scientific topic in any of the numerous excellent two-year colleges, would be equally well suited to continue with specialized course work. However, the skill and learning associated with the training of a scientific glassblower is such as to merit the award of a suitable degree.

The foregoing philosophy is the basis on which it is suggested that it should be possible to develop comprehensive programs for the training of graduates and undergraduates in the art of scientific glassblowing. The demand for trained and experienced personnel is increasing and will continue to increase far in excess of the numbers presently in training. Specialized courses should be made available to apprentices who would certainly welcome and profit by their existence. Scientific glassblowing is a very delicate combination of art and science. It is a profession of which anyone can be truly proud and one which many talented and intelligent individuals should be encouraged to join. The scientific glassblower and research worker are inter-dependent and everything should be done to promote compatibility between them. Noone knows better than an experienced research worker how restricted his activities are without the advice and assistance of an experienced glassblower and without the research worker no demand would exist for the art of scientific glassblowing.

THE PLACE of the GLASSBLOWER in RADIOCHEMICAL LABORATORIES

by

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Introduction

Some of the most effective methods used in modern research laboratories involve the use of radioactive isotopes. An ever-widening sector of the world's scientific literature deals with results made possible by the use of chemical reagents in whose molecules are atoms of some radioactive element. The use of a Geiger counter enables the fate of such a molecule to be followed through complicated industrial or biochemical processes, and aids in our understanding of just what reactions actually take place.

As in most chemical processes on the laboratory or pilot plant scale, the preparation, separation and processing of radioactive chemicals frequently require complicated glassware, and the inevitable maintenance and repair work needed may bring the glassblower into the vicinity of radioactive apparatus and materials. It is important that the original design of such glass apparatus take into account the requirements of possible on-the-spot repairs and changes.

The glassblower regularly employed in and around a radiochemical laboratory will be familiar with the safety requirements and will be subject to the discipline of the local safety supervisor. The glassblower not normally involved with radiochemicals may at some time be called upon for repair or alteration of radioactive glassware and, while he must accept all the instructions of the local safety supervisor, he should also have some personal knowledge and appreciation of the possible dangers, and the methods of avoiding them.

There is nothing about a radioactive material to indicate to the senses that the material is other than a normal chemical, unless the amount of activity be so great that light and heat are given off. The radiations emitted are detectable only with instruments. The most common radiations met with in this kind of work are:

Alpha particles, which are helium nuclei, of small penetrating power.

Beta particles, which are electrons and have more penetrating power than alphas.

Gamma rays, which are electromagnetic, like light rays of great penetrating power.

These radiations, in sufficient quantity, cause injury to humans by destroying body cells, and exposure may be either external or internal. External exposure is obvious, just being near an active source is enough.

Internal radiation may be liberated within the body from radioactivity ingested in contaminated food or air, from unwashed hands, or by solvent absorption through skin. Such bodily contamination very easily results through cuts and abrasions, and the glassblower is particularly vulnerable when his skin is broken in any way. He should not be in contact with active apparatus at such times.

Some active isotopes have an especial affinity for particular body tissues and may remain deposited there for long periods. For example radium or strontium in human bone.

The first knowledge of the effects of radiation upon humans was had from the history of early x-ray workers, and the atomic energy programs, benefiting from this experience and the knowledge that large amounts of ionizing radiation with its harmful effects would be involved, instituted precautionary measures to reduce or avoid the dangers.

Some of these safety precautions used in a plant producing radioisotopes, where radioactivity is present in massive amounts, are presented here for the information of glassblowers who may have to deal with radioactivity in their work. Strict observance of these safety regulations has resulted in an enviable safety record.

Radiochemical Laboratories

Where any radioactive materials are processed they should be confined to a special "active area" within the plant. To counteract the tendency of chemicals to get spread around the work area, scrupulous "housekeeping" must be applied and points of access to the active area should be guarded by barriers. At these points the visitor will be required to don protective clothing such as rubbers, lab coat and cloth cap. For work likely to contaminate clothing the laboratory must provide a complete change of work clothing so that one's own clothing will not be exposed to contamination.

Upon entry to the "active area", and after being outfitted in proper work clothes, the glassworker will be told how long he may safely work in the vicinity of the equipment he is to alter or repair. Specially trained personnel usually referred to as the "health physicists" will measure the radiation fields, and should discuss with the glassblower the methods he will use in carrying out the required work. This discussion will establish also a more accurate estimate of how long the glassblower may work in the vicinity with safety to himself and all others in the active area. In particularly severe conditions a dust mask, respirator, or complete plastic suit with attached fresh air hose may be necessary.

On all active jobs the glassblower will be issued a dosimeter which directly measures the radiation dose actually received. This should be checked routinely by the health physicist to determine if the glassblower must leave the vicinity. The glassblower will be provided also with a film badge which will accumulate a record of the radiation received during some fixed period, usually one week and during this period the same badge is used for each visit to the active area.

The laboratory equipment for radioactive work varies with the process, the amount of radioactive element, and also with the type of rays emitted by it.

Fume hoods are adequate for tracer amounts (microcuries) and low energy of radiation.

Glove boxes are required for larger amounts and higher energies.

Lead or concrete "caves" with remote manipulators will handle very large amounts, (kilocuries or megacuries) and the most penetrating radiations.

Protective Measures Used When Dealing with External Radiations

Massive shielding is the first requirement for gamma ray protection. Materials whose atoms are heavy are highly effective in absorbing the energy of the rays, e.g. lead bricks, concrete, iron, sand, and even water in large tanks has some applications. Lead glass is also used as a combination shield and viewing window. Detachable portions of the shielding may be removed for access to the equipment within. Mirrors or periscopes are often useful for studying a glass job beforehand without receiving radiation until necessary. The regular operator of the equipment will be requested to move any radioactive materials in the shielded enclosure into safe positions of storage behind shielding, or to take other precautions. This will lengthen the effective working time of the glassblower. It is preferable, too, that only the hands and arms become irradiated during the operation, while the body and head remain behind shielding.

Timing of work on active equipment will keep exposure to safe limits. The health physicist who has measured the radiation field in the exact working site with a long wand equipped with a terminal Geiger will state the safe working time there. If it is evident that more time will be required, other helpers must do the preliminary operations and leave the glassblower to do only those steps for which he is best qualified. Exposure is minimized by fast, well-planned, shared work.

Distance may be used as a safety factor, as radiation decreases rapidly as you recede from it. Doubling your distance reduces exposure four times. Whenever possible the direct handling of a radioactive object should be avoided, or made brief. The simple expedient of handling an active glass tube with tongs rather than gloved fingers will avoid a surprising dose of hand radiation. Radiation can actually destroy the skin and cause slow-healing radiation burns on the fingers. It is usually possible to make elaborate preparations at a safe distance from a job, then approach rapidly, finish the job fast, and withdraw at once. Most glassblowing can be done in a clean area, on clean new glass, and fashioned to fit neatly into place in a measured niche on the active equipment. The replacement unit is slipped quickly into place by assembling standard taper or ball joints, and if necessary one tubing arm may be heated to permit bending it into an exact fit.

Radioactive decay may make possible some jobs at a future date with a great reduction in exposure. E.g., a radio-iodine apparatus will be only half as radioactive in eight days time, and one quarter as active in sixteen days time. Duplicate equipment often makes possible alternate servicing on equipment made relatively safe by decay. Unfortunately most isotopes are longer-lived than this.

Proper design will prevent much exposure by avoiding the sequestering of glass equipment in hard-to-get-at places. All items should be within reach of both hands through such ports as are available, and preferably not through a thicket of equipment inside.

Rugged construction will reduce exposure by avoiding much repair work. Support of most units is desirable to prevent sagging when full of heavy liquid, and to counteract the twisting action of mechanical controls. As glass is weakened eventually by radiation, those parts are most likely to need replacement where the radioactive material will linger for some time, as in process units and storage reservoirs. It is well to have secondary containers such as stainless steel beakers around such units to catch possible spills as the glass deteriorates. A large metal tray should cover the floor under the whole process equipment. Glass lines should be constructed so as to drain free of liquid. Capillary lines are desirable for liquid transport as only a small volume of liquid is moving at one time, which minimizes radiation. Gentle suction also is best for liquid transport as it avoids pressure leakage at pipe joints, which spreads contamination. Provision for venting suction lines after use must be made to prevent creeping of liquids along them, and it may be desirable to have filters or scrubbers in suction lines to help contain the activity inside the shielding.

Spare parts for all critical units in an equipment should be available, and they should fit well into the places vacated by their predecessors to enable quick replacement. Sometimes a template can be kept to ensure an easy duplicate fit of connecting joints.

Stopcocks are a necessary nuisance in that the periodic servicing they require is the cause of much hand radiation. Sometimes they may be located in batteries with a shielding baffle between them and the main radiation fields. They may be supported firmly by fitted holders on Flexiframe rods, with quick-opening fasteners. The connecting tubes should be arranged so that the cock may be detached quickly and lifted out in a few seconds for servicing. Although normally turned with the gloved hand, in sites of high radiation cocks are turned remotely with rods and knobs. There is a limit to the number of these turning mechanisms that can be installed through thick lead walls, and unless shafts are flexible they are difficult to align properly. This means that the number of stopcocks is usually limited. Sometimes one turner may be made to service several lines by using one common five-way stopcock which will select the line to be evacuated or filled. Apiezon N has been found to be a reliable lubricant which is resistant to radiation and chemicals, and has better adhesion than teflon greases which tend to migrate along tubes. The teflon plug stopcocks serve very well until radiation deteriorates the plastic, which occurs only where massive radiation is involved.

Protective Measures Used to Prevent Internal Bodily Contamination

Ventilation of the whole "active area" by exhausting the air through filters up a high stack is important to the health of personnel therein. Equally important is the continual removal of air from glove boxes and "caves" to prevent their dusts, mists, or emitted gasses like radon from escaping into the laboratory air. This ventilation may be a problem during glassware repairs by the creation of drafts which may crack glassware being welded. Local ventilation in a hood, box or cave may have to be greatly reduced or shut off for the most critical minute or so, with the permission of equipment management. Draft shields of asbestos paper may be set up around the weld area instead.

Cleanliness in lab operations is necessary to avoid the general spreading of dusts by workers as they move about. The linoleum floor in the vicinity of apparatus being serviced should be checked frequently for activity and decontaminated promptly. Active scraps removed from equipment should be properly disposed of at once. Hands and gloves should be checked with the Geiger frequently.

Suitable clothing for the job at hand is dependent upon what has to be done. Lab coat, cap and gloves will suffice for tracer work. Coveralls are better for most jobs. For brief jobs involving quick reaches into radioactive equipment a pair of polythene sleeves may be pulled on, taped to the rubber gloves tightly with masking tape and taped to the shoulders of the coveralls. When withdrawn from the equipment these sleeves and gloves must be removed by the gloved hands of health physics personnel and disposed of before they touch anything else in case they are contaminated. Often it is necessary to wear a dust mask or respirator. Sometimes a complete suit of plastic with trailing air supply hose must be worn.

Personal hygiene is imperative around radioactive glass. Food, tobacco, gum must be forbidden in the active area. Hands must be kept away from the face, checked and washed frequently, particularly before going out for a meal. Skin areas can be decontaminated if not too active. Common abrasive hand cleaners are good, or other cleaners may be recommended by the laboratory workers in the area. A complete shower should be had after a radioactive glassblowing job, before changing back into ones own clothing.

The actual blowing of glass by the mouth, so characteristic of the trade, cannot be done on active work. Blowing may be done with a hand bulb and glass tee by placing a gloved finger over the stem of the tee and squeezing the bulb. An alternative is to have a slow stream of low-pressure air entering the equipment through a leaking hose, and to partially cover the leak with the gloved finger when inflation is required. Sometimes a second person can be trained to apply this inflation while the glassblower heats and manipulates the glass. This awkward procedure is a prime reason for trying to do most of the glassblowing in a clean area, and to confine active glassblowing to installation of prefabricated parts and removal of useless ones. Discarded units when lifted out should be smothered immediately in damp cloths and placed in a tight-lidded can for burial, to prevent spreading radioactivity around the area.

Separate glassworking tools should be kept in the active area. They need be only the simpler ones such as torch, tweezers, scratch cutter, and rubber bulbs. After active jobs they can usually be reduced to safe levels of radiation by decontaminating them with abrasive cleaners or detergents. They will be handled only with gloves.

Active area glassware should not be brought out casually to the clean shop of the glassworker for modification. If there is no glass torch in the active area, the glass piece should be accompanied by a certificate from a responsible health physicist declaring it to be free of activity and safe to blow by mouth.

Skin punctures by fractured tubing must be avoided, as enough active material may be taken into the body thus to exceed the maximum permissible body content considered safe, which is measureable in micrograms or less. Any cut should be encouraged to bleed, washed under a tap of clean water and taken for medical attention.

Well-placed joints will permit easy disassembly of glass. An active tube may be scratched and broken by the hot rod technique or by an incandescent wire. When active tube ends must be thrust into Tygon tubing the rubber-gloved hand may be covered by a heavy work glove, and the Tygon softened by immersion in a beaker of boiling water for a few minutes, when it will slip on easily and harden in place. Tygon hose is best sliced off glass tube ends with a single-edged razor blade.

Some of the procedures given here may be used at some time by glass men who may be called upon to alter or service radioactive equipment, or equipment in which other toxic materials are processed.

References

(1) Handbook 42, U.S. Dept. of Commerce, National Bureau of Standards.

(2) Safe Handling of Radioisotopes, Int. Atomic Energy Agency, Vienna, Austria, 1958.

REBOIL TESTING

by

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INTRODUCTION

Reboil has been a problem for many years in the glass industry where reheating of a glass is necessary for lampworking or sealing to itself or other glasses or materials.

A need was felt for a test that could produce reboil in a glass under controlled conditions. The reboil data obtained can be used as follows: (1) To compare glasses for reboil, and (2) To predict the performance of a glass in production sealing or reworking operations.

The test described in this paper can be used for control as well as development and research work.

APPARATUS

Figure I is a photograph of the complete reboil test equipment.

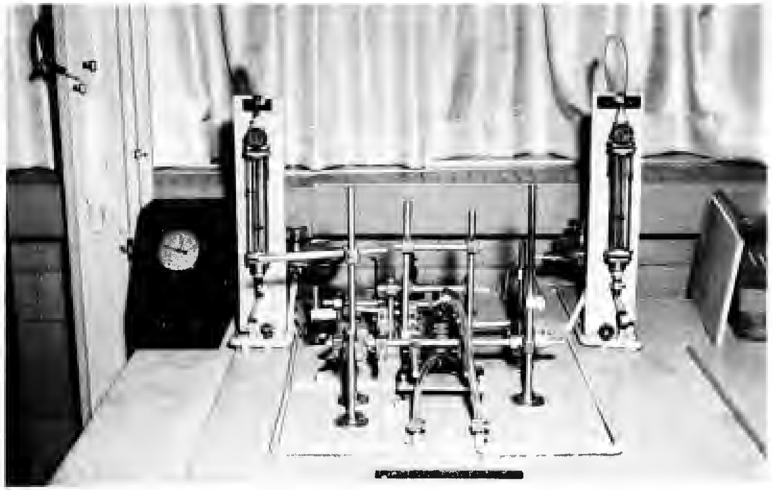

Fig. I PHOTOGRAPH OF COMPLETE REBOIL EQUIPMENT

A schematic diagram of the equipment assembly is given in Figure II.

The reboil equipment consists essentially of a frame assembly for positioning a glass rod sample quite accurately in relation with a commercial laboratory gas-oxygen blast burner with an invar tip. The invar tip minimizes changes in the size of the burner orifice due to thermal expansion. Since burner pressure is affected by orifice size, a constant orifice size is very important in maintaining stable burner operations.

The standard burner flame conditions are controlled by the following: (1) Gas flowmeter, low pressure gas regulator and water manometer, and (2) Oxygen flowmeter, two-stage oxygen pressure regulator, additional low pressure oxygen regulator along with a large volume expansion chamber and water manometer. The above controls maintain a reproducible constant flow of oxygen and gas at constant pressure to the burner.

