NBS TECHNICAL NOTE

429

Separation and Purification Section: Summary of Initial Activities February 1966 through June 1967

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards

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UNITED STATES DEPARTMENT OF COMMERCE
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NATIONAL BUREAU OF STANDARDS • A. V. Astin, Director

TECHNICAL NOTE 429

ISSUED FEBRUARY 1968

Separation and Purification Section: Summary of Initial Activities February 1966 through June 1967

Edited by David H. Freeman

Separation and Purification Section
Analytical Chemistry Division
Institute for Materials Research

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FOREWORD

The Analytical Chemistry Division was established as a separate division at the National Bureau of Standards on September 1, 1963, and became part of the Institute for Materials Research in the February 1, 1964, reorganization. It consists at present of nine sections and about 100 technical personnel encompassing some 45 different analytical competences from activation analysis and atomic absorption to vacuum fusion and x-ray spectroscopy. These competences, and in turn the sections which they comprise, are charged with research at the forefront of analysis as well as awareness of the practical sample, be it standard reference material or service analysis. In addition it is their responsibility to inform others of their efforts.

Formal publication in scientific periodicals is a highly important output of our laboratories. In addition, however, it has been our experience that informal, annual summaries of progress describing efforts of the past year can be very valuable in disseminating information about our programs. A word is perhaps in order about the philosophy of these yearly progress reports. In any research program a large amount of information is obtained and techniques developed which never find their way into the literature. This includes the "negative results" which are so disappointing and unspectacular but which can often save others considerable work. Of importance also are the numerous small items which are often explored in a few days and which are not important enough to warrant publication--yet can be of great interest and use to specialists in a given area. Finally there are the experimental techniques and procedures, the designs and modifications of equipment, etc., which often require months to perfect and yet all too often must be covered in only a line or two of a journal article.

Thus our progress reports endeavor to present this information which we have struggled to obtain and which we feel might be of some help to others. Certain areas which it appears will not be treated fully in regular publications are considered in some detail here. Other results which are being written up for publication in the journal literature are covered in a much more abbreviated form.

At the National Bureau of Standards publications such as these fit logically into the category of a Technical Note. In 1967 we plan to issue these summaries for all of our sections. The following is the first annual report on progress of the Separation and Purification Section.

W. Wayne Meinke, Chief
Analytical Chemistry Division

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SEPARATION AND PURIFICATION SECTION: SUMMARY OF INITIAL ACTIVITIES, FEBRUARY 1966 THROUGH JUNE 1967

Edited by David H. Freeman

ABSTRACT

This Report describes the initial growth and research activities of the Separation and Purification Section since its formal organization in February, 1966.

A research capability for the study and refined adaptation of ion exchange materials is described. There are new activities reported for the areas of extreme purification, chemical reagents, organic chemicals, including the use of crystallization for the achievement, protection, and measurement of chemical purity. Specific studies have been conducted in the purification of mineral acids, nitrobenzene, and the development of zone refining methods.

Key words: ion exchange, purification, reagents, zone refining.

1. PREFACE

The Separation and Purification Section was organized in February of 1966. Its creation was prompted by growth of interest in use of sophisticated separations techniques and by the increasing need for extremely pure and well characterized chemical materials. The Section was soon involved in responding to the needs of three larger bodies, the Analytical Chemistry Division, the Office of Standard Reference Materials, and the Institute for Materials Research. This can be illustrated by the following three examples. First, a number of unrelated reagent purification activities were brought under control by establishing a reagent cold storage facility, by bringing the purest samples of commercially available chemical reagents into a state of prompt availability, by eliminating most of the need to prepare such materials on an individual (and therefore quite costly) basis, and, finally, by freeing time for the study of reagent purity. The second example involves the initiation of concentrated study of ion exchange resin phenomena, their applications to problems in chemical analysis, and the relationship between ion exchange properties and the molecular structure of the resin network. The first results have provided progress toward the preparation and characterization of well-defined derivatives of copolymers of styrene and divinylbenzene. A direct product of this research has been the demonstration that individual resin beads show an important potential capability to perform as microstandards and, therefore, to provide the first precise means of setting detection limits and for performing analytical calibration of instruments that respond to a trillion atoms or less. The third area involves the preparation and characterization of purified organic chemical compounds. Presently, this task is divided between two groups where the first is studying analytical problems and the second is concerned with zone crystallization which is already established as one of the most

powerful purification methods known to science. A past heavy emphasis upon distillation has thus been shifted toward the more fundamental goal of charcterizing the purity of refined organic materials. A modern capability is now being built, including the provision of a -30°C laboratory for zone refining studies, and the use of gas chromatography, nuclear magnetic resonance, high resolution mass spectrometry, and infrared spectrophotometry.

The research activities of the Section are aimed at goals which include, and go beyond, publication in the scientific literature. A portion of our energy is spent in cooperative study of problems affecting the output of other groups at NBS, in government, in universities, and in industrial laboratories. These interactions are intended to be helpful and at the same time they provide interesting input statements of the "now" problems of these other groups. Finally, there is frequent consultation with the Office of Standard Reference Materials to determine areas where the effort of chemical characterization and the implied benefits can be made available to other technical and scientific laboratories.

In preparing this first report of the Section's activities and programs, it has been necessary occasionally to identify commercial materials and equipment. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

The assistance of Miss Ellen Matthews and Mrs. Rosemary Maddock in the preparation of this report is gratefully acknowledged.

David H. Freeman, Chief
Separation and Purification Section

Washington, D. C.

2. PROGRAM AND FACILITIES

The Section was formed with initial competences in the areas of vapor-liquid fractionation using analytical distillation, ion exchange research, and a limited activity that was aimed at meeting modern needs for purified reagents. The distillation activities were in serious need of reassessment since the current needs for chemical purity can now seldom be met by these methods alone. The ion exchange interests were in need of being coupled to the needs of analytical chemistry, and the reagent activities were accompanied by an overwhelming ratio of demand to capability.

The program of the Section is just barely emerging and its subject outlines have been used to organize this first Report. The Section is concerned with the basic interactions that are exploited during a separations method, with the development of an effective working concept of the obtainment of extreme chemical purity, and with the measurement and control of the related phenomena involved in both separation and purification.

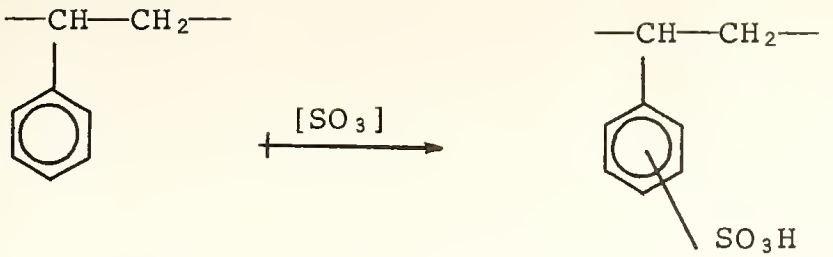
The facilities of the Section presently include the following: a sophisticated array of apparatus for the study of chemical interactions on the microscale with individual ion exchange beads, an assortment of analytical distillation equipment that is almost competitive with preparative gas chromatography; and a high precision apparatus for the measurement of freezing point. A basic complement of research and analytical measurement hardware is still needed; some of this gear, such as an infra-red spectrophotometer and a sensitive gas chromatograph, have just arrived. Plans for a low temperature environment laboratory are discussed later in this Report. In addition to the minor hardware of the research and analysis laboratory, the Section shares access to a nearby time-shared computer facility, to the general services facilities at NBS, and, in the foreseeable future, to the NBS reactor and the implied convenient use of radioactive indicators.