The test sample holder is so designed as to be adjustable for variations in rod diameter. The compensating adjustments are made using a screw assembly and dial gauge.

The heating cycle is timed using a precision timer that reads directly to 0.1 second.

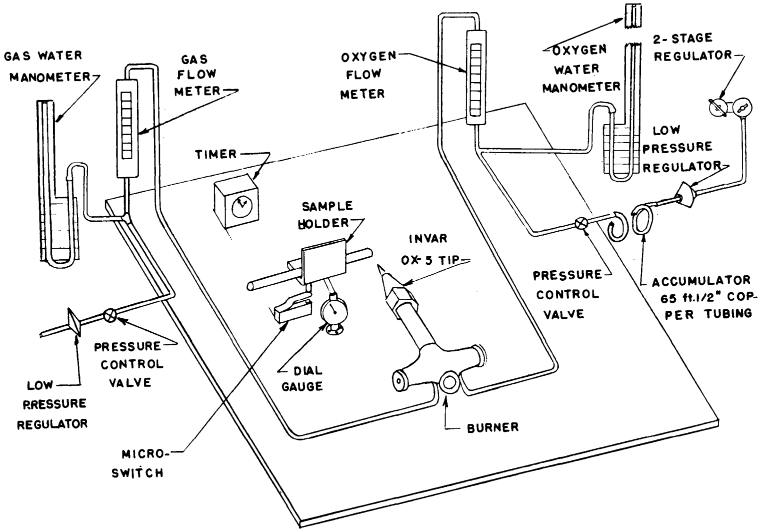

Fig. II SCHEMATIC LAYOUT OF REBOIL EQUIPMENT

PROCEDURE

1. Sample preparation

The first step in making a reboil determination is to select a glass rod that is straight in the axial plane. Rod with a camber of more than 3/64" in a 12" length should not be used.

The sample is then ground and polished using a 180 grit caborundum wheel. The polished end is inspected for scratches and chipped ends using a 10 power magnifying glass. Scratches and chips are cause for rejection in the one-third of the rod circumference facing the burner.

After measuring the diameter of the rod, the polished end is immersed in a 1% HF solution for 30 seconds. The sample is then rinsed in distilled water and dried with suitable source of electric heat (heat lamps). The sample is now ready for testing and the clean end must not be handled or placed in contact with any foreign material.

2. Equipment adjustment

The burner tip is checked for levelness and correct distances from the support board and sample holder. See Figures III and IV.

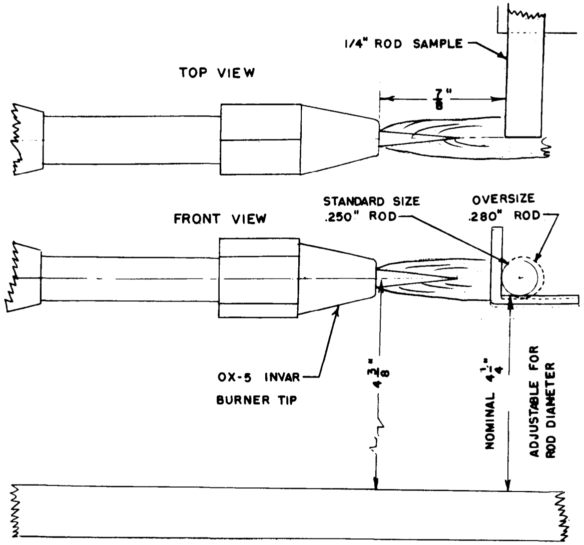

Fig. III DETAIL OF ROD POSITION IN FLAME

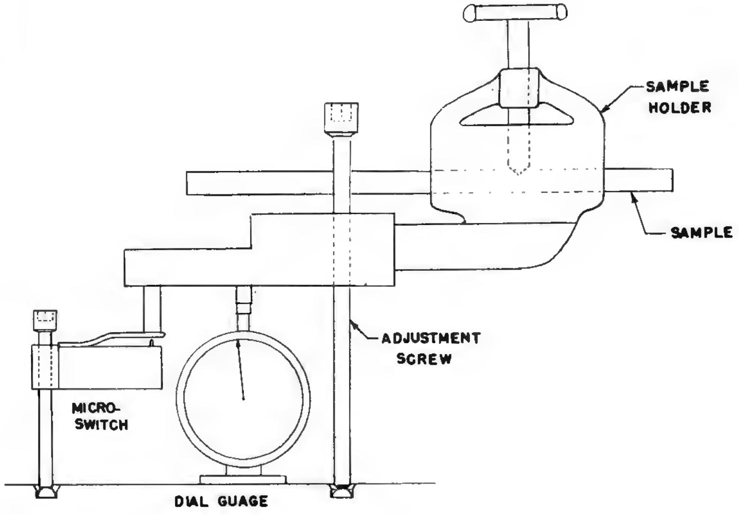

Fig. IV DETAIL OF SAMPLE HOLDER & DIAMETER ADJUSTMENT

Next, the burner is lighted and the flows and pressures adjusted as follows: (1) Natural Gas - 5.2 ft.^{3} /hr. at a pressure of 18" of water, and (2) Oxygen - 12.4 ft.^{3} /hr. at a pressure of 58 1/8" of water.

The sample and equipment are now ready for testing. The correction is now made for any variation in rod diameter from .250" (1/4"). A zero reading on the dial gauge is for a diameter of .250". If a larger diameter is encountered, the sample holder is moved downward and vice versa for a smaller diameter. The purpose of the diameter compensating adjustment is to keep the cane centered exactly in the flame.

The microswitch system is adjusted so the timer starts just as the sample holder reaches the correct position. An adjusting screw is used to position the microswitch in relation with the sample holder. See Figure IV for details.

The sample is now placed in the holder and positioned so that the flame is centered on the polished edge of the rod.

3. Test run

The test sample is lowered into the flame and allowed to remain for 8.0±.05 seconds. Figure V is a photograph of a sample during a test run. The holder is now raised and the sample placed in a furnace for annealing. After annealing, approximately 1/2" of rod containing the reboil is cut from the parent sample

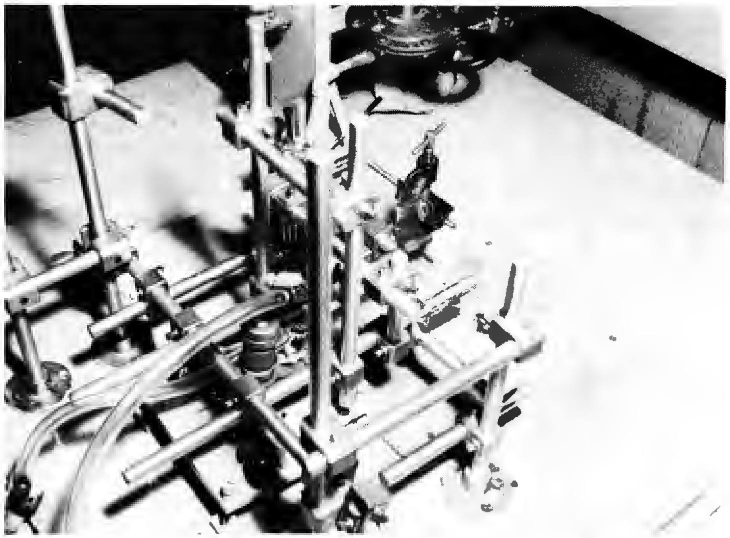

Fig. V CLOSEUP OF ROD SAMPLE

and weighed. The weighing is made on an analytical balance.

The densities of the reboil sample and parent sample are then obtained using a standard float sink method. The method is very similar to that used by Knight[1] and Duff[2]. The density of the sample is determined by observing the temperature at which it sinks in a heavy liquid, for which the temperature-density characteristics are known for the temperature range used.

4. Reboil volume calculations

The volume of reboil in the test sample is calculated by the formula:

$$V = W \left(\frac{1}{D} - \frac{1}{d} \right) \quad (1)$$

v = Volume of reboil sample (cubic centimeters)
V = Volume of reboil (cubic centimeters)
W = Weight of a sample (grams)
D = Density of reboil sample (grams/cubic centimeter)
d = Density of parent glass (grams/cubic centimeter)

The above formula has been derived based on the fact that the density of a material is expressed in terms of mass of unit volume and its dimension are M/V or ML^{-3}.

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[1] M.A. Knight, "Glass Densities by Settling Method" - Journal American Ceramic Society, 28 [11] 297-302 (1945).

[2] R.D. Duff, "Glass Density Determination by Sink-Float Method" - Journal American Ceramic Society, 30 [1] 12-21 (1947).

(2) $$\text{Density } (D) = \frac{W \text{ (Mass)}}{v \text{ (Volume)}} \quad \text{or} \quad v = \frac{W}{D}$$

Density of reboil sample glass.

(3) $$d = \frac{W}{v-V}$$

substituting $\frac{W}{D}$ for v from (2)

$$d = \frac{W}{\frac{W}{D} - V} \qquad \text{or} \qquad \frac{W}{D} - V = \frac{W}{d}$$

transposing and solving for V

$$V = \frac{W}{D} - \frac{W}{d} \qquad \text{or} \qquad V = W\left(\frac{1}{D} - \frac{1}{d}\right)$$

Volume is in cubic centimeters if W is in grams and D and d are in grams/cc.

RESULTS AND DISCUSSION

Reboil has been a problem in the glass industry as well as associated industries where glass has to be lampworked or sealed to itself or other glasses or materials.

The reboil test described in this paper was designed and set up to produce reboil under a set of standard conditions. The test can be used to evaluate many of the important factors in the formation of reboil: namely, (1) burner conditions used in lampworking or sealing, (2) contamination of the glass surface, (3) heating rates during lampworking or sealing, (4) glass composition, and (5) tank or pot melting conditions.

1. Effect of burner conditions on reboil

The volume of reboil produced in a glass will depend on the burner conditions. The standard burner conditions for the test were purposely set on the oxidizing side to prevent reduction in those glasses containing lead or other reducible metals.

Changing the standard burner conditions by varying the oxygen flows by ± 5% produced reboil volume changes of ± 3%. Reboil volume changes of ± 25-30% were obtained when the oxygen flows to the burner were changed by ± 10%. The data are given in Table I. Since oxygen and gas flows can be maintained to 2-3% using present equipment, the burner conditions can be maintained within the necessary limits for reproducible results.

2. Effect of contamination on reboil

The volume of reboil produced in a glass sample due to surface contamination may completely overshadow the volume differences due to base glass variation.

Table I

Effect of Burner Conditions

Burner Conditions	Volume of Reboil
Standard Burner Conditions*	.0033 cc.
5% Decrease in O_2 Flow	.0032 cc.
5% Increase in O_2 Flow	.0034 cc.
10% Decrease in O_2 Flow	.0025 cc.
10% Increase in O_2 Flow	.0042 cc.

*Standard burner conditions:

Oxygen Flow -- 12.4 ft.^{3} /hr. at 58 1/8" Water Pressure

Natural Gas Flow - 5.2 ft.^{3} /hr. at 18" Water Pressure

Invar Burner Tip Equivalent to National OX-5 Tip

Distance From End of Invar Burner Tip to Rod Sample - 7/8". See Figure III.

Table II

Effect of Contamination on Reboil Volume

Sample	Volume Reboil
Base Glass	.0008 cc.
Base Glass Contaminated with Transite	.0096 cc.
Base Glass Contaminated with Supramica	.0353 cc.

Test Conditions

Glass Temperature - 600°F
Sample Temperature - 600°F

Base glass pulled across contamination sample 12 times at temperature indicated.

Glass run through standard reboil test.

A test in which acid-cleaned glass was contaminated with transite and supramica produced volumes of reboil 12-45 times the volume produced in the base glass. This test shows the extreme case where hot glass was intentionally contaminated, but it points up the fact that even a small amount of contamination can have an important effect on the reboil produced in a sample. The data are given in Table II.

Production tests have shown that hot glass parts handled in the sealing area with asbestos-covered metal tongs produced reboil when sealed. Other parts made at the same time, but handled without touching the sealing area, exhibited no reboil when sealed.

The standard test procedure calls for the glass surface to be cleaned in a 1% hydrofluoric acid solution to minimize surface contamination.

3. Effect of heating rates on reboil

The rate at which glass is heated will determine whether any reboil is produced at all and also in what amounts. The standard test was set up to produce the practical maximum amount of reboil in a 1/4" diameter glass rod. The standard glass was Kimble's K-52 lead-barium glass formerly used for black and white television bulbs.

An average heating rate of 400-425°F/second was found to produce the greatest volume of reboil in the shortest time and still control or keep the glass sample in the flame. Faster average heating rates or heating times longer than eight seconds, caused the glass rod to bend or drip out of the flame, before the volume of reboil could reach a maximum. Obviously, the glass heating rate during the first 2-3 seconds is much higher than the average rate of 400-425°F/second. Rates of approximately 1000-1100°F/second have been measured.

The volume of reboil produced with the test equipment decreases as the heating rate decreases. When the average rate dropped below 275-300°F/second, no reboil was produced in the sample.

Production sealing experience has shown the importance of proper heating rates to reduce or eliminate reboil.

An objectionable amount of reboil was being produced in the seal area during the sealing of two glass parts. It was determined that the initial rate of heating of the parts prior to sealing was quite high. A two-stage heating arrangement

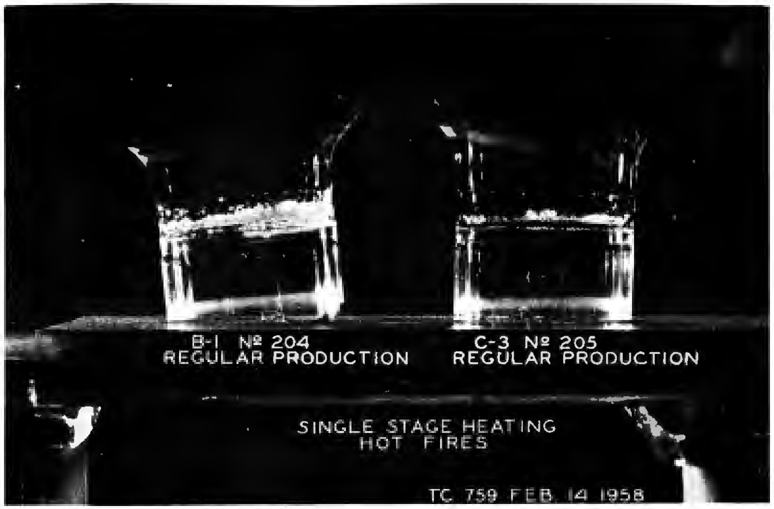

Fig. VI REGULAR PRODUCTION - SINGLE STAGE HEATING

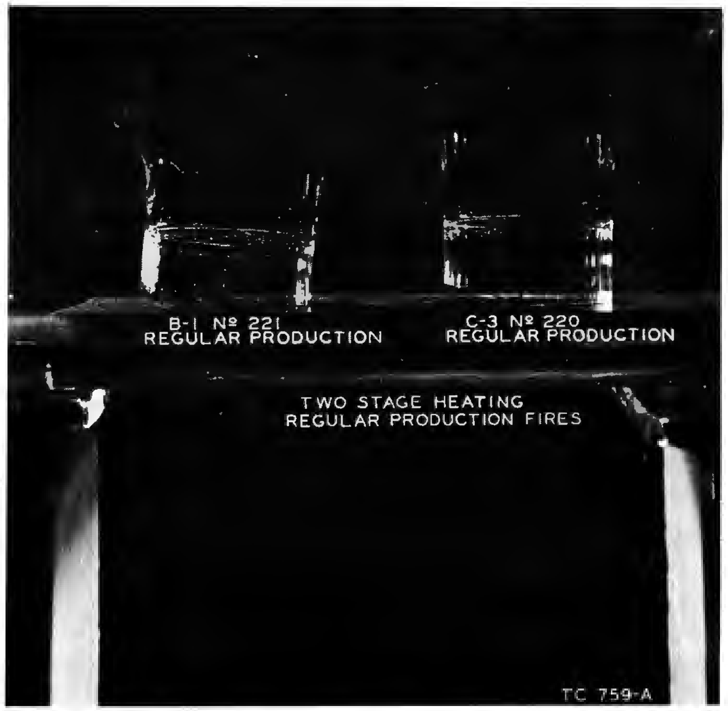

Fig. VII REGULAR PRODUCTION - TWO STAGE HEATING was installed in the sealing process. The combination of a slower heating rate during the first stage and a proper, but much higher heating rate during the second stage, produced essentially reboil free seals. See Figures VI and VII. Actually the two-stage heating cycle was achieved without increasing the total heating time over that used originally.

The above production problem illustrates the practical use of reboil test data as it concerns heating rates.

4. Effect of glass composition on reboil

Glass composition plays a significant part in the production of reboil in a glass. All normal glass can be made to reboil, but the volume of reboil produced under a given set of standard conditions will vary depending on the composition.

A comparison of the reboil produced in several commercial glass compositions is given in Table III. The data indicate that of the glasses tested, the borosilicate produced the least reboil with the soda-lime, lead-barium, and the potash-soda-lead glasses following in that order.

The standard reboil test described in this paper can be used to evaluate new and old compositions for their tendency to produce reboil during lampworking or sealing operations.

5. Test reproducibility

The reboil produced in a sample from test to test can vary as much as 10% from the average of two runs. However, the normal variations range between 0-5%. The data are given in Table V.

Conclusions

1. A reboil test has been developed that produces reboil under controlled conditions. The reboil produced is calculated on a volume basis.
2. The reboil produced in a sample under standard conditions can vary as much as 10% from the average of two runs.
3. The volume of reboil produced depends upon burner conditions. Volume changes of ± 3% were obtained when the oxygen content of the flame was varied by ± 5%. However, when the oxygen content of the flame was further changed to ± 10%, the volume of reboil obtained varied by ± 25-30%.

Table III

Reboil Volume Versus Composition

Glass	Volume Reboil
KG-33 (Borosilicate Low Expansion)	.0001 cc.
A 3015 Flint (Soda-Lime)	.0023 cc.
K-52 (Lead-Barium)	.0029 cc.
KG-12 (Potash-Soda-Lead)	.0119 cc.

Table IV

Effect of Heating Rate on Reboil Volume

Average Heating Rate (°F/second)		Volume Reboil
0-3 sec.	0-8 sec.	
1000-1100°F	400-425°F	.0029 cc.
850- 950°F	350-375°F	.0015 cc.
650- 700°F	275-300°F	None

Glass - K-52 (Lead-Barium)

Table V

Reproducibility of Test Data

Run No.	Volume of Reboil			
	Sample A (cc.)	Sample B (cc.)	Sample C (cc.)	Sample D (cc.)
1	.0028	.0041	.0026	.0038
2	.0030	.0045	.0028	.0046
Average	.0029	.0043	.0027	.0042
Variation From Average	3½%	5%	4%	10%

4. The volume of reboil produced in a sample due to surface contamination may completely overshadow the volume differences due to base glass variations. Intentionally contaminated samples produced volumes of reboil 12-45 times the volume produced in the base glass.
5. Heating rate is a very important factor in the formation of reboil. Production tests have shown that glass can be lampworked or sealed without appreciable reboil if the proper heating rates are used throughout the process.
6. The volume of reboil produced in a sample under standard test conditions will depend upon the glass composition. The test data indicated that of the samples tested the borosilicates produced the least volume of reboil with the soda-lime flint, lead-barium and potash-soda-lead glasses following in that order.

Acknowledgement

The writer wishes to express his appreciation to E. M. Tom for the many stimulating discussions which have materially aided in the development of this test and to C. J. Hudecek for making many of the reboil test determinations.

A Plate Type Glass Laboratory Fractionating Column and Low Hold-Up Still Head

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In many industries, distillation may be a part of a process to make a finished or semi-finished product, but in the petroleum industry the process of distillation is almost basic.

By distillation, crude petroleum is first separated at the refinery into relatively few products, which may in turn again be distilled, cracked, treated, filtered, reformed, blended, etc., to make hundreds of finished petroleum products and/or be part of many thousand other products.

In order to control, develop, and to improve these plant products, both from a product and economical standpoint, is usually the function of the laboratory chemist or technician.

To more nearly match plant conditions and to distill enough product in a normal working day, for the petroleum chemist or technician to work with, were the primary reasons which led to the design of this all-glass laboratory fractionating column and low hold-up Still head.

This is perhaps the direct opposite approach to those interested in fractional distillation, who are always seeking designs that will produce the greatest separation efficiency for any given height of column and rightfully so. This is referred to as H.E.T.P. (height of equivalent theoretical plate)

There are many designs of laboratory fractionating columns that will give efficiencies of over 100 plates, but the quantity of product produced in a normal working day is limited, and therefore are usually constructed to operate continuously.

The apparatus described and illustrated herein is a practical and sturdy borosilica glass laboratory fractionating column which is rather easily made by the scientific glassblower. It has been in use for many years in the laboratories of the Research and Development Department of The Atlantic Refining Company, Philadelphia, Pennsylvania, and in the laboratories out in their plant area, on daily routine service.

The basic idea in this design is that the necessary liquid seal between each section of the column is made by the use of a glass capillary tube from which the cap is also blown and in which the capillary is small enough to cause the liquid in the column to coalesce and make the liquid seal, but yet large enough to allow the reflux liquid to flow down the column, and at a rate fast enough so the column will not flood except under very abnormal conditions.

Figure 1 shows the cross-sectional design of the first column constructed to test whether the basic design of using a capillary tube to make and retain a liquid seal during distillation was possible. The column was provided with the usual provision at the bottom to attach a boiling flask, and a vapor line to a condenser at the top.

During the subsequent distillation the column functioned well and the capillary bore remained full of liquid even while the cap showed considerable motion.

The next logical step was to find out the largest capillary bore that would remain full of liquid. This in fact would determine the reflux capacity of the column and through experimentation was found to be between 2.5 to 2.7 mm. (bore).

A quick test with water, which has a relatively high surface tension, allowed a 30 cc per minute flow through this size capillary at room temperatures and with no hydrostatic head. This rate would, therefore, be higher when distilling materials that normally would be used in the column such as petroleum distillates and other light organic liquids.

The next step in the development of the column was the construction

CROSS SECTION
PLATE TYPE COLUMN

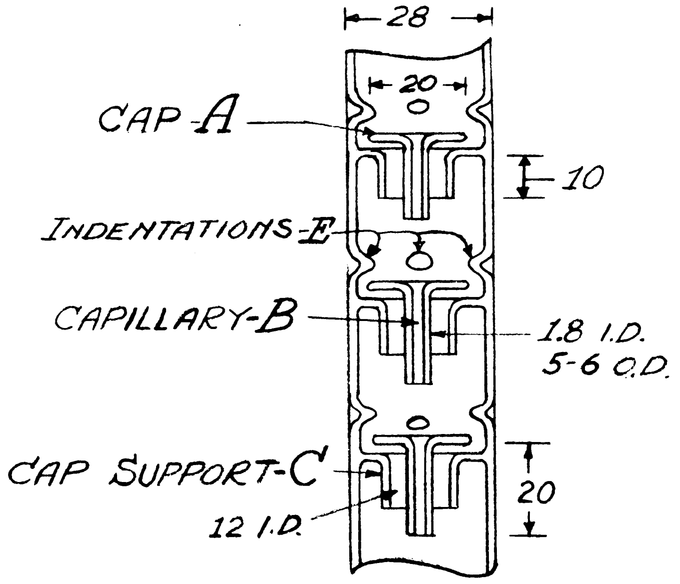


FIGURE-1-

- ALL DIMENSIONS IN MILLIMETERS -

SCALE: ACTUAL

0 1 2 3 4 5 CM

of a ten-section column in which the dimensions of each of the sections, like those in Figure 1, would be varied and to determine by actual operation what each of these ten different modifications could contribute to the final design.

To go into the design detail of each of these ten sections, perhaps, would be interesting to some readers but would add materially to the length of this paper; therefore, a discussion of the final design as shown in Figure 2 will have to suffice.

Figure 2 shows a cross-section of three sections of the final column design scale 1 1/2 : 1 and includes the best features of the ten-section experimental column. In operation the vapor ascends up the column until it condenses, either by heat loss through the column walls or at the reflux condenser in the Still Head at the top of the column.

The reflux returning to the column seals off the capillary tubes "B" in the caps and those in the Still Head. When these seals are made, the ascending vapor will lift the cap "A", mix with the descending liquid between the cap "A", and cap support "C."

It is this, the mixing of vapor and liquid at each of these sections, which affects a separation of the components in the material being fractionated. The lighter or lower boiling components continuing up the column and the heavier or higher boiling components going down the column.

While indentations "E" keep the cap "A" from getting out of position, indentations "D" catch the reflux from capillary "B" and guide it to the side of the column wall to be mixed with the liquid on the cap support "C" instead of dropping directly on and going down capillary "B" of the cap below which would lower the efficiency of the column. Indentations "E" and "D" are made alternately around the column as shown in Section A-A, Figure 2.

The cap support "C" are cut on a bevel and the bevels are installed on alternate sides during fabrication, as shown in Figure 2.

Efficiency of Plate-Type Column

As in similar investigations to test the relative separation efficiency

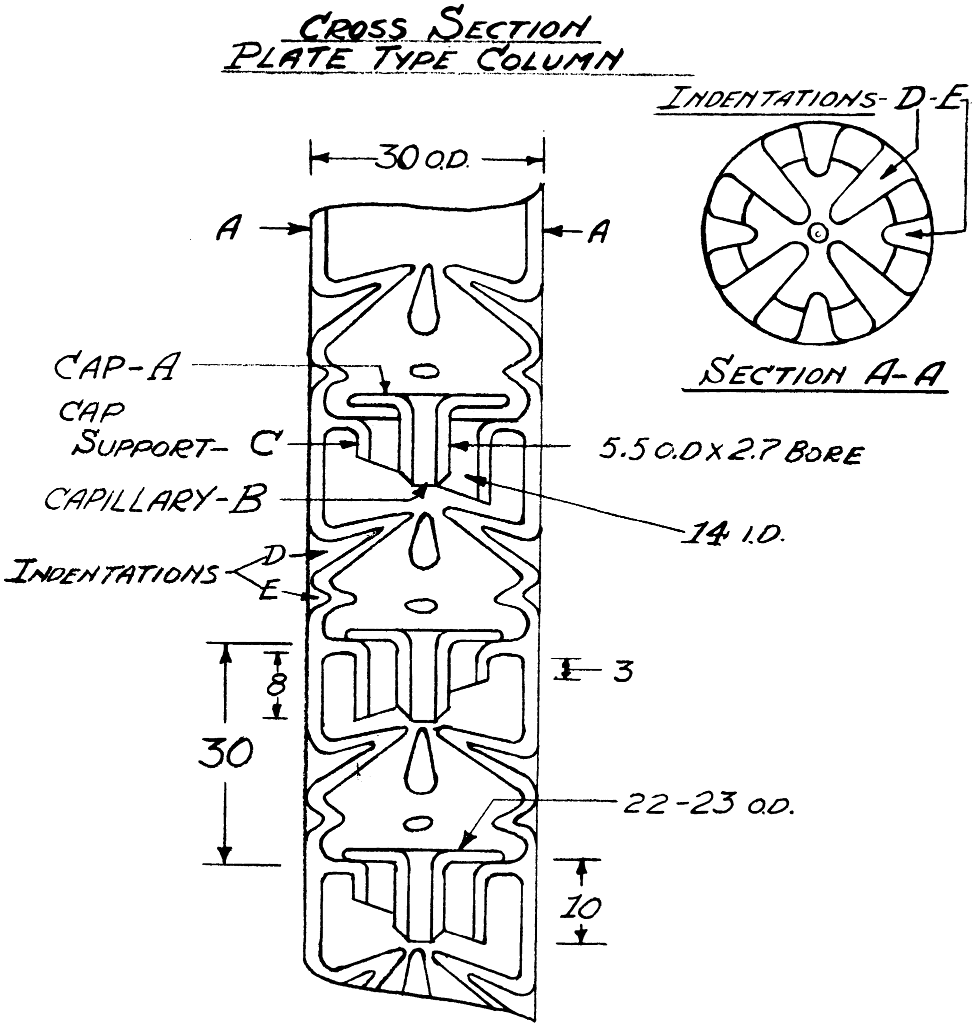


FIGURE-2
ALL DIMENSIONS IN MILLIMETERS
SCALE: 1½ : 1

of fractionating columns, a binary mixture of carbon tetrachloride and benzene were used to test a 15-section column.

The results showed that it gave a value of 7 1/2 actual plates, or that it takes two sections to equal one theoretical plate, and as the distance between the sections was 30 mm. the height equivalent to a theoretical plate (HETP) would therefore be 60 mm.

The efficiency probably could be improved by reducing the distance between sections to 20 or 25 mm. but other factors may be adversely affected. For example, to bring the sections closer than 25-30 mm. and operate the column at the rate it was designed to run might cause entrainment (mixing) of the liquid between sections, thereby decreasing its efficiency.

Probably the best way to evaluate most anything including this plate-type column is to compare it with another somewhat similar and well-known type column, the Snyder Ball Column. Figure 3 shows the original design of Snyder Ball Column (1); and the Atlantic modified Snyder Ball Column, and which was the forerunner of this plate-type column being presented. The advantages of the Atlantic-modified Snyder Ball Column over the original Synder Ball Column are several, however, most important is the use of a flanged tube to act as a seat for the ball instead of a constriction. This makes for a more sturdy construction and hence is less fragile and less prone to breakage. The second advantage is the ease of construction. The Snyder Ball Column is usually made starting with a long piece of glass tubing while the Atlantic modified Snyder Ball Column, as well as the plate-type column, is fabricated section by section. The third advantage over the Snyder Ball Column is that the seat for the ball is perfect, in fact, too perfect, and four small indentations (See Detail Figure 3) had to be made where the ball and seat meet to allow the reflux liquid on the seat and around the ball to drain back to the flask

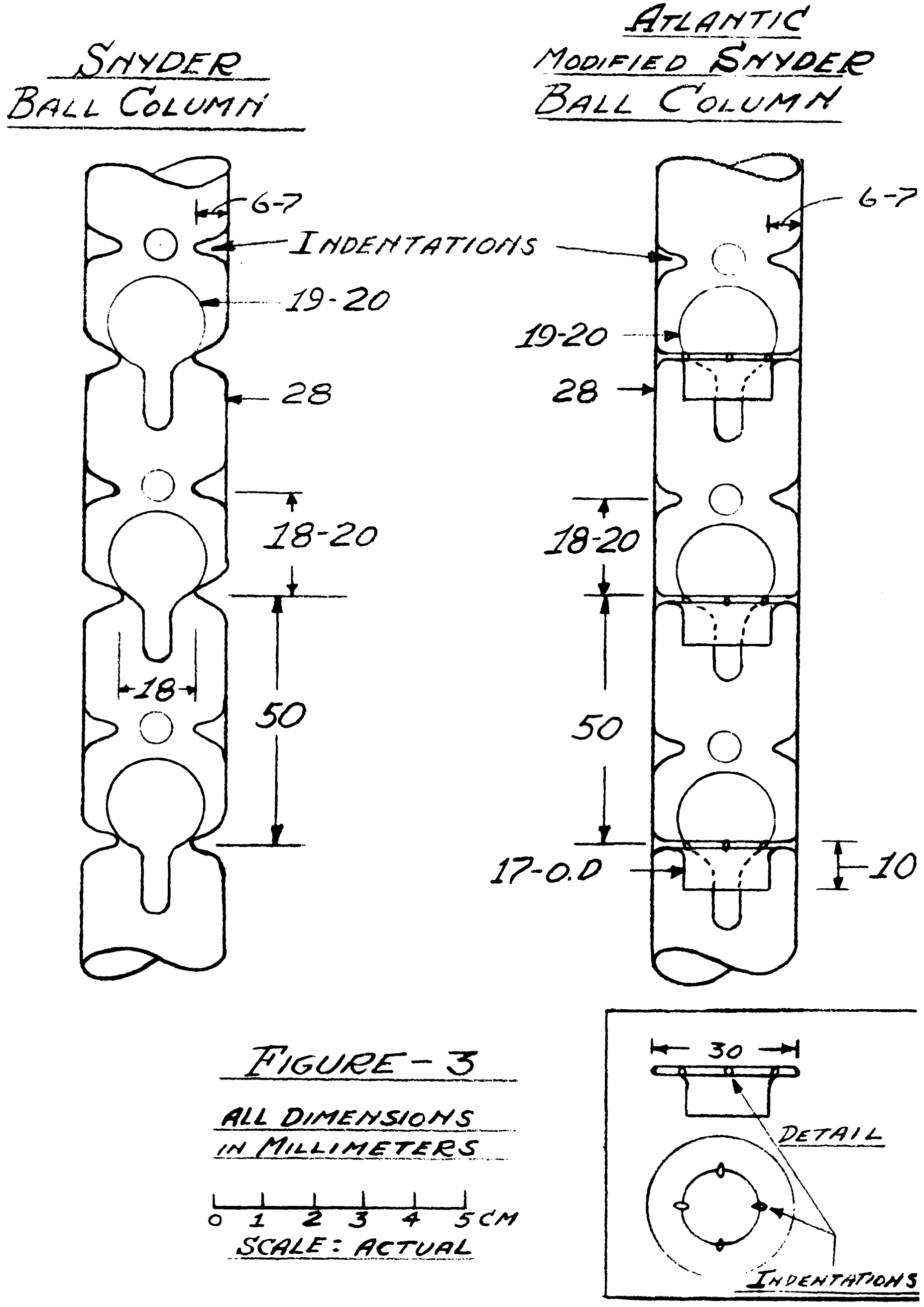


FIGURE - 3

when the distillation is stopped.