3. ION EXCHANGE

Ion exchange resins have a remarkable flexibility for solving many types of chemical problems, not the least of which is their repeated use in the separation and discovery of new elements. Over one million publications describe properties and processes involving a wide variety of ion exchange materials. Their economic influence is substantial; it includes the control of waste recovery, product purification, isolations of radioactive elements, and the concentration of sparsely distributed matter, including the mining of gold from sea water. While the ion exchange process is simply conceived and easily applied, there is little precision of agreement in the quantitative prediction of the properties of any given ion exchange material. This stems partly from of experimental difficulties in making such physical measurements accurately, the fundamental lack of refined theory and fundamental understanding of ion-ion and ion-solvent interactions in concentrated polyelectrolyte gels, and from disagreements and misunderstandings concerning the properties and molecular structure of the non-crystalline ion exchange materials. The interest in ion exchange at NBS is primarily oriented toward the understanding and establishment of highly characterized materials. One immediate goal is to provide a precise basis for the broad calibration of ion exchange measurement.

The present interest is focussed upon copolymers of styrene and divinylbenzene, the structure of which is shown in figure 1. Their outstanding feature is the expected high degree of chemical uniformity in their structure. The copolymer network is a gigantic molecule whose dimensions are limited only by the surface of its particulate form. Ion exchange resins are subsequently prepared by a derivative reaction, such as the sulfonation process used to prepare

cation exchange resin:



Sulfonation is able to reach a limit in which the SO_3 group is added singly to each aromatic group in the copolymer structure. Assuming that no side reactions occur to change the crosslinking, the sulfonated cation exchanger has a network molecular structure that is topologically identical to that of the parent copolymer.

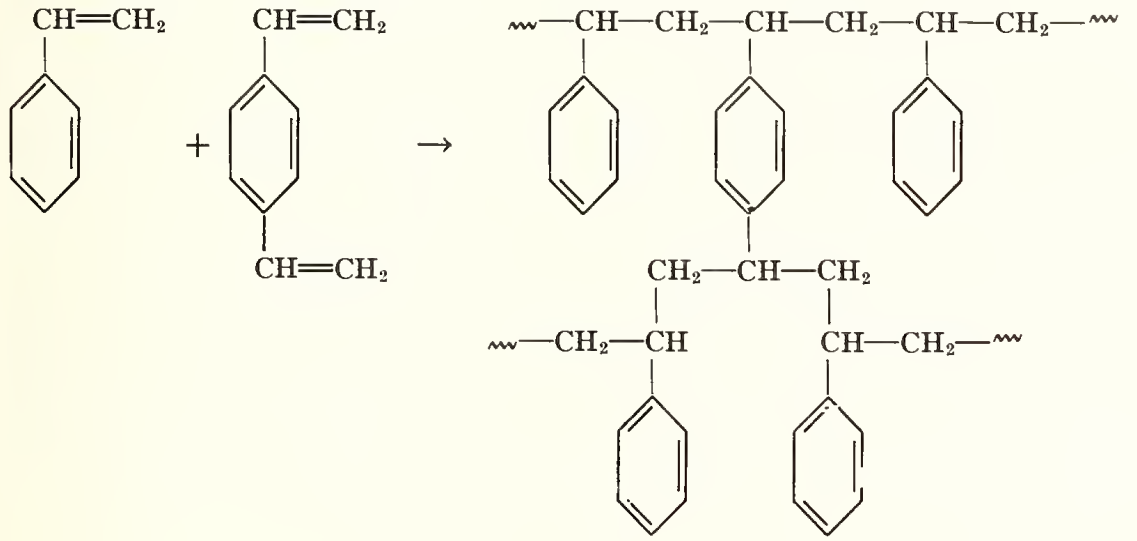


Figure 1. The copolymeric network that is formed by reaction of styrene and divinylbenzene is a three dimensional structure, a portion of which is indicated in the above drawing. The inherent structural flexibility, as well as the requirement of an ultimate swelling limit, is a direct result of the divinylbenzene crosslinks. Note that the structure is four-connected, as required by the fact that polystyrene chains emanate in four different directions from each divinylbenzene that is incorporated as a crosslinking unit in the network structure.

Ion exchange resins are hydrophilic to an extreme. For example, the sudden addition of water to completely dried resin usually causes the resin beads to react explosively, thereby destroying their spherical shape and optical clarity. When fully hydrated ion exchange resin beads are spun on a porous filter in a centrifuge, capillary action causes liquid to be retained in appreciable quantity wherever the beads are in contact with each other. This causes serious difficulty in using this technique to obtain the wet weight, or wet volume, of the water-swollen material. While similar difficulties tend to plague many experiments in which many - particle ion exchange systems are to be measured accurately, it is possible to carry out highly refined experiments on single beads through the use of microscopic measurement. With microscopy, individual bead diameters may be measured with provable accuracy since the microscope is capable of refined calibration. The intrinsically high sphericity of resin beads with diameters that do not vary by more than 0.1% within a single bead implies a basis for accurate measurements of swollen resin volume, weight, and related properties. With the use of radioactive isotopes, an entire chemical study can be carried out on a single resin bead. These important tools for precise ion exchange measurement have been discussed by us in detail in a chapter of a recently published book on this subject [1].

A. Homogeneity of Ion Exchange Resin

The concept of homogeneity requires that a system be uniform throughout all of its parts. The term does not apply to the smallest components of atomic structure in which nuclei, electron clouds, and the intervening microscopic spaces are different and, in part, discontinuous. Instead, homogeneity is a microscopic term that may be applied to microscopically dispersed gases, liquids and solutions where matter is arrayed in random order, or to the crystalline state where matter is orderly repeated. The absence of either order may be correspondingly defined in terms of long range disorder. As part of a working definition, one may refer to refraction and diffraction phenomena that may be used to distinguish optical clarity from aggregated particulate mixtures.

Copolymers of styrene and divinylbenzene can be prepared under conditions that, *a priori*, should cause a random distribution of the divinylbenzene crosslinks throughout the copolymer structure. There should be similarly random distribution in space; the linear polymer or block structure (of polystyrene occurs between the crosslinks. There is experimental evidence in support of this. For example, copolymer beads are optically isotropic in both the unswollen and equilibrium swollen states. Spherically symmetric birefringence is readily introduced during non-equilibrium swelling changes; this has been reported [2] and is shown in figure 2. Thus, conventional copolymers are unstrained structures. The extreme optical clarity of swollen copolymers is another indication of optical homogeneity.

The interferometric microscope provides a uniquely suitable tool for determining the possible presence of structural voids. In the past several years we have had occasion to use double beam interference at the facilities of E. Leitz, Inc., in New York City, at the Dartmouth Medical School in Hanover, New Hampshire, and at the NIH - NIND in Bethesda, Maryland.