Both the Snyder Ball Column and the Atlantic modified Snyder Ball Column have to be constructed with approximately 50 mm. between each section to avoid entrainment (mixing) of the reflux liquid from one section to the other. This is due to the fact that during the distillation there is approximately 2 cc of liquid around each ball while in the plate-type column there is only 1/2 cc.

This low hold-up for the plate-type column of only 1/2 cc compared to 2 cc for the Ball Column is one of the factors which makes the plate-type column more effective because the rectifying or separation efficiency will be working on 1/4 the amount of liquid than is in the ball column.

Designing of Laboratory Fractionating Columns

An efficient fractionating column, whether it be for the laboratory or plant, can usually be designed for a given set of conditions or specifications is the separation desired, rate, volume, pressure, space and type of materials to be processed, etc. are known.

However, it is the writer's opinion that as yet there is no universal design for a laboratory fractionating column.

Todd [2] and Podbielniak [3] attempted to solve this problem by supplying several columns of different diameters but the same length with the similar adapters at each end of the columns and which were interchangeable in their adiabatically controlled jacket.

Therefore, before the construction of a laboratory fraction column is started, adequate design specifications to give the desired results should be approved by all those concerned.

Construction Details and Information to Fabricate a Glass Plate-Type Laboratory Fractionating Column

(Note: The author, a scientific glassblower and aware of the difficulties of constructing and/or fabricating apparatus from the description in published articles, which in many cases do not give sufficient information or dimensions, has tried to correct this by including drawings that do have sufficient dimensions and written instructions in this paper.)

Specifications

Construct 15-section, plate-type (Figure 4) column using 30 mm. standard wall tubing 30 mm. apart, a 35/25 spherical joint on the bottom of the column, with a drip top about 75 mm. above the spherical joint and 30 mm. below the first section; provide a lagging jacket of larger outside

PLATE TYPE COLUMN AND LAGGING JACKET

ALL DIMENSIONS IN MILLIMETERS

SCALE: ACTUAL

0 1 2 3 4 5 CM

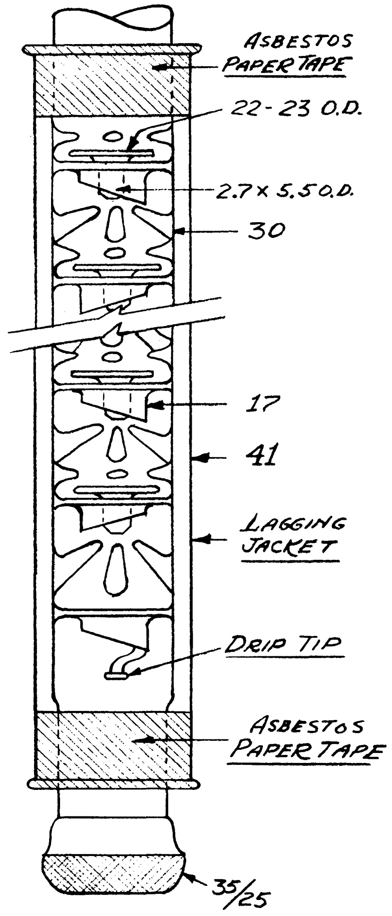


FIGURE — 4

diameter glass tubing, sealed at the top and bottom with asbestos paper tape, covering as much of the column as possible to provide a dead air space around the column and also to strengthen it. Still Head to be sealed to the top of the column with a cold finger condenser and a 18/9 spherical joint on the top of the Still Head to provide for an extra condenser if necessary and a means of collecting distillate and controlling the reflux ratio; column to operate at atmospheric pressure and have an operating efficiency of 7-8 actual plates at total reflux, with a moderate degree of separation when operated at a minimum of 10:1 reflux ratio on light and medium petroleum distillates or other organic liquids of similar densities.

Preparations for the Fabrication of the Plate-Type Column

There are only three essential parts to each column section, the tubing pieces, the cap support, and the caps themselves. All these parts for the 15 sections of the column should be made and assembled first ready to be fabricated into the fractionating column.

The tubing pieces (15) are cut on the glass slicing wheel, 30 mm. long from a 30 mm. O. D. Standard wall glass tube. These are rinsed in clean water, dipped in 26% hydrofluoric acid to remove any loose grind from the cut edge, rinsed again in clean water, and dried.

The cap support is made from a 13-14 mm. I. D. standard wall glass tube, heated on the end, rolled on an adjustable Vial Makers Roller, and the heated end flared at right angles to the tube with a carbon rod to make a flanged end approximately 2 mm. wider (32 mm.) than the column. The tubing beyond the flange is then cut on a bevel about 3 mm. from the flange on the short side of the bevel and 8 mm. on the long side of the bevel. In fabricating these plate or cap supports the position of the bevel should alternate.

The caps or plates are made from a 5.5 to 6 mm. O. D. x 2.5 to 2.7 mm. bore capillary tubing. A piece of this capillary tubing, approximately 100-110 mm., is sealed to a 5" or 6" piece of 10-12 mm. tubing to facilitate rolling on the vial makers rollers. The open end of the capillary is then closed and a bulb of approximately 13 or 14 mm. is then blown (see gauge for cap, Figure 5) with average wall thickness. The bottom of the bulb is then blown open, reheated, flared out into a flange, 22-23 mm. in diameter, in the same manner the cap supports are made. The capillary tube is cut 8-10 mm. below the flange and ground to a point. This ground service is not fire polished. The average weight of these caps should be about 1.5 gms. All the caps should be weighed and installed with the heaviest caps at the bottom of the column.

As the column is fabricated from the bottom up, the heaviest cap or plate would, therefore, be installed first. The purpose of this is to have the weight of the caps correspond somewhat to the density of the liquid in the column during a distillation where the heavier components of the material being distilled from petroleum would be at the bottom of the column.

The writer has constructed these plate type columns from 28-30 mm. O. D. glass tubing. However, if critical dimensions are properly evaluated, there is no reason why these plate-type columns could not be made larger or smaller to fit requirements. For instance, the 2.7 mm. bore capillary reflux tube carrying the liquid down the column may not be large enough if the capacity (not diameter) of the column were doubled. Should flooding occur in the scaled-up column, then some modification of the capillary reflux tube would be required.

Sequence Used in Assembling the Column

It is assumed at this point that all the parts to assemble the column are made. The tools that have been mentioned needed to make and fabricate the column are (1) Vial Makers Rollers, (2) a carbon rod, (3) gauge for cap, (4) a glass holder, (5) a carbon tool, and (6) a tungsten lance. All but the Vial Makers Rollers and carbon rod are shown in Figure 5.

A piece of 30 mm. O. D. tubing, 150 mm. long, is slightly flared on one end to take a cork. The other end, fire polished to begin the assembling of the first section of the column. This longer piece of tubing is necessary as a handle to hold the column during fabrication and while rolling it on the Vial Makers Rollers to keep the column straight.

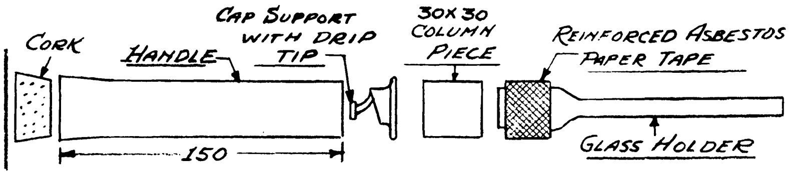
The first seal is a cap support that has a "drip tip" sealed to the lower edge of the level. The purpose of this "drip tip" is (1) to deliver the reflux liquid to the center of the column, and (2) to provide a point at the bottom of the column from which the total reflux distillate can be measured. It is the ratio of this reflux rate compared to the overhead distillate rate which determines the reflux ratio. And in general, this reflux ratio should not be less than 10 reflux to one overhead.

To make the seal, the cap support (with drip tip) is held by a carbon rod and centered against the end of the handle piece. Both are heated until the edges stick together. Next,one of the 30 mm. lengths of 30 mm. tubing which is held by a glass holder (see Figure 5) with asbestos paper tape in between, is centered against the cap support and both heated vigorously and sealed. The glass holder is removed, the seal reheated, rolled and paddled to align it, and the carbon tool (Figure 5) inserted to form a square corner at the seal and at the same time keep the cap support at right angles to the column. The heaviest cap is inserted next and 4 short indentations equally spaced around the column using the Tungsten lance (Figure 5) are made about 4 mm. above the cap to keep it in place but still allow the cap to rise high enough as not to constrict the vapor going up the column. (Section "A-A" - Figure 2)

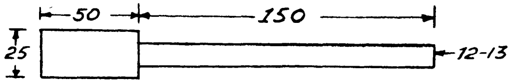
While the seal is still hot, a spot is heated about 6 mm. above the cap support below and while holding the column in a verticle position a long indentation is made to about 1 mm. from the capillary tube of the cap with the tungsten lance - 3 more of the indentations are now made in the same manner and equally spaced around the column. These long indentations catch the reflux liquid and guide it to the side of the column and prevent it from dropping directly on the center of the cap below. This same sequence of fabrication is followed until all the 15 sections are completed, ready to install the Still Head.

Still Head

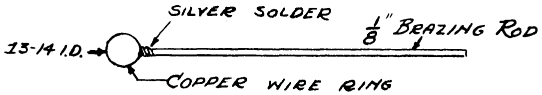
There are probably as many designs for Still Heads as there are for fractionating columns, however, they all should condense the vapor and return it to the column with the minimum loss in temperature. In this way



ASSEMBLYING SEQUENCE



CARBON SHAPER



GAUGE FOR CAP

TUNGSTEN LANCE

FIGURE -5

the column has only to furnish the necessary heat to revaporize the reflux, rather than to furnish additional heat to bring the reflux up to its vaporization temperature.

If the reflux has cooled down too much, it may cause flooding at the top of the column due to excessive condensation of the ascending vapor. Therefore, reflux liquid from a Still Head should return to the column at a temperature just below its boiling point.

Another common fault in Still Head design is the length the reflux liquid (distillate) has to travel after it is condensed.

It is not logical to have a fractionating column that will do a good job of separating a material into its various components and then to have them mixed again by running them down a long condenser tube or mixed in a large liquid reflux proportioner.

Most of these objectional features have been eliminated by the design of the Still Head, shown in Figure 6, and several advantageous features added as follows:

(1) Should the material being processed have a high vapor pressure, there is an 18/9 outer spherical joint at the top where additional condensing area can be had by attaching another condenser, preferably a spiral (Graham) condenser.

(2) The Still Head is also designed so all the reflux liquid (distillate), whether it be condensed by the cold finger condenser or the spiral (Graham) condenser, all meet and drop off at one point in the reflux proportioner. This is of considerable help to the operator in determining the reflux ratio.

Construction of the Still Head

The drawing in Figure 6 has all the necessary dimensions for the average scientific glassblower to construct the Still Head; however, should some dimensions other than shown in Figure 6 seem necessary, a scale (0-50 mm.) is included on the drawing to scale such dimensions.

The only part of the Still Head that needs some explanation is the reflux proportioners.

In constructing the proportioner, after the 12 mm. tube with the drip tip is sealed into the end of the 28 mm. tube which forms the body of the proportioner, the 5.5 O.D. x 2.7 mm. capillary tube is also sealed into the side. When these two seals are made, a round bottom is made on the 28 mm. tube, 40 mm. from the 12 mm. seal. While the rounded end

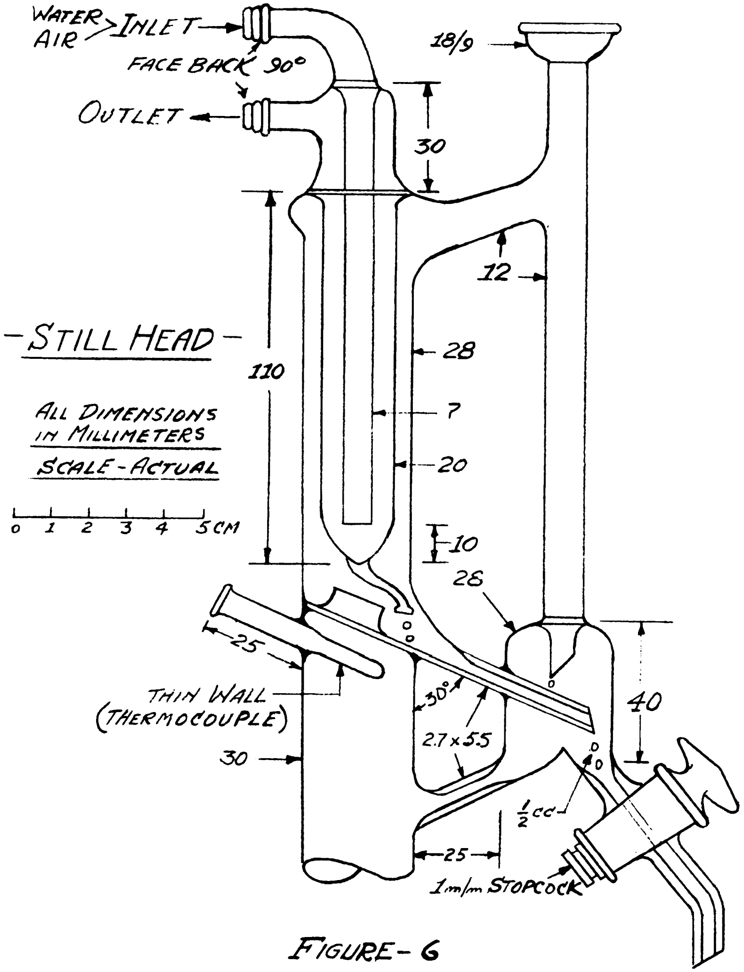


FIGURE - 6

is still hot, a groove is made in the middle with a piece of thin sheet metal. This divides the bottom into two reservoirs. To one reservoir, the 1 mm. bore stopcock, used to control the reflux take-off rate, is sealed close and to the other reservoir, a 5.5 x 2.7 mm. capillary, is sealed.