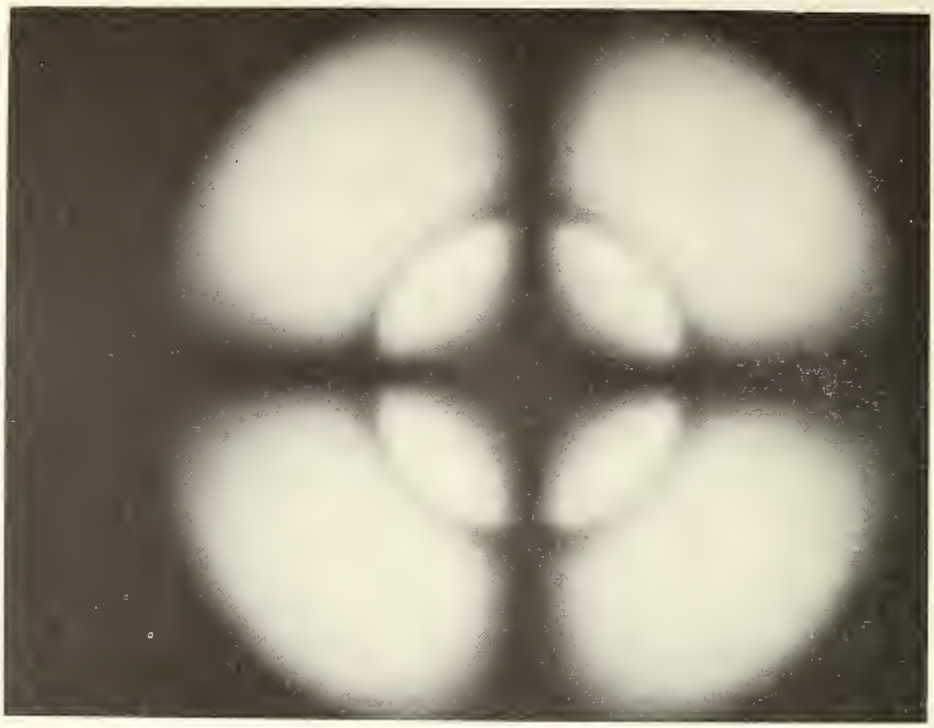


Figure 2. Birefringence during the uptake of an organic solvent is apparent during microscopic examination with crossed polarizer and analyzer.

In the course of repeated examining of samples of resins and copolymers, we were able to observe but one instance in which structural voids were definitely present. A photomicrograph of this material is shown in figure 3 and the small circular interference patterns indicate structural discontinuities whose optical path lengths are in the vicinity of one wave length (5500 Å). This is measured as a typical phase difference where light passing through resin is retarded in comparison to the faster light passing through a structural void which we may assume to be filled with solution having the same optical properties as that present surrounding the bead externally. The retardation can be related to the actual void dimension using the expression:

$$\Gamma = (n_V - n_S)\, d$$

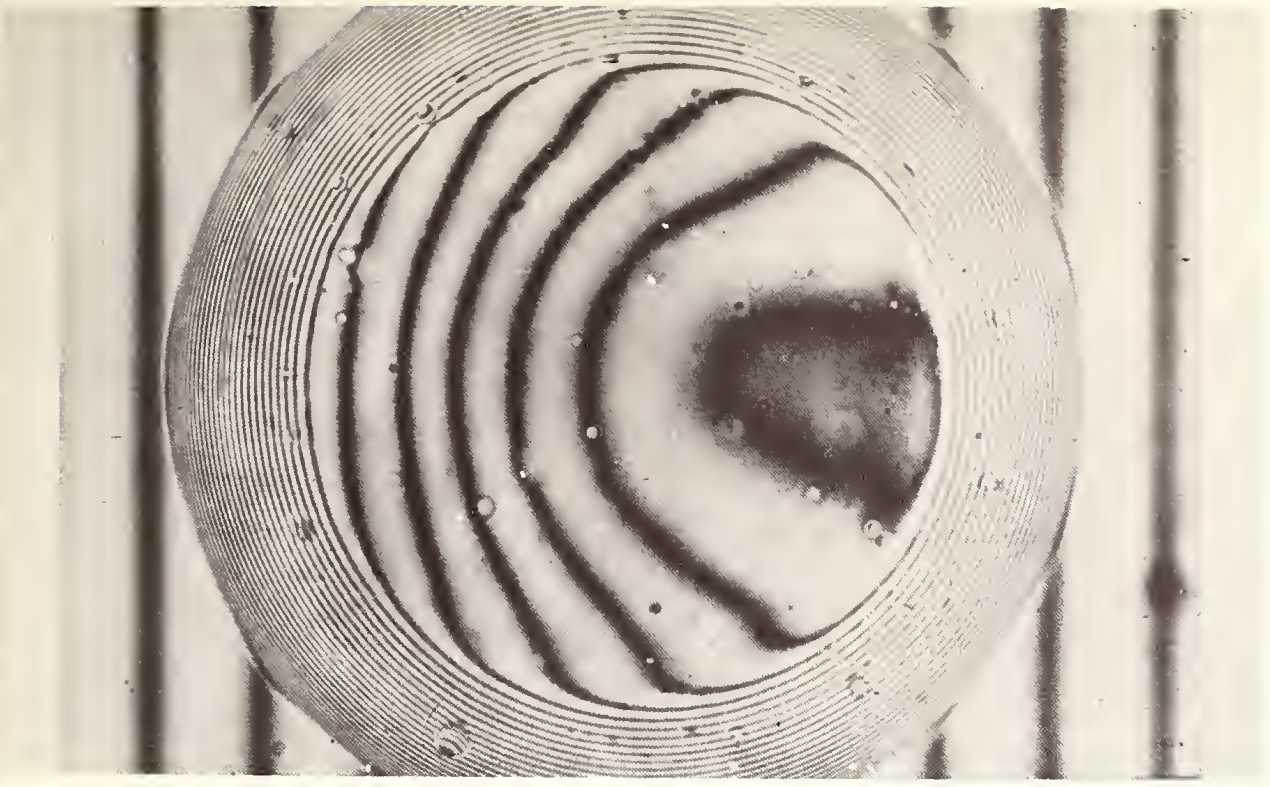


Figure 3. This interferometric photomicrograph exhibits the finding that ion exchange resin gel derivatives of styrene divinylbenzene copolymers have structural voids. This finding, however, it not known to be typical for this type of material.

where n_v and n_s are the respective refractive indices of void (i.e., solution) and gel structure, d is the actual void thickness.

The homogeneity of a particulate sample depends upon a further requirement that all particles are chemically and physically uniform. Strong inferences on this question can be based upon measurement of the swelling properties of individual beads. As shown by figure 4, the swelling ratio q = V(swollen)/V(unswollen) may be plotted in terms of its deviation (ζ) from the average value $\bar{q}$, where $\zeta = q_i - \bar{q}$. Since $\bar{q}$ is a physical property that must be characteristic of the material, it is required to be an intensive variable

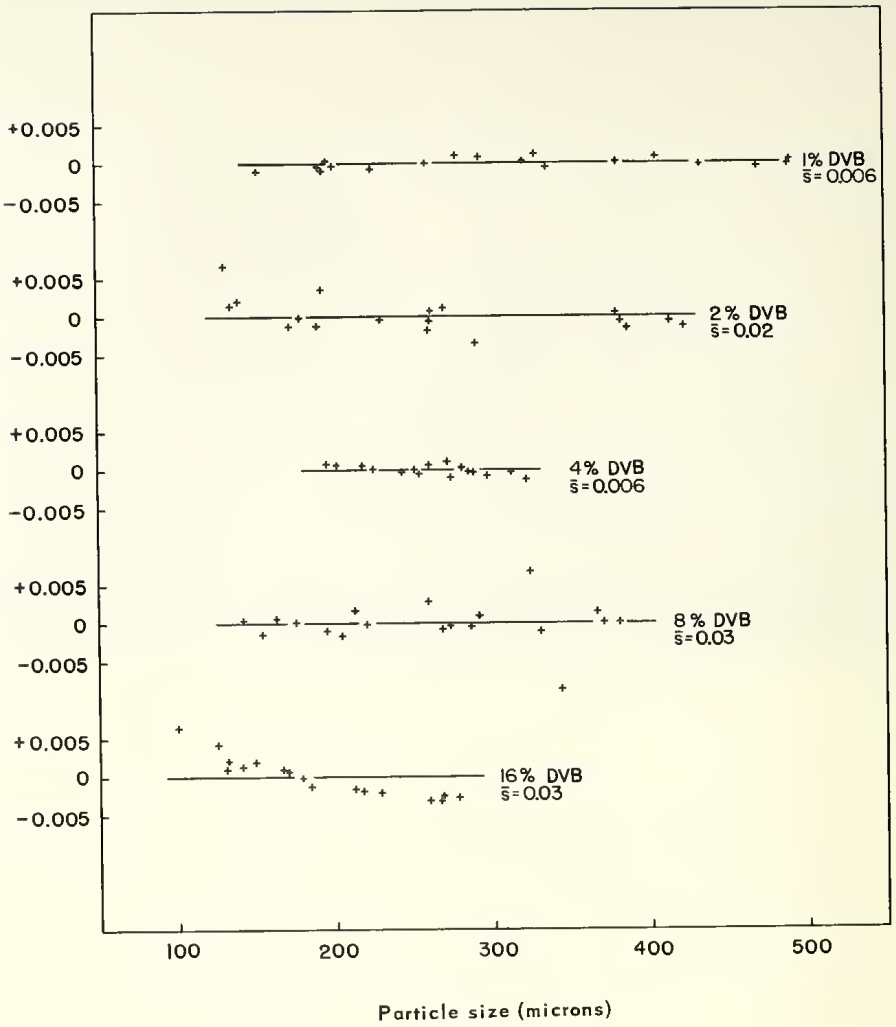


Figure 4. Deviations in swelling of different particles from variously cross-linked copolymers samples. The quantity $(q_i - \bar{q})/\bar{q}$ is plotted, vs. particle size, where q_i is the individual measurement and $\bar{q}$ is the average. The samples with 8%, or less, DVB are evidently homogeneous, and the 1% DVB particles show a high degree of interparticle uniformity.

for a homogeneous system of many particles. The swelling deviations for the 16% DVB crosslinked particles show a marked trend with particle size and, accordingly, this material is heterogeneous. The less highly crosslinked systems are more consistent with interparticle homogeneity.

The application of the foregoing intensive properties requirement for single beads is also suitable for determining the homogeneity of derivative ion exchange resins. As published elsewhere [3], we have found that a variety of resin samples exhibit marked variations in the swelling ratio and in the concentration of exchange sites C (meq/ml) as measured with tracers on individual particles. Figure 5 shows the variation of these quantities for a heterogeneous sample of ion exchange resin and figure 6 shows the intensive behavior that, though infrequent, has at least been observed.

Finally, we add to this picture the results of a preliminary and incomplete study that we have carried out at Oak Ridge National Laboratory through the courtesy of Dr. George E. Boyd. A Philips EM 200 electron microscope was used to provide direct images of cation exchange resin (sulfonated styrene divinylbenzene) structure. The resin was converted to the monovalent thallium counterion form in order to achieve maximum opaqueness to the electron beam. Over a thousand electron photomicrographs were taken, but the effort was constantly hampered by the fragility of the structure. To illustrate, when the electron beam was turned up to sufficient intensity to permit accurate focussing, it would then destroy the structure. Partial success was achieved by collecting colloidal ion exchange resin fragments directly upon a thin carbon film coating upon collodion. While study of the electron micrographs is being continued, the concept of homogeneity is gaining strength as an accurate description of the randomly oriented structure of these materials, provided the distance scale is sufficiently large to permit definition of the uniformity. The present findings suggest that a 100

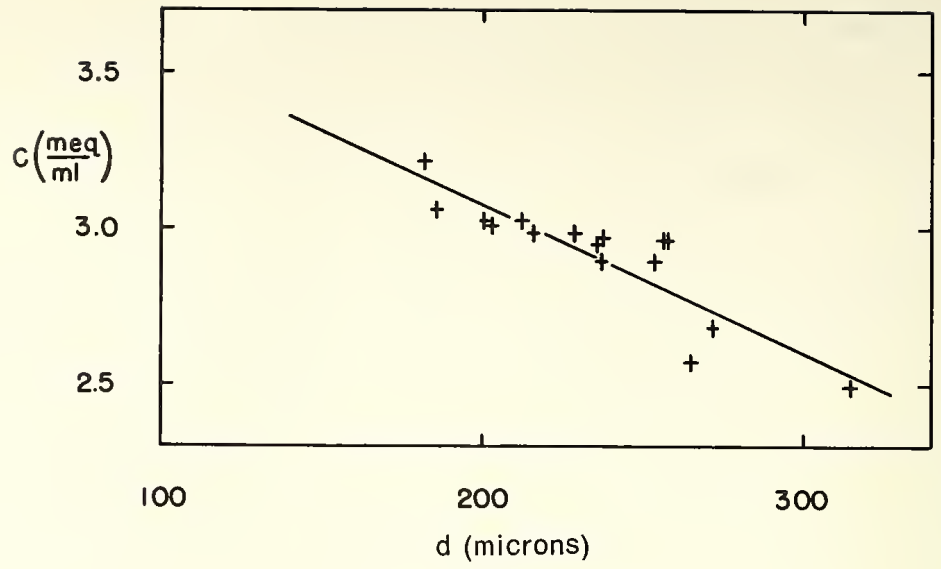


Figure 5. The above measurements are strongly indicative of non-uniformly sulfonated cation exchange resin which, on this basis, is defined as having marked interparticle heterogeneity.

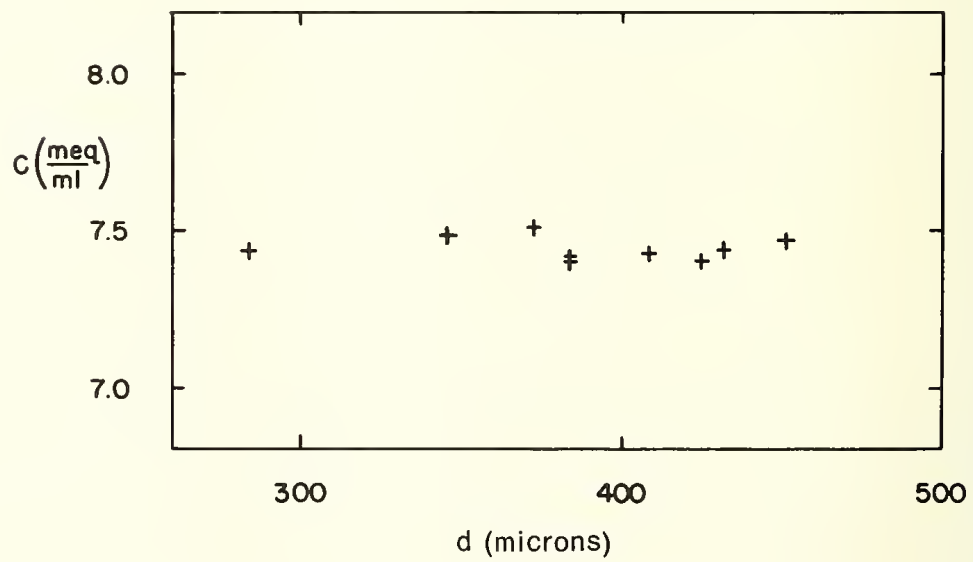


Figure 6. In contrast to figure 5, these results provide a strong inference that uniform sulfonation has occurred and, on that basis, the material exhibited interparticle homogeneity.

angstrom domain may be adequate to provide statistical uniformity.