The purpose of this groove is to act as a weir or dam over which the reflux liquid flows through the capillary back to the column. The capacity of the pool of liquid is about 1/2 cc and the dripping of the reflux liquid into this pool constantly keeps fresh (distillate) liquid in the pool.

In Conclusion:

The Plate-Type Column has the following features:

1. Good thruput
2. Little tendency to flood
3. Low hold-up of liquid per plate
4. Complete drainage
5. Durable and serviceable
6. Easy to construct
7. Complete column can be oven annealed
8. Plates close together
9. Good separation efficiency

The Still Head contains the following features:

1. Low liquid hold-up
2. Cold Finger Condenser
3. Short reflux return path
4. Designed to add extra condensing area, if needed
5. All condensed liquid (reflux) directed to one point
6. Easy to construct

References:

(1) Earl O. Snyder, Olney High School, Philadelphia Public School System, Philadelphia, Pennsylvania

(2) Floyd Todd, Todd Scientific Company, Springfield, Pennsylvania Efficient and Versatile Laboratory Fractionation Assembly, Ind. & Eng. Chemistry, Vol. 17, pg. 175, March 15, 1945

(3) Walter J. Podbielniak, Ind. & Eng. - Anal. Edition
Part 2 - 5 - 119 - 1933
Podbielniak, Inc., Chicago 11, Illinois

Development of a High Temperature Electronic Glass

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This is the story of the development of a new glass. It is well known that most commercial glasses are fused mixtures of metallic oxides with silicon dioxide being the common oxide. Since there are an infinite number of mixtures of oxides possible, there are also an infinite number of glasses available. However, only a few glasses have the right combination of properties to make them useful. Each oxide or group of oxides contributes to the final property of the glass, but the presence of some oxides in the glass will affect the contribution of one or more of the other oxides. Glasses are therefore classified with respect to these contributing oxides. The types include fused silica, borosilicate, phosphate, soda-lime, barium, and lead glasses. Recently, aluminosilicate glass was added to this list. These glasses can be defined as alkaline earth alumina silicates with low alkali content. A glass of this type will be followed through the research and development stages.

The initial step in the development of a new glass is usually a compilation of the desired glass properties. These would normally include at least the annealing point, softening point, thermal expansion, chemical durability; and in the case of an electronic glass resistivity, dielectric constant and loss factor. The properties and composition of every experimental glass melted by our laboratories are retained on IBM cards for easy accessibility. Once the desired properties are known the research begins with a search of the IBM file and the literature. Although a glass which precisely fits the property requirements is rarely found, a number of glasses are usually found which help to guide the research.

The property requirements in this case were rather broad. They included a softening point temperature greater than 500°C, good chemical durability, low electrical loss, and low thermal expansion. The high softening point eliminated most glasses, but some early melts of aluminosilicate glass were found in the IBM files. It appeared as though these glasses would satisfy the high softening point requirement. Several other glass types were also studied, but it was decided that aluminosilicates had the most promise. Therefore, a compositional field was outlined using the data from the earlier melts, published phase equilibrium diagrams, and the practical knowledge gained from other systems.

Experimental glass melts are made in platinum crucibles to eliminate contamination and to assure reproducibility. Usually four pounds of glass are melted to provide a sufficient amount of sample for property measurements. The materials for the glass batch are chemically analyzed and these analyses are used to calculate the raw batch. The resultant glasses are also analyzed, because errors can occur due to variations in raw materials and vaporization during melting. Thus, property measurements can always be associated with a known glass composition and the data has much more meaning.

After the glasses are melted and annealed property measurements are made. These usually include liquidus, thermal expansion, softening point, resistivity, and dielectric constant. As each group of glasses is melted and the properties are determined the results are used as an additional guide for formulating the next melts. Thus by a system of balance and rebalance the glass which most nearly fits the requirements is achieved. Usually this only requires a few melts and the accompanying chemical analyses and property measurements, but sometimes a hundred or more must be made. However, in some systems there are so many potentially useful glasses that the entire system is studied in detail. In these cases, hundreds of melts and property measurements are made. Property contributions can then be related to each oxide in the system and later requests for glasses with specific properties can be met with a minimum of new melts.

Since the aluminosilicate system had not been extensively studied before, a large number of melts were needed. A glass numbered 51-26E (51 indicates the initial melt was made in 1951) eventually evolved as the optimum glass for the properties required. Therefore, a larger experimental melt was made to obtain a variety of samples such as tubing, rods, and discs. These samples were needed to conduct further property measurements and to supply outside laboratories with samples for evaluation. The laboratories showed considerable interest in the properties and potential applications of aluminosilicate glasses, and a pilot commercial melt was recommended and made. Since this was a commercial melt the composition was given a commercial number, EE-2. The first E signifies electronic and the second E the composition type.

A variety of tubing, rod, and bulb sizes were made available for further testing and evaluation. The results of these tests and the interest shown in aluminosilicate glasses were encouraging. Although EE-2 was a very satisfactory glass for the original requirements it did not fulfill all of the applications to which it was put. In other words, aluminosilicate glasses with slightly different properties were also needed. A whole family of glasses with a range of thermal expansions, softening point, etc., were possible in this system. Therefore, it was decided that a more thorough study would be profitable.

In several areas the need for a more complete study was apparent. During sealing, these glasses had a greater tendency to reboil than most other glasses. The outgassing characteristics, effect of nuclear radiation, complete viscosity-temperature relationship, and sealing behavior were relatively unknown. A comprehensive program was therefore established.

One of the first areas of study was the melting and refining of these glasses. During pilot melting it was noted that aluminosilicates differ from most glasses in their melting temperature, and their ability to be refined by ordinary refining agents. Since this is a relatively new glass type very little is known about the reactions which take place during the melting process. A study of these reactions was initiated concurrently with an evaluation of some twenty refining agents. Recently a large melt was made which utilized the information gained thus far. The resulting glass was greatly improved in quality over the earlier melts.

The composition study is covering the entire field of aluminosilicate glasses and will eventually provide information to correlate the glass composition with properties. A phase study of the system will identify the crystalline phases present when the glasses devitrify and will yield information about the glass and crystalline phases in equilibrium at various temperatures. Since reboil during sealing is a problem with these glasses a complete program has been organized to fully understand the phenomena. Reboil tests are run as a standard property measurement and the sealing study has already yielded data which is being used to provide better seals. An outgassing study which utilizes a high vacuum system and a mass spectrometer is yielding information on the amount and variety of gases evolved from these glasses at high temperatures and low pressures or under electron bombardment. Nuclear radiation tests have shown that these glasses are unaffected by levels of radiation which are very harmful to some other glasses. The studies are being conducted on a number of compositions in

Figure 1 - VISCOSITY OF ALUMINOSILICATES COMPARED TO BOROSILICATES

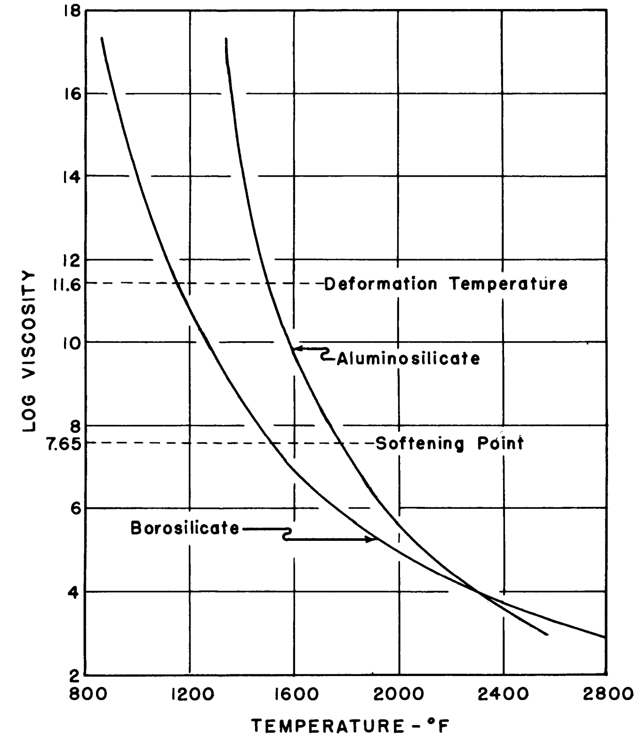
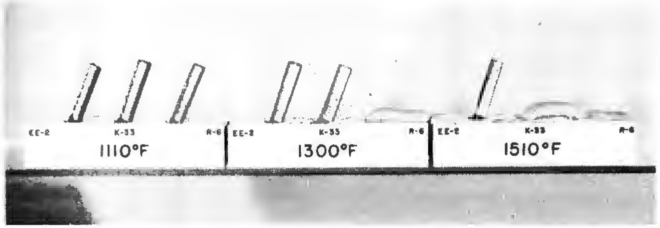


Figure 2 - COMPARISON OF DEFORMATION TEMPERATURES



EE-2 – ALUMINOSILICATE GLASS
K-33 – KIMAX-BOROSILICATE GLASS
R-6 – SODA-LIME GLASS

Figure 3 - SOME PROPERTIES OF ALUMINOSILICATE GLASSES COMPARED TO SODA-LIME AND BOROSILICATE GLASSES

	SODA-LIME R-6	BOROSILICATE K-33	ALUMINOSILICATE EE-2
SOFTENING POINT - °F	1300	1510	1780
THERMAL EXPANSION 0 to 300°C	92	32	44
LOG RESISTIVITY AT 350°C	5.2	6.4	12.5

the aluminosilicate system so that each property can be related to the oxide variation.

Finally, all of the property data must be assembled, correlated, and conclusions must be drawn. Of course, this is usually done on a continuing basis throughout the study, but in the final form the data will be the most useful. It will then be possible to tailor a glass to fit certain property requirements. New applications for these glasses should also become apparent when all of the properties and characteristics are known.

Since EE-2 was used to illustrate this development some of the properties of the glass might be of interest. Figure 1 illustrates the viscosity of a typical aluminosilicate compared to a borosilicate glass. Shown in Figure 2 are comparisons of the softening temperatures of EE-2 with two other glasses. Figure 3 shows a comparative listing of the properties of EE-2 and other glasses. The high resistivity and low thermal expansion coefficient are typical of aluminosilicate glasses.

In this paper an attempt has been to trace the development of a new glass. It should be pointed out that most, if not all, of the glasses on the market today had to go through a similar development before they reached the glassblower or consumer. Of course, research and development does not cease with production melting of the recommended glass. Efforts are constantly being made to improve established glasses by continuing research.

GAS ADSORPTION ON SOLID SURFACES

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A considerable portion of modern industrial technology may be said to depend, directly or indirectly, upon the phenomenon of adsorption; that is, upon the interaction of various substances either in the liquid or the gaseous state with a surface. In the petroleum industry, for example, present day methods of oil refining have been made possible by the use of a variety of solid catalysts whose surfaces have the ability to transform chemically the molecular species constituting crude oil into specific products having commercial value; this transformation or catalysis involves as an essential step the adsorption of the oil components onto the surface of the solid. Similarly, the large scale fixation of nitrogen, an extremely important technological achievement, was the result of the discovery from 1900-1925 of catalysts capable of adsorbing, and thereby activating, elemental hydrogen and nitrogen in such a manner that the formation of ammonia therefrom was energetically feasible. The refining of sugar, the separation and purification of gases, the manufacture of reinforced rubber stock, these are all examples of industrial processes dependent upon adsorption by solid surfaces.

Because of these facts a great deal of research has been carried out during the last fifty years or so in the general field of adsorption both by academic institutions and by industrial laboratories with the result that a variety of experimental techniques has been developed which may be used to investigate interactions with surfaces. The application of these techniques has depended, of course, upon the availability of the proper experimental equipment and this in turn has been dependent to a large extent upon the glass blower's art and the physical properties of the glasses he employs. The present article has as its purpose the providing of a brief introduction to the techniques commonly employed in studying adsorption and to the type of glass fabricated equipment required. Due to limitations of space, the discussion will be restricted to the adsorption of gases by solids with the principal emphasis being devoted to the field of heterogeneous catalysis. Those facets of the subject which have been covered elsewhere will be passed over rather briefly by simply providing references for the interested reader. A further limitation in the present article is that no attempt will be made to discuss those methods requiring ultra-high vacuum ($<10^{-6}$ mm Hg); such techniques have unique problems associated with them and really require separate consideration.

It is perhaps well to start by defining what is meant by the word adsorption. If a gas, when brought into contact with a solid, adheres to the surface of the solid, then the gas is said to be adsorbed and the process involved is one of adsorption. The solid is usually referred to as the adsorbent while the gas being adsorbed is called the adsorbate. In general, two types of gas adsorption may be observed. The first type, physical adsorption, is caused by the same forces that are operative in condensation phenomena and usually, although not always, is a rather weak form of adsorption. The second type, chemical adsorption or chemisorption, is generally stronger in nature than physical adsorption and, as the name indicates, involves a chemical interaction or reaction between the gaseous species and the solid surface. It is this latter type of adsorption which is associated with the phenomenon of heterogeneous catalysis. For a given gas-solid system the extent and nature of the adsorption process is a function of time, temperature, and pressure. A knowledge of this function will in many cases yield valuable information as to various properties of the adsorbent. Thus the physical adsorption of a gas such as, say, nitrogen by a solid catalyst may be used to determine the surface area and the physical topography (i.e., pore size distribution) of the catalyst. Similarly, the chemisorption of hydrogen by a metal-containing catalyst may provide information as to the concentration of metal at the catalyst surface.

In general, a determination of the amount of gas adsorbed by a solid involves the following steps:

(1) preparation of the adsorbate
(2) pretreatment of the adsorbent
(3) maintenance and measurement of the adsorbent temperature
(4) measurement of the adsorbate pressure
(5) measurement of the amount of adsorbed gas.

The equipment used in carrying out the above operations will be described forthwith. Basic, of course, to any experimental work in the field of adsorption is the necessity of producing and maintaining a vacuum. Usually this involves simply the use of a good oil or mercury diffusion pump backed by a mechanical pump along with suitable cold traps. Since general vacuum technique has been admirably described elsewhere[1], there is no reason to elaborate further at this time.

Adsorbate Preparation - Generally it is quite important that the gases used in adsorption work be free of contamination, the absolute degree of purity required being determined by the particular nature of the system under study. Obviously, one must either purchase pure gases, clean up impure commercial gases, or make the gases himself. For many purposes tank gases such as hydrogen, helium, nitrogen, etc. may be purified adequately by rather simple means. A useful arrangement for purification of such gases has been described by Joyner[2]; further details may be found in a book by Farkas and Melville[3]. In some cases very pure gases may be obtained commercially; generally, these are provided in sealed-off glass containers. When tank gas cannot be sufficiently purified, as is often the case with carbon monoxide, or when the purified gas cannot be purchased directly, then one is forced to make the gas by some specific chemical reaction. Thus very pure nitrogen may be obtained by the thermal decomposition of sodium azide, while carbon monoxide can be made by the sulfuric acid decomposition of formic acid. Similar preparations have been described for many gases[3] Regardless of the source, provision must be made for storing the pure adsorbate in some convenient manner, usually by placing it in a large glass bulb at a pressure greater than atmospheric. A superior type of storage facility which uses mercury cutoffs rather than the usual stopcocks to isolate the storage bulb has been described by Joyner[2].

Adsorbent Pretreatment - In most cases of powdered adsorbents, it is necessary to rid the surface of adsorbed impurities (i.e., water) before starting any adsorption measurements. Often this may be accomplished simply by evacuating the adsorbent at an elevated temperature while in other instances one may have to subject the adsorbent surface to some chemical reaction in order to clean it. Thus oxygen can be removed from a metal surface by reduction in hydrogen followed by evacuation to remove any adsorbed hydrogen. Where reduction or oxidation procedures of this nature may be required, it is convenient to make permanent arrangements to purify a stream of tank oxygen or hydrogen and

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[1] S. Dushman, "Scientific Foundations of Vacuum Technique", John Wiley & Sons, Inc., New York, 1949.

[2] L. G. Joyner, "Scientific and Industrial Glass Blowing and Laboratory Techniques", ed. by W. E. Barr and V. J. Anhorn, Instruments Publishing Co., Pittsburgh, Pa., 1949, Chapter 12.

[3] A. Farkas and H. W. Melville, "Experimental Methods in Gas Reactions", Cambridge University Press, 1939.

pass it over the adsorbents. A purification train consisting of reduced copper gauze at 400°C, a $MgClO_4$ drying tube and a -78°C cold trap is generally suitable for oxygen, while a "Deoxo" unit, a $MgClO_4$ drying tower, and an activated charcoal trap at -195°C will purify tank hydrogen quite nicely. Useful discussions of the preparation of clean surfaces have been presented by Trapnell[4] and Brunauer[5] and these authors should be consulted for details.

Temperature Control - Adsorption phenomenon is, in general, extremely sensitive to temperature and is especially so in the case of physical adsorption. Thus one of the major problems facing the experimentalist is that of controlling and measuring the temperature of the adsorbent. Elevated temperatures are usually obtained by electrically heated furnaces or baths of one kind or another and various temperature control devices are available which may be employed in their operation. Low (<0°C) temperatures, however, present more of a problem. Certain fixed temperatures may be obtained by use of materials undergoing first order phase transitions. Thus a temperature of -78°C may be maintained with solid carbon dioxide and a temperature of -195°C with liquid nitrogen. In many cases of physical adsorption, however, it is necessary to vary the temperature. For example, in determining the thermodynamics of, say, argon adsorption on a particular solid, it is required that the adsorption be measured over a temperature range near the boiling point of argon and that any particular temperature be maintained as constant as possible. To meet such requirements various cryostats have been described in the literature[6-10]. A convenient cryostat used in the Gulf Laboratories is shown in Fig. 1. The operation of this latter is basically quite simple. The adsorbent is placed in the sample bulb (3) and the sample bulb sealed to the vacuum system at the points indicated (20). After the adsorbent has been pretreated by evacuation through stopcock B, the cryostat components

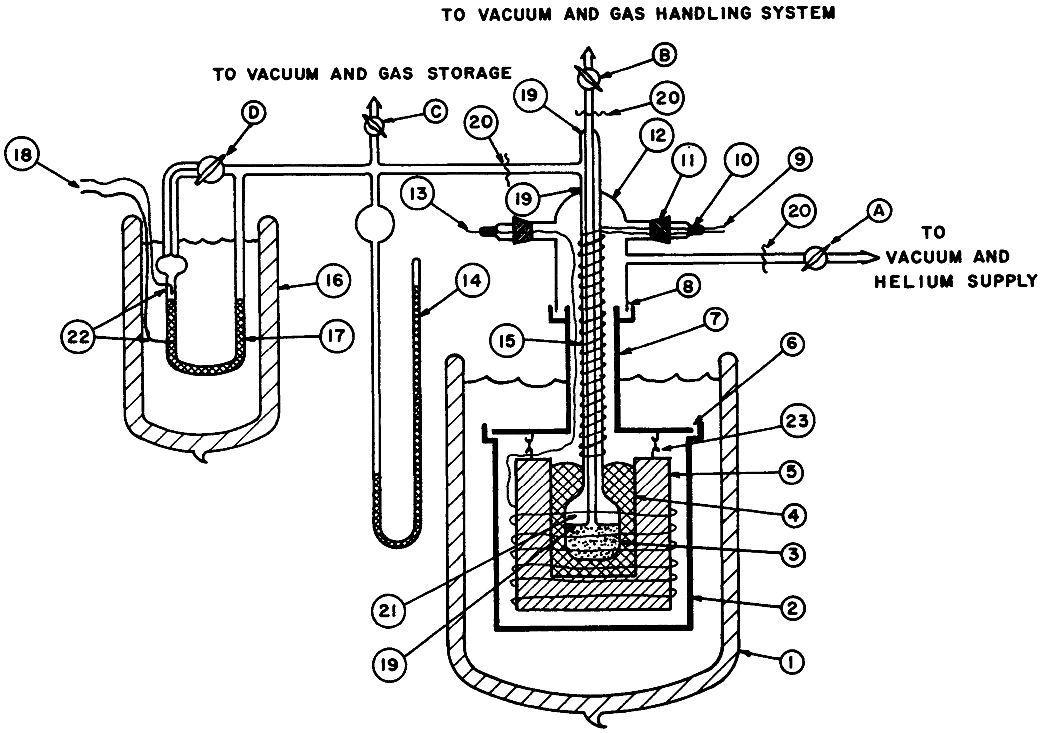

FIG. 1. Low Temperature Adsorption Cryostat.

(1) Glass dewar containing liquid nitrogen. (2) Brass can. (3) Pyrex adsorbent bulb. (4) Mercury. (5) Copper block. (6) Wood's metal seal. (7) Stainless steel tube. (8) Vacuum wax seal. (9) Preheater leads and thermocouple. (10) Glass press. (11) Ŧ 10/30 joint. (12) Pyrex cryostat head. (13) Copper block heating leads. (14) Mercury manometer. (15) Preheater. (16) Glass dewar containing ice. (17) Mercury manometer. (18) Leads to thermoregulator. (19) Ring seal. (20) Butt seals. (21) Condensation chamber. (22) Tungsten-through-Pyrex electrical contacts. (23) Nylon thread suspension.

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[4] B. M. W. Trapnell, "Chemisorption", Butterworths Publications, Ltd., London, 1955.

[5] S. Brunauer, "The Adsorption of Gases and Vapors", Princeton University Press, 1943.

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[7] A. G. Keenan and J. M. Holmes, J. Phys. & Colloid Chem. 53, 1309 (1949).

[8] S. Ross and H. Clark, J. Am. Chem. Soc. 76, 4291 (1954).

[9] B. B. Fisher and W. G. McMillan, J. Chem. Phys. 28, 549 (1958).

[10] J. A. Morrison and D. M. Young, Rev. Sci. Instr. 25, 518 (1954).

are assembled in the manner indicated. With stopcock D open the manometer system is evacuated through C and then a gas added which, when liquefied at the temperature of the experiment in the chamber (21), will have an appreciable vapor pressure. The cryostat is then evacuated through A and several hundred millimeters pressure of helium added. The liquid nitrogen dewar (1) is then raised about the cryostat and the latter allowed to cool. The temperature in the sample tube is followed by noting the vapor pressure in the condensation chamber (21) on the manometer (14). When the desired temperature is reached, stopcock D is closed and the thermoregulator (not shown) is turned on. This latter is actuated by the manometer (17). Thus when the mercury in the left arm of the manometer is not in contact with the upper electrical contact, the thermoregulator provides heat to the copper block (5) via the heating element (13); the temperature of the sample bulb (3) and the condensation chamber (21) is thereby raised until the vapor pressure of the liquid in the chamber becomes great enough so that contact is made between the mercury and the upper electrical contact. At this point the thermoregulator shuts off and the sample cools via heat loss to the liquid nitrogen until contact is broken. The cycle then repeats itself. The current from the thermoregulator and the pressure of helium in the cryostat are adjusted to give an optimum on-off cycle time. In order to prevent condensation of gas in the tube leading to the condensation chamber, a preheater (15) is provided which maintains the tube at a higher temperature than the copper block; the temperature of this preheater is measured with a thermocouple. In principle, the cryostat is capable of temperature control for an indefinite period at any temperature between -195°C and room temperature. Experience in this laboratory has been confined to temperatures from -195° to -180°C; over this range it has been possible to control for weeks to within ±0.005°C. The cryostat has been described in some detail in order to illustrate the lengths one must often go in order to achieve satisfactory control of the adsorbent temperature; the importance of precise and uniform temperature regulation over the entire adsorbent bed cannot be over-emphasized.

Adsorbate Pressure Measurement - Since the extent of adsorption is usually quite responsive to pressure changes, some attention must be given to manometric devices. For most work a mercury manometer of the type described by Joyner[2] is very satisfactory; with such a manometer one can read pressures from 1 to 1000 mm Hg to within ±0.1 mm Hg. When greater precision and/or lower pressures are demanded, a wide bore (20-30 mm I.D.) mercury manometer and a sliding microscope cathetometer will enable readings down to 0.01 mm Hg to be made to ±0.001 mm Hg. In some cases manometer oils can be used in place of mercury thereby gaining a factor of about 10 in sensitivity. When pressure measurements below 1 mm Hg are required one is usually forced to resort to other means of pressure measurement. If the gas being used is nearly ideal, the familiar McLeod gauge is probably the simplest and most reliable low pressure manometric device that one can employ. Several excellent discussions of McLeod gauge construction and design are available[1]. It is strongly recommended, however, that the comments of Los and Morrison[11] on the effects of capillary depression be considered in McLeod gauge design. Various other manometric devices such as ionization gauges, Pirani gauges, etc. have been described[1] and these may often be used to advantage. In these Laboratories, for example, the thermistor gauge of Rosenberg[12] has been quite useful. It is well to bear in mind, though, that such instruments are no better than their calibrations and that frequent recalibration is to be recommended. As a concluding remark, it should be

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11. J. M. Los and J. A. Morrison, Rev. Sci. Instr. 22, 805 (1951).
12. A. J. Rosenberg, J. Am. Chem. Soc. 78, 2929 (1956).

pointed out that novices in the field often overlook the effects of thermal transpiration when working at low pressures and low temperatures. Corrections for this effect must often be made; the necessary correction data for a number of gases have been summarized by Bennett and Tompkins[13]

Adsorption Measurements - We are now in a position to consider the problem of actually measuring the amount of gas adsorbed by a solid at some specified temperature and pressure. There are two general techniques for this purpose, the so-called volumetric method and the gravimetric method. The former consists essentially of a measurement of the decrease in volume of the adsorbate due to the adsorption process while the latter involves, as the name implies, a determination of the corresponding increase in weight of the adsorbent. Both methods have certain inherent advantages and will, therefore, be considered separately.

In the volumetric method one simply measures the volume of adsorbate before and after bringing it into contact with the adsorbent; obviously, the difference is the amount adsorbed. The measurements are usually carried out in an all-glass system of known geometric volume equipped with suitable temperature and pressure measuring devices and gas handling facilities. A large number of such systems have been described in the literature; an excellent review by Joy[14] discusses many of these designs and gives an extensive bibliography which may be consulted with profit by anyone planning work in this field. Joyner[2] gives a detailed description of the construction and operation of a typical volumetric system and additional information may be obtained in the books by Trapnell[4] and Brunauer[5].

A fairly typical volumetric system used in the Gulf Laboratories is shown, schematically, in Fig. 2. In this design major emphasis has been on versatility, provisions being made

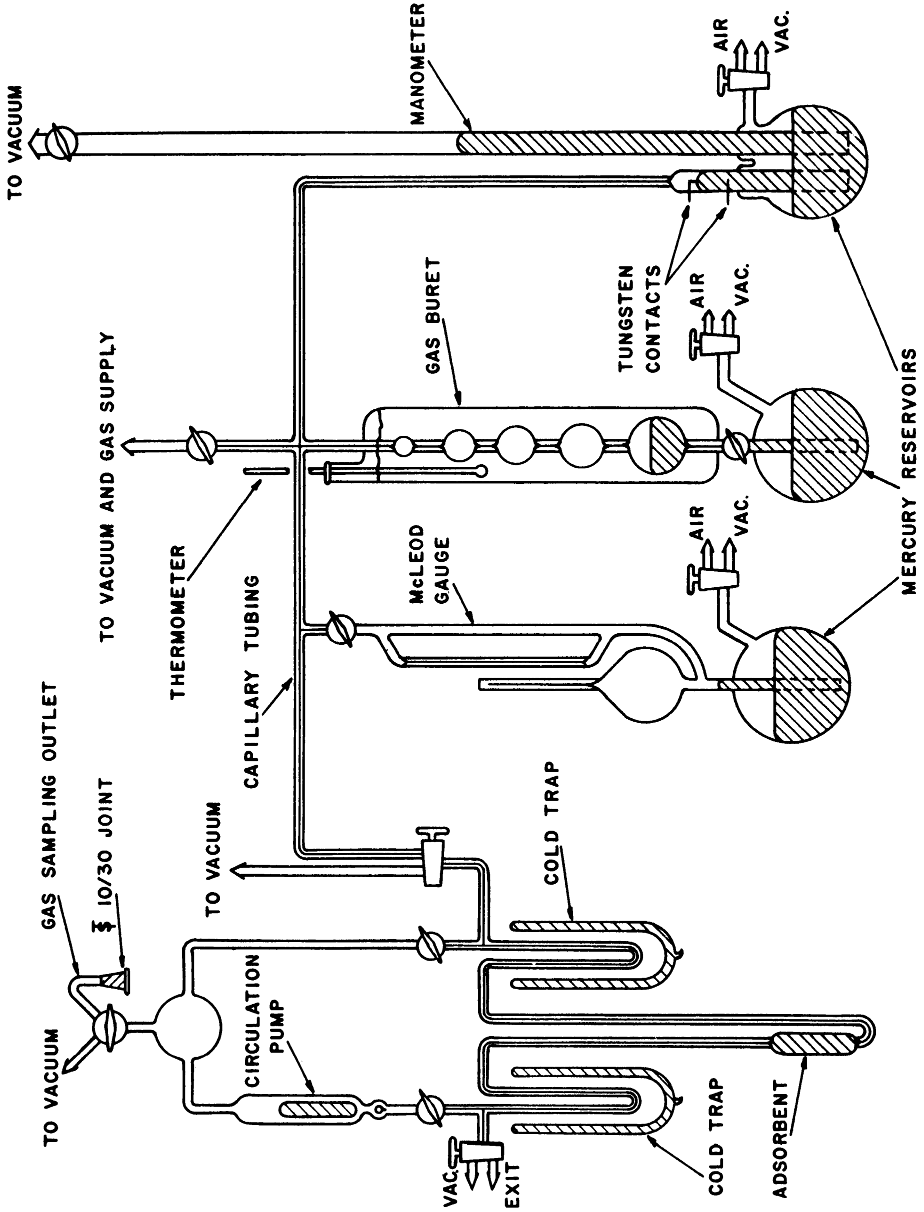

FIG. 2. Volumetric Adsorption System

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[13] M. J. Bennett and F. C. Tompkins, Trans, Faraday Soc. 53, 185 (1957).

[14] A. S. Joy, Vacuum 3, 254 (1953).

for conducting a variety of experimental work. Pressures may be read from 1000 to 1 mm Hg on the manometer and from 10 to 10^{-3} mm Hg on the McLeod gauge; for some applications the latter may be replaced with, say, a thermistor gauge. The adsorbent is protected from contamination by mercury or stopcock grease with cold traps and the adsorbent tube is provided with both an inlet and an outlet line. This latter allows one to flow gases over the adsorbent for pretreatment purposes; in fact, the adsorbent tube can serve as a catalytic reactor, the reactant stream passing over the adsorbent and into some analytical device such as a chromatography unit or a mass spectrometer located down stream from the exit stopcock. An all-glass gas circulation pump[15] is provided which enables one to circulate a gas over the adsorbent; if desired the circulating gas may be analyzed by withdrawing small samples via the gas sampling outlet. This feature is often helpful in studies of solid catalysts. For example, the system in Fig. 2 has been used to study hydrogen adsorption on certain oxides by circulating a mixture of hydrogen and deuterium and observing the rate of reaction between the two; the degree to which the two species reacted was indicative of the extent to which the hydrogen was chemisorbed.