B. The Molecular Structure of Ion Exchange Resin

There is no reason to assume any condition that precludes the exact definition and experimental determination of the structure of a random oriented network structure such as that of the ion exchange derivatives of copolymers of styrene and divinylbenzene. The feasibility of structure characterization has certainly been established with biological substances that exhibit individual variation of an ordered molecular structure, and there is good intuitive reason to expect this is also true of statistically uniform polymers that have a randomly oriented structure. Whether this concept is entirely meaningful or not depends directly upon a high degree of definition and control of the network synthesis, including an exact knowledge of reactant composition, mixing uniformity, and heat exchange during polymerization, so that the structurally significant criterion of statistical uniformity is consistently realized. Similar requirements must apply to any subsequent reactions that produce ion exchange resin, plus the knowledge that the network structure undergoes no change of topology during substitution of the ion exchange sites. Within this framework, the conformation of the copolymer and that of the ion exchanger have but two important differences: the nature of the distribution of derivative functional groups in space and the distribution of the functional groups among the available aromatic ring positions.

C. Fractional Sulfonation of Styrene Divinylbenzene Copolymer

Homogeneous sulfonation may occur under two entirely different sets of experimental conditions. In the first, diffusion controlled reactions may be used to achieve rapid sulfonation that reaches the ultimate limit of one sulfonate group per aromatic ring in the copolymer network. When this

limit is reached, the network is as homogeneously sulfonated as the network itself was originally distributed. In the second instance, reaction conditions are controlled so that fractional sulfonation occurs isotropically. In both instances, homogeneous substitution implies uniform distributions of the sulfonate group both spatially and in terms of its substitutional arrangement, where the functional group position on the aromatic rings must be either unique and constant, or variable and random. Fractional substitution is an ultimate challenge to the control of the experimental conditions of substitution of a crosslinked network and there is no reason to assert that it must be achievable. However, it was estimated that the temperature dependence of diffusion effects should be smaller than that of the sulfonation reaction. Accordingly, lowering the temperature was predicted to lead toward an decreasing ratio of the relative rates of chemical to diffusional processes. Experimental tests of this prediction were investigated and the results showed that fractional homogeneous sulfonation was feasible under the relatively unspectacular experimental requirements of a mild and dilute sulfonation agent to carry out the reaction at room temperature. This work was published in the August 1967 issue of Analytical Chemistry [4].

D. Development of a Standard Reference Material for Ion Exchange Research

The significance of ion exchange measurements depends directly upon meaningful definitions of the measured and measuring systems. Heterogeneous material is always difficult to characterize adequately, and precise attempts to attain characterization of ion exchange resins have included some results that suggest experimental inconsistency. Some important examples can be cited: the chloride-perchlorate equilibria on the ethanoldimethylbenzylammonium anion exchange resin have been reported twice in the published literature; the two sets of

measurements differ both in trend and numerically, the latter reaching two magnitudes (a factor of one hundred) of disagreement [5,6]. Discrepancies this large are not generally found among reported measurements of ion exchange equilibria, but they are routine among the various reported measurements of electrolyte uptake processes. In other areas, some researchers have published inferences that the ion exchange materials they have studied are heterogeneous and non-uniform. These findings may be correct, but have been taken as applicable to ion exchange resin materials in general, although the basis for this more extended inference is not established. Such conflicts produce a state of confusion that is entirely out of keeping with the requirements for scientific measurement. To help resolve the general problem of making valid comparisons in ion exchange research, the Office of Standard Reference Materials at NBS has formally approved efforts to develop styrene and divinylbenzene copolymer materials to serve as a constant research pool. Negotiations for the material are now being pursued. The most important single factor in the effort is that NBS will examine and test until the achieved homogeneity is established as adequate. The present activities are focussed upon issuance of the standard reference material during the summer of 1968.

E. Development of Ion Exchange Beads as Microstandards

Homogeneous ion exchange resins are composed of spherical particles that are chemically identical. The counterion composition of a single bead may be predetermined, and scavenging procedures are available for the removal of all extraneous substances not directly associated with either the counterions or the bead matrix. These considerations are especially interesting when applied to small sizes of beads, as illustrated in the following calculation. Consider the equivalent weight per unit counterion charge, ε_{RH}(grams/equivalent), of a cation exchanger in the hydrogen form, RH. This is related

to the concentration of ion exchange sites (C(meq/ml) = 1000X $\rho_{RH}/\varepsilon_{RH}$)where ρ(grams/ml) is the resin density, and a typical value for fully sulfonated RH is C = 7.7(meq/ml). Now, assume that the resin is partly converted to a mixed counterion state in which each $i^{\underline{th}}$ element occupies an equivalent fraction y_i of the available sulfonate exchange sites. The equivalent weight of the composite resin is given by

$$E = \varepsilon_{RH} + \sum y_i(\varepsilon_i - 1) \qquad (1)$$

from the foregoing equation it is easily shown that the weight w_i of the i^{th} element in a single bead of diameter d(cm) is given by

$$W_i = \frac{\pi d^3 y_i \varepsilon_i \rho_m}{6\ E} \qquad (2)$$

where ε_i is the equivalent weight of the i^{th} counterion based upon ion charge, and where ρ_M is the density of the bead in the mixed counterion form. For a specific example, consider a pure calcium form resin so that $Y_{Ca} = 1$, ε_{Ca} is 112.4/2 or 56.2, and E = 185 + 55.2 = 240.2. Then, for a bead that is 2.0 microns in diameter, and assuming a bead density of 1.5 grams/cm^3, the weight of calcium is obtained

$$W_{Ca} = \frac{(3.14)(2.0\text{x}10^{-4})^3(1.5)(1)(56.2)}{(6)(240.2)} = 1.5\text{X}10^{-12} \text{ grams} \qquad (3)$$

showing that a reasonable size of resin bead can be marked for precise calibration on the picogram (10^{-12} gram) scale. This type of calculation is just as easily carried out in principle with beads that are composed of a homogeneous multi-element mixture. Various weights of beads in any one counterion form are in the same ratio as the numbers of exchange site equivalents, and this can be used as the basis for predetermining a final mixture of the homogeneously distributed counterions in a desired microstandard particle. This mixing should be reliable if the beads all have the same surface to volume ratio, i.e., if they are monodisperse.

4. ULTRAPURE REAGENTS

A. Introduction

Ultrapure materials, by definition, should not contain detectable quantities of contaminants. There is a growing interest and importance in the preparation of chemical reagents having such extreme purity. The nature of the problem is very broad since the difficulty of reaching high purity depends upon a degree of contamination control considerably above that necessary for obtaining conventional levels of chemical purity.

The present project was prepared with a central idea of meeting modern and future needs of trace analytical chemistry. In the past, each such need has been approached as an isolated problem. The implied lack of coherence was recognized and this led to the formation of the present project in which experience is accumulated and focussed much more effectively.

The first such efforts were discouraging since the project was quickly saturated with many specific requests for individual reagents and very few of these requests could be met by the same material. Some of these requests were met as described in the following paragraphs. Other requests could not be met because there was not enough time, or equipment, to conduct the effort. To avert this situation leading to non-illuminative immersion in endless detail, a materials bank was started so that the purest commercially available reagents could be accumulated for immediate issuance. The approach has effectively relieved the project from many of its routine aspects.

The present approach to reagent purification has an accumulative information benefit. Since each reagent is used in such a way that its composition becomes more fully determined, the usefulness (or the non-usefulness) of a particular reagent is thus allowed to increase as a simple consequence of the keeping of good records. Some early features of the reagent effort are indicated by the following.

B. Hydrochloric Acid

Hydrochloric acid was prepared by anion exchange extraction followed by distillation in a quartz apparatus that was measured to have between seven and eight theoretical plates. The results of polarographic titration showed that the concentrations of a number of elements were reduced appreciably, as shown by the following:

Results of
Purification of Hydrochloric Acid
(Concentration in parts per million.)

Element	Reagent	Purified Reagent
Cu	0.021	0.004
Pb	0.013	0.003
Na	0.13	0.0008
Ca	0.035	0.004
Fe	0.15	0.15

Among the more significant findings is that the iron content is essentially unchanged. The cause for this was later uncovered. Microscopic examination of the containers, made of poly-fluorocarbon materials, showed the presence of small opaque particles that were embedded within the container, and there were frequent instances where these were located on or near the surface. Laser microprobe techniques were used for determining particle compositions. Nearly all of these particles were found to contain iron as a major constituent; magnesium, aluminum, silicon and zinc were also found to be present. This source of container contamination is possibly more widespread than is commonly realized and we are now engaged in a more general study of the problem.

C. Hydrobromic Acid

Hydrogen bromide gas was added from a cylinder into water in a quartz vessel submerged in a cold bath. The amount added was followed by monitoring the cylinder weight. A 48% HBr reagent solution was obtained and this was subsequently used

for analysis of selenium of moderately high purity. Analysis for sulfur, however, showed that the reagent blank was 10 ppm in the aqueous hydrobromic acid. Upon refluxing the acid in quartz distillation apparatus, and subsequent distillation, the sulfur content was decreased to 0.1 ppm.

D. Extraction of Uranium From Silica Gel

An activation analysis procedure was designed to depend upon direct neutron activation of silica gel following thin layer chromatography. The required absence of uranium contamination in the gel is obvious if one is to avoid confusion between the activated element and a corresponding fission product. Various grades of silica gel were compared with and without treatment with circulating hot nitric acid solution. No improvement was realized from the original level of 0.12 ppm uranium in the best grade of silica gel. Other attempts were made, including extensive anion exchange resin extraction from a system containing the silica gel, concentrated hydrochloric acid, and the resin. The removal of uranium was not improved. Investigation showed that the laboratory working area had trace contamination with uranium that was just barely detectable, although the contamination mechanism was not made clear. Although clean room facilities would be called for next, the present work now avoids direct activation of the silica gel.

E. Extraction of Filter Paper

A requirement for filter paper that was especially free of calcium and aluminum was approached with an effort to use ammoniacal EDTA as an extractant, washing with ammonia and then with water, and drying under partial vacuum. The interesting feature of the method was that a polyethylene container was used for extraction, washing, drying and for storage of purified paper, thus minimizing the risk of possible airborne contamination. Thus far, the presence of the two elements has not been confirmed in the purified paper.

F. Bis(ethylhexyl)hydrogen phosphate

This extractant is known to be contaminated with inert organic substances, the mono-ethylhexyl dihydrogen phosphate, and various unidentified contaminants. Purification was carried out using the procedure described by the Oak Ridge National Laboratory report, ORNL-3548, the only modification being an attempted final step involving molecular distillation. (The material forms a glass upon cooling so zone refining is not easily carried out.) However, the distillation caused consistent degradation of the material in the warmer regions of the distillation unit. No distillate could be collected when the temperature was lowered below the decomposition temperature.

G. Reagent Storage in the Cold

Reagent deterioration, or contamination, generally occurs when reagents remain constantly exposed to light, heat or air-borne contamination. As one answer to this problem, we have started to refine and evolve the practice of storage of our purest reagents in a freezer that will hold a temperature of -20°C. Some reagents such as water and 50% sodium hydroxide solution become frozen at that temperature, and while in a solid state, diffusion processes are effectively stopped. Other reagents such as hydrochloric acid are not frozen, nor would they tend to be unless extremely low temperatures, such as -90°, were achieved. One possible way to cause freezing is to increase the acid concentration up to about 15 molar where the acid forms a trihydrate and, accordingly, should freeze at -30°. At present approximately 25 different reagents are available in storage for trace analytical chemistry, and there has been favorable user response based upon the convenience of having this facility available. At the same time, we are learning more about the needs of trace analytical chemistry through a system of depending upon the users to supply any compositional information which they obtained, including

whether the reagents were satisfactory for the specific purposes. It should become possible to determine a basis for preparing particular reagents for which there is highest need and significance.

H. Water

One of the fascinations about water purification is a paucity of methods of establishing water composition (including particulate matter) in terms of measured contaminants, or their removal, at levels in the parts per billion region or below. Organic contamination is probably common at the level of one hundred parts per billion level and it may be high if ion exchange resins have been used. Plans are now being evolved for preparing water by distillation and by crystallization.

I. Low Temperature Environment Laboratory

The recurring need to depend upon low temperatures to minimize reagent deterioration and the need to purify reagents using crystallization procedures have caused a taxing of our available low temperature facilities. On more than one occasion we have had to play "musical freezers" when the zone refining experiments of one group required the cold storage space that was already in use for something else. This reached sufficient proportions to justify a major investment in a large low temperature environment laboratory that would be adequate for meeting both storage and research needs. The plans were completed in the fall of 1966, and a sketch of them is shown in figure 7.

J. Fluid-Borne Contamination

In these laboratories there has been a history of concern for particulate matter as a possibly common source of trace contamination. Light scattering methods may be used to detect particulate matter, and there are methods of collecting filtered samples for analysis. A very simple and relatively