Operation of the system in Fig. 2 is fairly simple. The gas buret is calibrated with mercury before installation; when the system has been assembled the remaining volume enclosed by the gas supply stopcock and the stopcock leading to the adsorbent tube is determined by a series of pressure-volume measurements using helium, the volume of the system being varied by changing the level of the mercury in the gas buret. Once this volume is known then the amount of gas in the calibrated portion of the system is readily computed from a knowledge of its pressure and temperature. The glass tube containing the adsorbent is then sealed onto the system. The sample is subjected to the necessary pretreatment and finally brought to the temperature at which the adsorption is to be studied. A volume of helium is measured out in the calibrated portion of the system and then expanded into the evacuated sample tube. The "dead volume", that is, the volume of the sample tube minus the apparent volume of the sample, is easily calculated from the resulting decrease in pressure. Helium is generally employed for such calibrational purposes because it is not adsorbed by solid surfaces except at extremely low temperatures. Having obtained a value for the dead volume, the helium is pumped out of the system and the stopcock leading to the sample closed off. A volume of adsorbate is measured out in the gas buret and then brought into contact with the adsorbent. Because the dead volume is known, the amount of adsorbate in the gas phase may be computed by noting the temperature and pressure; the difference between this and the original adsorbate volume gives directly the amount of adsorption. The gas pressure and hence the volume adsorbed may be readily varied by raising or lowering the mercury in the buret.

By careful calibration, close temperature control, and precise pressure measurement, the volumetric method is capable of detecting quite small quantities of adsorbed gas. Thus, without much trouble one can measure out a gas volume corresponding to as little as 10^{-5} to 10^{-6} grams of adsorbate. As a further example, Halsey and his co-workers[16] have developed a volumetric adsorption system capable of measuring gas volumes to within a precision of between 1 and 2 parts per 10,000. In addition to its high precision, the volumetric method has the further advantages that it requires, in the majority of cases, relatively simple equipment and that it is a flexible type of measurement. Thus, with respect to the last point, one can readily switch from sample to sample over wide ranges of adsorptive capacity without any modification in design. These favorable features

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[15] F. Porter, D. C. Bardwell, and S. C. Lind, Ind. Eng. Chem. <u>18</u>, 1086 (1926).

[16] G. Constabaris, J. H. Singleton, and G. D. Halsey, J. Phys. Chem. <u>63</u>, 1350 (1959).

have resulted in the widespread use of volumetric methods of one kind or another; in the field of physical adsorption, in particular, the large majority of the work has been carried out volumetrically.

Despite its advantages, however, volumetric techniques have several shortcomings. By its very nature, a volumetric method is restricted to adsorbates for which reliable equations of state are available and which can be quantitatively manipulated in a glass system. Thus water vapor adsorptions are often difficult to measure volumetrically. Further, the amount of adsorption is defined here as the difference between two gas volumes, and if the ratio of adsorbed to gas phase material becomes too small, one is forced to take a small difference between large numbers. If this difference approaches the error of volume determination, then the adsorption measurement becomes quite inaccurate. Thus one is in effect limited to a certain range of adsorbent area to adsorbate pressure ratios.

In order to overcome these and other disadvantages of the volumetric method, recourse may be had to gravimetric techniques. These involve the determination of the weight of adsorbed gas by means of a suitable microbalance of which two general types are available. The first type is the so-called beam microbalance. The beam of such a balance may be supported on a knife edge or attached to a fine torsionless wire and the adsorbent suspended from the beam. One then determines the amount of gas taken up by the adsorbent by noting the resulting deflection of the beam. In the other type of microbalance the adsorbent is suspended on a delicate spring and the adsorption determined by measuring the spring extension.

A number of beam microbalances have been described in the literature[17-21], and useful discussions of them given by Jennings[22], Rhodin[23] and Gulbransen[24]. Such balances have several distinct advantages including very high sensitivities. Thus it is possible to obtain a sensitivity of 10^{-8} to 10^{-9} grams for loads up to, say, 0.5 grams. Furthermore, beam microbalances can often be made to record automatically any weight changes, a feature which is useful when one is interested in the rate of an adsorption process. Opposed to these advantages, however, are several adverse features, the most important being that beam microbalances are quite delicate, require special skills in their construction and usually must be operated by highly trained personnel. For these reasons such balances in the past have usually been custom made for special studies and have not been generally employed in routine work.

A more common gravimetric method of studying adsorption involves the spiral spring type of balance developed by McBain and Bakr[25] The balance consists of a fine quartz helix suspended in a vacuum chamber with a small pan (usually quartz) containing the adsorbent fastened to the lower end. Weight changes are followed by measuring the concurrent extension in length of the helix by means of a suitable microcathetometer. The sensitivity of the helix is easily determined beforehand by placing known weights in the pan and measuring the resulting length changes. With modern quartz handling techniques, helices may be produced which are both quite sensitive and at the same time fairly robust; these are commercially available at relatively reasonable prices.

A more or less typical gravimetric adsorption system employing a quartz helix is shown in Fig. 3. This system con-

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sists essentially of a thermostatted case for the helix (the sensitivity of a quartz helix is somewhat temperature dependent), an adsorption chamber in which the adsorbent is suspended, and a mercury manometer (or other pressure measuring device). In order that adsorbates such as benzene which are soluble in stopcock grease may be handled, the usual high vacuum stopcocks have been replaced with mercury cut-offs. The helix has been provided with an internal quartz reference rod suspended from the top of the helix; this serves to compensate for slight displacements of the unit due to thermal effects. Weight changes are determined by measuring the distance L between the end of the reference rod and some fixed point on the helix. For the study in which the system in Fig. 3 was used it was necessary to protect the adsorbent at all times from contamination by stopcock grease vapors or by mercury. The helix, therefore, was suspended in the case by lowering it through an opening at the top of the case; this opening was then sealed off and the cold traps put into place. It will be noticed that the arrangement in Fig. 3 is such that a stream of gas may be flowed over the adsorbent if it is so desired. The temperature of the adsorption chamber is controlled with a constant temperature bath or a furnace of some kind. Another feature of the system which is sometimes useful is the ballast bulb shown in Fig. 3. If one is interested in the rate of adsorption, there are theoretical reasons why this should be measured at constant pressure; the purpose of the ballast bulb is to minimize any pressure drop during the course of the adsorption process by making the ratio of adsorbed to gas phase adsorbate quite small. As an example of the sensitivity of the method, the system shown in Fig. 3 has been employed in a study of oxygen chemisorption using a helix having a sensitivity of 1.8×10^{-3} g/mm and a cathetometer reading to within ±0.001 mm; with such equipment it was possible to detect adsorptions amounting to as little as 6×10^{-6} grams, the total load being 0.2 grams.

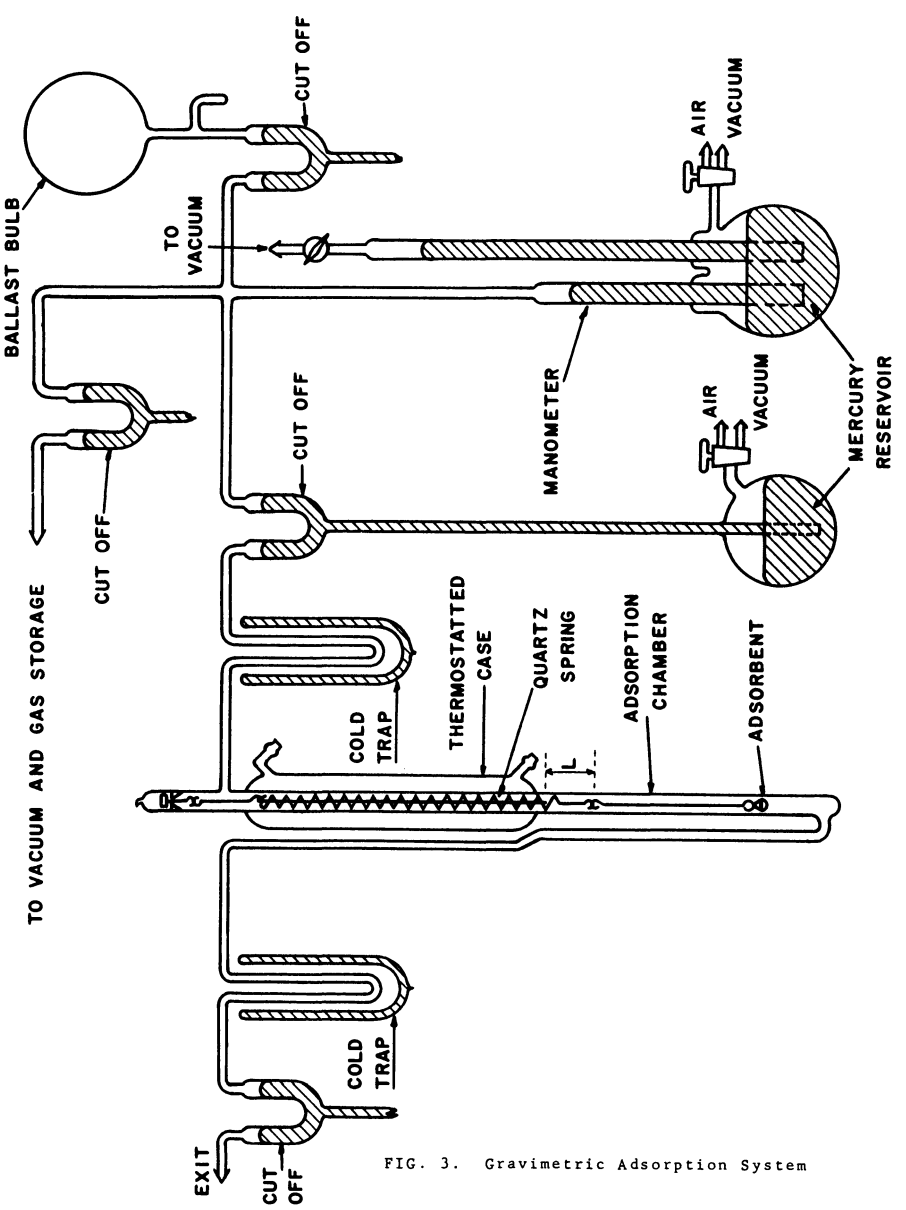

FIG. 3. Gravimetric Adsorption System

One of the pleasing features of a quartz helix balance is its inherent flexibility. In addition to straightforward adsorption measurements, balances of this nature have been used for purposes such as studying the magnetic susceptibility of adsorbed gases[26] and measuring the rate of thermal decomposition of solids[27] An interesting automatic recording adsorption apparatus employing a helix in conjunction with a linear variable differential transformer has been described by Klevins, Carriel, Fries, and Peterson[28]; the remarkable feature of this piece of equipment is that, in addition to the recording aspect, it combines high sensitivity (10^{-6} gram) with large load capacity (20-25 g). Finally, it may be mentioned that by employing an arrangement in which several balance cases are attached to the same gas manifold a series of helices can be used to carry out a number of adsorption measurements simultaneously[29]

This brief account of techniques and equipment can hardly be expected to do justice to a field such as adsorption where experimentation has been so varied and intricate. However, it is hoped that what has been presented will provide some indication of how one goes about measuring adsorption and what the problems are which one must face. The references provided should serve as a starting place for those interested in pursuing the subject further. Because of the complex glass equipment often called for by research in the general area of surface chemistry and adsorption, the glassblower has played a very important role in this field of the physical sciences and will undoubtedly continue to do so in the future.

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Schaefer, Walter A.	Esso Research & Eng'g. Co., P.O. Box 51, Linden, N. J.
Schilling, William F.	Kimble Glass Co., Vineland, N. J.
Schlott, Rudolf W.	Mellon Institute, 4400 Fifth Avenue, Pittsburgh 13, Pa.
Schipmann, Robert H.	Food Machinery & Chem. Corp., Princeton, N. J.
Scholtz, R. C.	General Electric Co., Nela Park, Cleveland 21, Ohio
Schultz, Elwood	Univ. of North Carolina, Chapel Hill, N. C.
Schwickert, Russell C.	U.S.Army Signal R. & D. Lab., Evans Signal Lab., Belmar, N. J.
Scott, William J.	Macalaster Bicknell Co., 243 Broadway, Cambridge, Mass.
Searle, R. H.	E. I. DuPont Co., Aiken, S. C.
Seckman, J. W.	Lockheed Aircraft Corp., Missiles & Space Div., P. O. Box 504, Sunnyvale, Calif.
Sheward, O. A. Jr.	Florida State Univ., Tallahassee, Fla.
Silk, John A.	General Atomic, San Diego, Calif.
Sill, Gustave A.	Mellon Institute, 4400 Fifth Ave., Pittsburgh 13, Pa.
Simon, Richard H.	S. C. Johnson & Son, Inc., 1525 Howe St., Racine, Wis.
Sites, George A.	Houdry Process Corp., Hewes Ave., Linwood, Pa.
Skinkis, Wm. B.	Retired - Westinghouse Res. Labs., Beulah Rd., Pgh, Pa.
Slominski, Harry J.	Union Carbide Chem. Co., Niagara Falls, N. Y.
Smith, Howe	Fischer & Porter Co., Warminster, Pa.
Smith, Robbie E.	Rohm & Haas Co., Redstone Arsenal Res. Div., Huntsville, Alabama
Smith, Thomas L.	Union Carbide Metals Co., P.O. Box 580, Niagara Falls, N. Y.
Smith, W. C.	Corning Glass Wks., Houghton Park, Corning, N. Y.
Snidow, R. D.	Sandia Corp., Albuquerque, N. Mex.
Snyder, Carl R.	Philco Corp., Church Rd., Lansdale, Pa.
Snyder, Dale	Dow Chem. Co., Midland, Mich.
Souza, Raymond L.	Watertown Arsenal Lab., Watertown, Mass.

Spessard, Lewis C.	Martin of Baltimore, Middle River, Maryland
Spindler, G. P.	Bell Telephone Labs., Mountain Ave., Murray Hill, N. J.
Squeo, Guy J.	Standard Oil Co., 2500 New York Ave., Whiting, Ind.
Staiger, W. A.	Staiger Inst. Co., 86 Urban Ave., Westbury, N. Y.
Standing, George	Machlett Labs., Inc., 1063 Hope St., Springdale, Conn.
Stanley, L. J.	Union Carbide Chem. Co., P.O. Box 8361, Tech. Center, South Charleston 3, W. Va.
Stanley, Russell	Infrared Industries, Inc., Warminster, Pa.
Stauffer, Douglass S.	Bethlehem App. Co., Inc., Hellertown, Pa.
Steers, John E. Jr.	Jones & Laughlin Steel Corp., Pittsburgh, Pa.
Stein, Melbourne J.	Bell Telephone Labs., Murray Hill, N. J.
Stone, Francis X.	Allegheny Electronic Chemicals, Bos 529, Bradford, Pa.
Sullivan, Frank R.	M.I.T. Lincoln Lab., Lexington, Mass.
Szalkowski, Bruno	Wilt Glassblowing, Watervliet, N. Y.
Taylor, Roger K.	W.R.Grace & Co. Washington Res. Center, Clarksville, Md.
Teske, Charles W.	Naval Ord. Lab., White Oak, Silver Spring, Md.
Thomas, George B.	Fredericks Co., Bethayres, Pa.
Thompson, Gordon P.	U.S.Bureau of Mines, 4800 Forbes Ave., Pgh. 13, Pa.
Tiley, John	Philco Corp. Computer Div., 3900 Welsh Rd., Willow Grove, Pa.
Tobin, Robert B.	Mellon Institute, 4400 Fifth Ave., Pittsburgh 13, Pa.
Trechel, Eugene J.	Mooney Bros. Corp., 195 Paterson Ave., Little Falls,N.J.
Tropsa, Frank	Machlett Labs., Inc., 1063 Hope St., Springdale, Conn.
Trudell, John	Polytechnic Inst. of Bklyn., 55 Johnson St., Brooklyn, N. Y.
Uthman, Paul W.	Alcoa Res. Lab., New Kensington, Pa.
Voyer, Lucian A.	L. A. Voyer Co., 791 Tremont St., Boston, Mass.
Walrod, A. H.	Varian Associates, 611 Hanson Way, Palo Alto, Calif.
Walther, Karl H.	Brookhaven Nat'l. Lab., Upton, L.I., N. Y.
Warren, Louis	Texaco Inc., Box 509, Beacon, N. Y.
Weismann, T. J.	Gulf Research, Harmarville, Pa.
Weiss, G.	O. H. Johns Glass Co., Ltd., 219 Broadview Ave., Toronto, Ont., Canada
Weir, Harry E.	Atlas Powder Co., Wilmington 99, Del.
West, Joseph	West Scientific Glass Co., 903 - 87th St., Niagara Falls, N. Y.