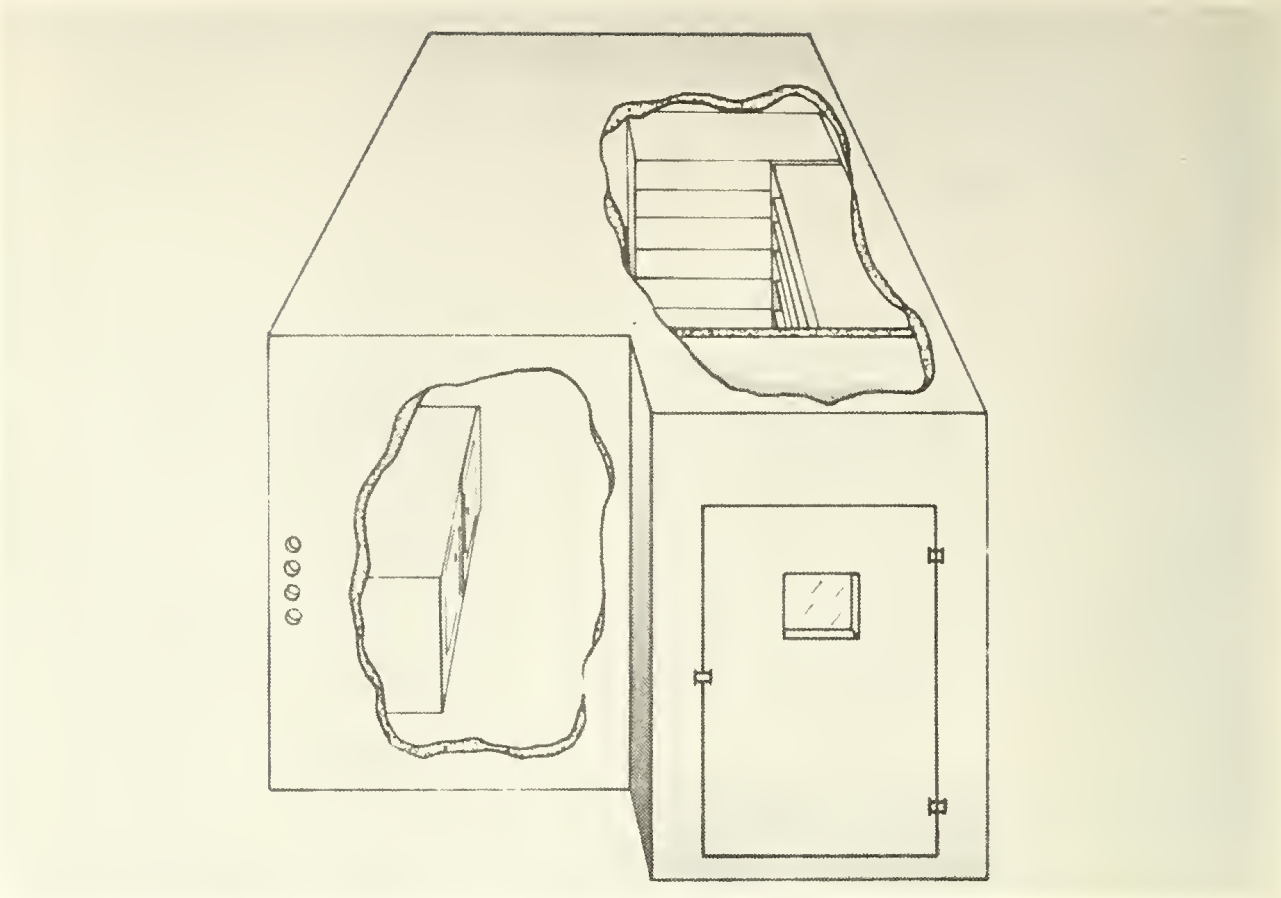


Figure 7. Artist's sketch of the planned low temperature research laboratory. The design calls for continuous operation at -30°C.

inexpensive method was developed as a result of our efforts to assist the physics department at the U. S. Naval Academy with their interest in studying the Brillouin scattering of a laser beam by carbon tetrachloride. We were asked to help remove the particulate matter scattering that obliterated the signal of interest. In this effort, our use of filtration was combined with the laser beam scattering observations. Eventually the source of the dust was identified within the cell used to contain the liquid. Upon realizing the effective information obtained from this apparatus, we determined that an inexpensive laser would be a helpful addition to our laboratory facility. A standard curve for polystyrene latex spheres was developed using the apparatus as shown in figure 8.

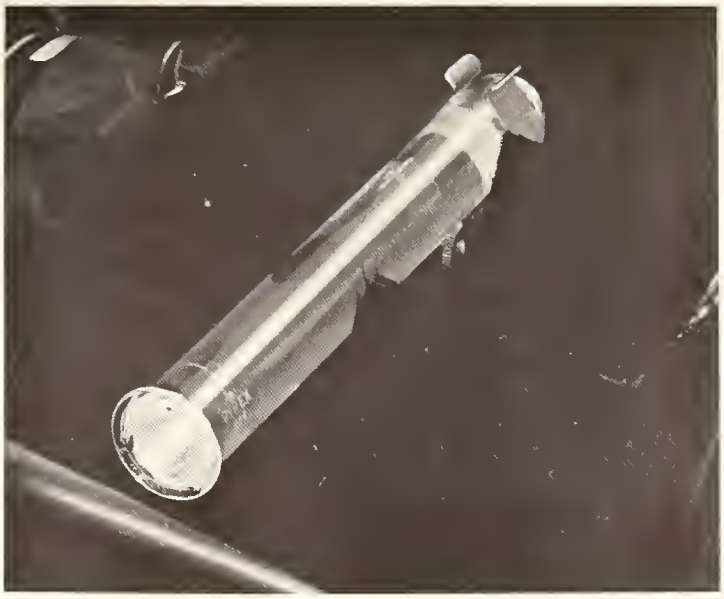


Figure 8. The above photograph shows the concentrated Tyndall effect produced by a laser beam passed through a liquid. In the arrangement above the light scattered, approximately in the perpendicular direction, is measured by a photomultiplier.

To a first approximation, spherical particles scatter light according to the concentration by weight of the particles present. As a matter of curiosity, a sample of water from the NBS pond was examined and a crude estimate of the solids content of the water is at a level of 1 ppm, as shown in figure 9. The apparatus is being rebuilt to provide a more precise measurement. In the meantime, an inexpensive laser device is being used as a qualitative detector for liquid-borne dust. Among our first findings was the demonstration that ethanol, which was dried using molecular sieve material, was contaminated with suspended particulate matter.

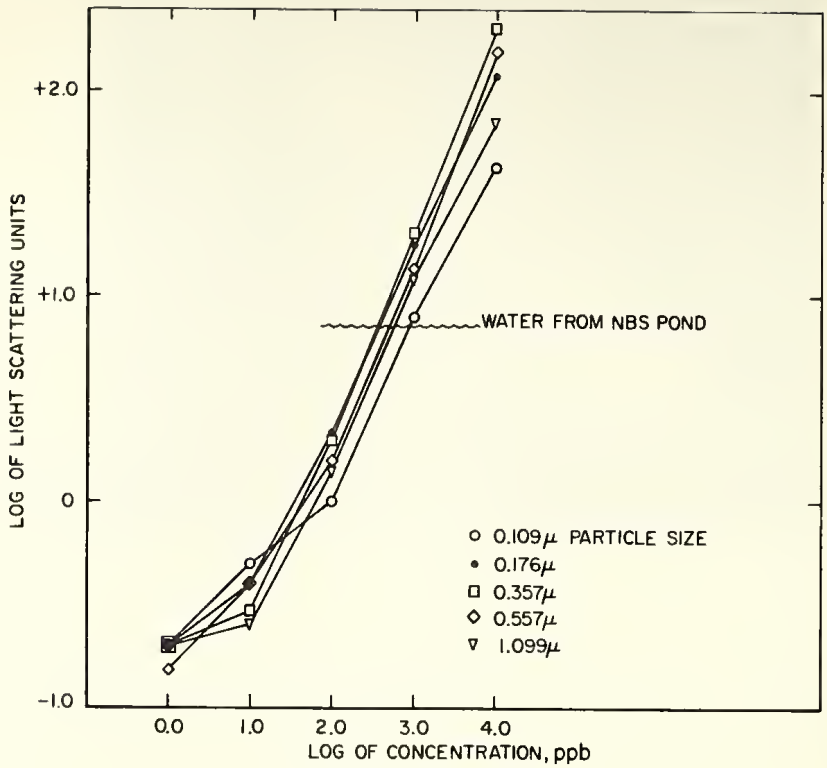


Figure 9. Calibration curves of light scattering versus concentration of spherical particles.

5. STUDIES ON THE PURIFICATION OF ORGANIC CHEMICAL MATERIALS

A. Introduction

Many interests in organic chemical materials are directly concerned with the need for increasing requirements for chemical purity. Purified materials serve such diverse roles as chelating agents, dye indicators, acid or base standards, crystals with interesting energy states, and as supporting solvents, to name but a few. Traditionally, our laboratory has been called upon to provide routine distillation services, and these activities have enjoyed important roles which included the facilitating of measurements which would otherwise be much less reliable; other distillation studies have been carried out in cooperation with the International Union of Pure and Applied Chemistry. In the past sixteen years, over ninety-five organic compounds were either distilled, or, as occasionally required, recyrstallized from suitable solvents. Over two years ago, however, it became clear that the continued reliance upon distillation and recrystallization procedures was not meeting general purification requirements. A major difficulty in finding a more effective purification approach is related to the varying needs of different users who are particularly sensitive to those contaminants which affect their special requirements. This is the characteristic pattern of the end-use orientation of chemical purification procedures. The search for improvement poses no small problem. As pointed out by Sloan [7], "Unfortunately, there is no really good absolute criterion of purity for highly purified samples. ... (one) approach to the estimation of purity is to identify the impurities present in a given sample and assay each of them. This method is tedious, but it has the advantage of providing information useful in relating specific physical effects to the presence of certain impurities." Our past average purification rate of one compound every six or eight weeks would be drastically slowed if a thorough investigation of contamination

were to accompany each purification. The major problem is how to avoid extensive study of each compound requiring purification.