Williamson, Harry G.	U. S. Steel Corp., Clairton, Pa.
Wilt, William A.	Wilt Lab. Glassblowing, Watervliet, N. Y.
Woltz, Charles R.	Westinghouse Elec. Co. Applied Res., Balt., Md.
Woodall, E. L.	Gen. Elec. Co., 1133 E. 152nd St., Cleveland 10, Ohio
Woods, Richard M.	Pittsburgh Coke & Chem. Co., Neville Island, Pgh., Pa.
Wrbican, Sam	Alcoa Research, P.O. Box 772, New Kensington, Pa.
Wurster, Kurt	K. W. Thermometer Co., 19 Hillcrest Rd., Whippany, N.J.
Yeager, Paul Vincent	Convair, 414 J. St., Chula Vista, Calif.
Younker, Waldo J.	Kettering Lab., Eden & Bethesda, Cincinnati, Ohio
Zandhuis, Jan	Carnegie Inst. of Tech., Schenley Pk, Pittsburgh 13, Pa.
Zelt, Raymond J.	Lansdale Tube Co., Church Rd., Lansdale, Pa.
Zoellner, Franz	Eck & Krebs Inc., 27-09 40th Ave., L.I.City 1, N. Y.
Zwirblis, Henry	125 Harding Ave., Hicksville, N. Y.

American Scientific Glassblowers Society

FIRST ANNUAL EXHIBIT

Held in conjunction with the Fifth Annual Symposium - at the Penn-Sheraton Hotel

Listed at right are the companies who participated, as exhibitors, in the First Annual Exhibit.

Exhibit management was provided by

RICHARD RIMBACH ASSOCIATES, INC.
845 Ridge Avenue, Pittsburgh 12, Pa.

EXHIBITORS - PRODUCTS - BOOTH NUMBERS

Ace Glass, Inc., Vineland, N. J. 4
Exhibiting: Equipment of interest to glassblowers.

Bethlehem Apparatus Co., Hellertown, Pa. 14
Exhibiting: Improved Lab-Lathe, New Sharp Flame Hand Torch; Bench Burner; Gas-oxygen Ribbon Burners and other glassworking accessories.

Burrell Corp., Pittsburgh 19, Pa. 22
Exhibiting: Laboratory Glassware, Glass Tubing; Glass Blowers Tools.

Carlisle Gas Burner Corp., Millville, N. J. 2
Exhibiting: Gas Burner Equipment.

Corning Glass Works, Corning, N. Y. 16
Exhibiting: Pyrex, Vycor, Corning Brand Laboratory Glassware.

Eck & Krebs, Inc., Long Island City 1, N. Y. 15
Exhibiting: Laboratory Glass Apparatus and Supplies.

Engelhard Industries, Inc., Newark 2, N. J. 1
Exhibiting: Fused Quartz.

Fischer & Porter Co., Warminster, Pa. 23
Exhibiting: Glass Products.

Fisher Scientific Co., Pittsburgh 19, Pa. 18
Exhibiting: Hoke Torches; Burners; Vycor Ware; Tube and Beading Kit; Accessories.

General Electric Co., Lamp Glass Dept.,
Willoughby, Ohio 17
Exhibiting: Fused Quartz-Tubing, Rods, Ingots, Fabricated Shapes, Laboratory Ware.

Glass Products Development Lab., Seaford, N. Y. 10
Exhibiting: Glass Graded Seals; Metal-Glass Seals; Conductive Coatings, Specialized Glass Ware.

W. H. Haak, Lafayette, Ind. 9
Exhibiting: Glassblowing Burners.

Instruments Publishing Co., Pittsburgh 12, Pa. 8
Exhibiting: "Scientific and Industrial Glassblowing and Laboratory Techniques" by W. E. Barr and V. J. Anhorn.

Kimble Glass Co., Toledo 1, Ohio 19, 20
Exhibiting: Kimble Laboratory Glassware.

Kontes Glass Co., Vineland, N. J. 6, 7
Exhibiting: Kontes Brand Laboratory and Technical Glassware Products.

Labglass, Inc., Vineland, N. J. 3
Exhibiting: Scientific Glassware and Research Apparatus.

MacAlaster Bicknell Co., Millville, N. J. 13
Exhibiting: Glassblowing Tools, Equipment, Sundries.

H. S. Martin & Son, Evanston, Ill. 11
Exhibiting: Scientific Glassware.

Pioneer Neon Supply Co., Pittsburgh 22, Pa. 12
Exhibiting: Luminous Tube Transformers; Glass Tubing; Stopcocks, Flashers.

Wilt Lab. Glass Blowing, Inc., Watervliet, N. Y. 21
Exhibiting: Glass Annealing Oven.

Reprint

INSTRUMENTATION • SYSTEMS • AUTOMATIC CONTROL

Published by the Instrument Society of America

Purifying Instrument Mercury

by James B. Lawrence
Bethlehem Apparatus Company, Incorporated
Hellertown, Pennsylvania

Reprinted from the February 1959 issue of the ISA Journal

Purifying Instrument Mercury

Many instrumentmen are unaware of the purity requirements of mercury for use in instruments. Some apparently believe there are no requirements! Are you one of those who thinks "Our mercury is just used in flowmeters, so it doesn't have to be clean?"

by ***James B. Lawrence***
Bethlehem Apparatus Company, Incorporated
Hellertown, Pennsylvania

ALTHOUGH IT'S NOT generally recognized, dirty mercury downgrades the performance of any type of instrument, because it flows sluggishly under slight forces, a characteristic known as "stiction." Also, in glass-tube instruments, dirty mercury makes reading the meniscus difficult, and sometimes impossible, because of a "skin" which sticks to the inside tube wall. Too, dirty mercury is hazardous, for its skin clings to hands, clothing, and apparatus.

How to Check for Pure Mercury

You can check mercury purity simply by looking at its surface. If it is bright, lively, and mirror-like, it's suitable for all types of instruments. With this simple "appearance test" you actually are determining its purity to less than one part per million with respect to all base-metal residues! CAUTION: It takes practice to carry out an effective appearance test. Here is the way to do it. Draw off a mercury sample into a *chemically clean* culture dish. Cover and allow to stand *at least one hour.* Uncover, and *immediately* inspect by focusing a flashlight on its surface at a low angle. Guard against dust settling from the air.

How Does It Get Dirty?

Mercury is contaminated by 1. dissolved base metals and 2. floating impurities. Some common metals which dissolve in mercury and form a skin are lead, tin, zinc, and cadmium. Common floating impurities are dust, oil, dirt, grease, and water. When you examine a mercury surface, it's hard to tell which contaminant you see—dissolved or floating. So, it's wise to assume you have both, and purify to remove both.

How mercury comes in contact with base metals is sometimes a mystery. Frequently, the mercury is contaminated when you buy it. Sometimes, it's through ignorance on the user's part regarding metals which dissolve in mercury. I remember one worker who drained mercury from a meter into a galvanized pan! Common materials which do *not* contaminate mercury are glass, iron, or steel, stainless steel, and the plastics.

How To Clean Mercury

Cleaning methods for mercury include distillation, acid washing, and oxidization—all three designed to re-

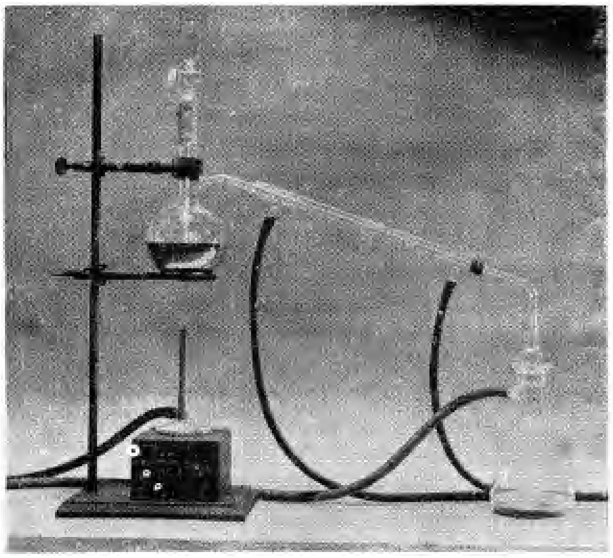

Figure 1. Laboratory set-up for distillation purification of mercury. You must carefully regulate the heat for slow evaporation, to ensure complete purification, and to avoid 'bumping"—the carry over of contaminants.

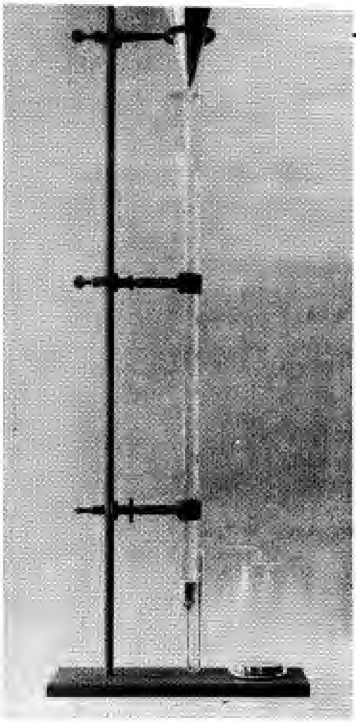

Figure 2. Laboratory-type nitric acid tower for purifying mercury. Mercury falls in fine droplets through 5% nitric acid. Goose-neck tubing at bottom acts as a trap.

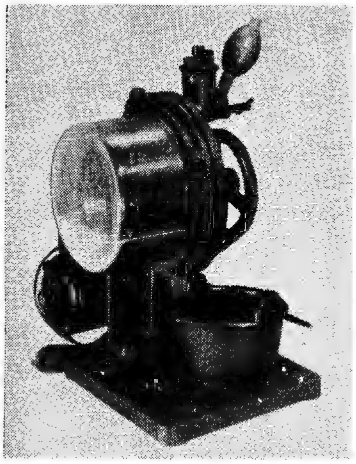

Figure 3. The Bethlehem "Oxifier" which purifies mercury by oxidizing its contaminants. Mercury in the half-filled, tightly-closed case is broken into a fine spray and forced into intimate contact with the air by revolving paddles.

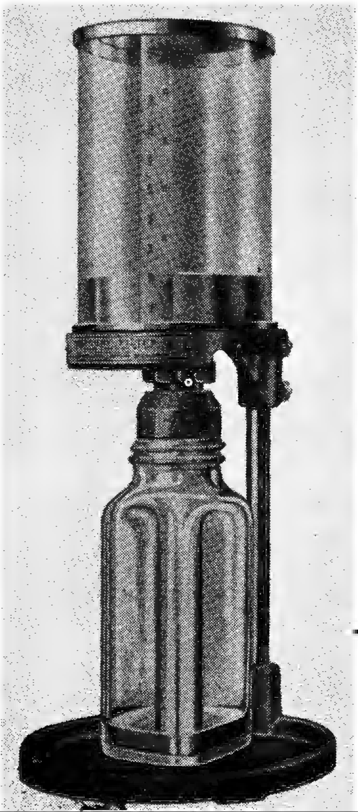

Figure 4. A gold adhesion mercury filter. All mercury flowing down from upper tank must pass through an aperture surrounded by a gold ring. Since mercury "wets" gold, the ring is a positive seal against impurities which otherwise would pass down with the clean mercury.

more dissolved metals. Floating impurities must be removed by filtering.

Distillation. Distillation purifies because mercury evaporates at a temperature lower than do its dissolved contaminants. Originally, mercury was distilled at atmospheric pressure. But *vacuum* distillation permits distillation at a much lower temperature (Figure 1). "Bumping" is especially hard to avoid in mass distillation when several hundred pounds of mercury are evaporated in a single operation. It is good practice to distill mercury *three* or more times; thus the term "triple distilled."

Acid Washing. The disadvantages of distillation—slow speed, necessity for repetition, risk of mercury poisoning—led to use of chemical purification, of which the nitric acid wash is the best known (Figure 2). Several passes through the column are necessary. But, there is a limit, because mercury is somewhat soluble in nitric acid, and nitrate of mercury will accumulate in the column. It is reported that 3 to 9% of the mercury is attacked after three passes, requiring the solution to be treated.

In spite of the mercury trap, acid gets through into the treated product (drops of acid can be seen on the surface). So you must wash the mercury several times by shaking it in distilled water, and then dry it. Following such treatment, your mercury is bright and lively; however, if oxide skin begins to form after standing, you must treat it further.

Oxidization. Oxidization cleaning is widely used because it has several advantages over both distillation and chemical methods. It is faster and safer, requires less handling, and assures better results. It works because oxygen combines with all base-metal impurities, but at room temperature, does not readily attack the mercury. Until recently, all types of oxygen purifiers operated by forcing air or oxygen through mercury, a technique called "bubbling." Sometimes water or acid was added to the mercury. The major drawback of this method is the time required. It is reported that a cadmium impurity of one part in ten thousand is not entirely removed in four days: we ourselves have observed instances where a complete cleanup took three days. Such great lengths of time are required because mercury bubbles are large, and total surface area is small.

To overcome such difficulties, we developed in 1948 an oxidizing apparatus (Figure 3). Here, mercury is forced through air, rather than air through mercury. As the droplets are of minute size, total surface area is large, and oxidation proceeds rapidly. The paddles also break up the oxide skin as it is formed, carrying it into and through the mass of mercury and releasing droplets entrapped in the scum. For light contamination, the air in the cylinder is sufficient for complete oxidation of the charge; for heavy contamination, means are provided for renewal of the air. In two hours, all base metals are changed to fine oxide powder which floats on the surface.

Each method of cleaning listed above must be followed by filtering to remove the floating impurities.

An effective way to do this is with a "gold adhesion filter" (Figure 4).

Don't Hurry

Always remember in handling mercury that, when it is agitated in contact with oxides, dust or other finely-divided particles, the particles are so completely submerged in the mercury that it takes a long time for them to float to the surface. Finely-divided aluminum, for example, keeps rising for three days. So an essential part of mercury cleaning is *a period of standing.*

We have learned that many instrumentmen find it unfeasible to purify their own mercury. To accommodate them, we offer a service whereby we send them empty iron cylinders for storing their dirty mercury, which they exchange for cleaned mercury. (Figure 5).

Beware

I often am asked, "Is mercury really poisonous?"* I can say this much: where mercury is heated, as in distilling, you must be extremely careful not to breathe even a trace of its vapors. At our plant, to be on the safe side, we do all mercury distillation out of doors. If this is impractical, be sure to use a ventilated hood. However, *clean* mercury at room temperatures offers no particular hazard when you follow good housekeeping rules.

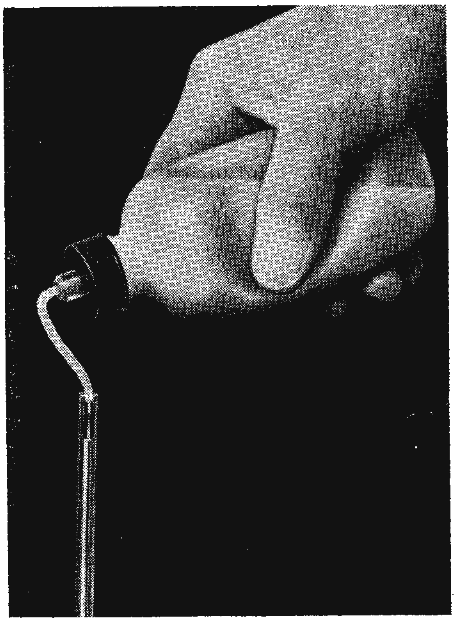

Figure 5. This unbreakable polyethylene bottle has a dispensing tip convenient for filling instruments in the lab or plant—simply squeeze.

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*If you are interested, author Lawrence would be pleased to supply a **Chemical and Engineering News** reprint on the subject.