In the spring of 1966, a determination was made to consider some material whose purification was needed, where the method of purification would not be expected to involve the well-trodden path of hydrocarbon separations, and where there was a good prospect for suitability of several different approaches whose relative effectiveness could be studied. This interest was focussed upon nitrobenzene. The effort was initiated with the thought that we would try to determine if a high degree of purification could be obtained, and what would have to be done to prove the purity. The present study is directed toward the logic and fundamentals of the control of purification and the measurement of purity. The following discussion will describe the results of the study during the past nine months.

B. Nitrobenzene Purification

This substance has the interesting property of becoming birefringent in the liquid state when a strong electric potential is applied. The birefringence, or Kerr effect, is a repetitive function of electric potential so that theory requires a cycling appearance and disappearance of the birefringence as higher and higher voltages are reached. Complications to the possible use of this material for high voltage calibrations arise as a direct result of polarization phenomena which vary significantly with the purity of the liquid. Furthermore, this material is in a group of highly polar compounds which includes the low molecular weight alcohols. The resistivity of acetone is reported by Felici [8] to change by three or more magnitudes as a result of removing residual water and of deionization by treatment with dry ion exchange material.

Distillation of a test sample of nitrobenzene was carried out at reduced pressure at 50°C (see figure 10). Gas chromatographic analysis showed that water and benzene concentrate in the first fractions, and become undetectable in the middle and last fractions. Concentrations of water (0.04%) and benzene (0.004%) were determined in the starting material by adding known quantities of these substances and by linearly extrapolating to the intercept on the composition axis. The results after distillation, for the best middle fractions distilled, were not distinguishable from the noise level of 0.0025% for benzene and 0.02% for water. The effect of careful distillation alone, however, does not provide an electrical resistivity of greater than 10^9 ohm/cm^2.

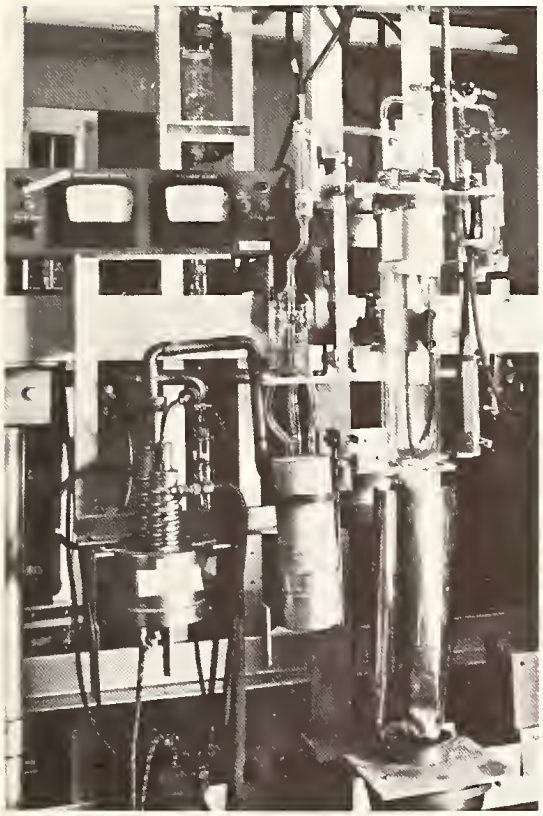


Figure 10. Still used for fractionating nitrobenzene under its own vapor pressure. The distillation column is surrounded by foil and is of the Stedman sieve type with 36 actual stages. Reflux is controlled by a Dewar condenser above the column. Distillate is collected by a smaller Dewar condenser at the top left of the still.

Upon passing the liquid through an alumina column, the resistivity could change from 7.3×10^7 to 4.3×10^{10} Ω/cm, and is fully comparable to the observations made by Ferraci [8]. The filtration through alumina yielded a set of colored bands, the first being quite dark and indicative of the collection of suspended particulate matter, the second bright yellow, then tan, light purple or green, and finally lavender. The yellow material bleached upon acidifying, and it was removed from the alumina column after acidification and elution with ethanol. GLC study then showed the appearance of a peak whose retention time agreed precisely with that obtained by adding known amounts of o-nitrophenol with a detection limit of 0.08%. A rough estimate of the amount of the o-nitrophenol in the original sample was 0.06%. Under the conditions for gas chromatography, the other isomers of nitrophenol were not detectable; the particular volatility of the ortho-substituted nitrophenol is a result of hydrogen bonding that gives a ring chelate. Further, thin layer chromatography of the leached components from the yellow band indicated that a least two other contaminants were also present; one of these is m-nitrophenol and the other is fluorescent and has the lowest retention index of any contaminant from the alumina as examined by TLC.

The presence of o-nitrophenol is sufficiently spectacular that passing a small sample of nitrobenzene through a 6 mm column of alumina permits a microscale test, although it is probably not very specific. This is shown in figure 11 and 12. However, in the present case, we were able to show that the usually very effective nature of low temperature distillation, at least as far as water and benzene are concerned, is apparently not applicable for o-nitrophenol whose presence in various distillation fractions suggests a rather ubiquitous tendency to by-pass the usual rules for fractional volatilization. This result alone may imply the ineffectiveness of simple distillation in the purification of nitrobenzene for Kerr effect studies.

Figure 11. Activated alumina provides an excellent trap for acid and polar impurities in organic solvents. The intensely colored impurities that remain in 99.7+% pure material become obvious when a small liquid sample is passed through the tube.

Figure 12. Chromatograph column for removing contaminants from nitrobenzene. Colored zones on activated alumina (neutral) are visible in the extra column section at the base of the stand in the photo. This apparatus is the same as that in figure 11, but on a larger scale and therefore useful for preparative work.

6. CRYSTALLIZATION PROCESSES

A. Introduction

Estimating the purity of materials by use of cryoscopic behavior is now a well-established technique and no attempt will be made to list the voluminous amount of material which has been published on the subject. Basic principles involved in the estimation of purity by cryoscopy as employed in this laboratory have been described in detail by Glasgow, Streiff and Rossini [9]. Cryoscopy is the study of the change in temperature as a function of the change in ratio of the solid phase to the liquid phase in ideal or nearly ideal solutions. This laboratory employs two of the more commonly used cryoscopic techniques. The first is the time-temperature freezing method in which the solid-liquid ratio is determined as function of time. The second is the static method where an adiabatic calorimeter is used to determine the solid liquid ratio as a function of heat content of the material.

All of the cryoscopic methods are useful in obtaining precise and accurate values but they depend upon precise heat of fusion data for final purity computation from the cryoscopic measurements.

The thermometric method has been used at NBS for many years in estimating the purity of various materials in the range 99.0 to 99.999 mole percent. Recently construction of an adiabatic calorimeter has been undertaken and this instrument is now in the final stages of assembly and testing. It will be used to provide a further increase of capability in the field of thermal analysis.

Crystallization from the melt has been used for high temperature purification and, recently, it has been adapted for work at ordinary temperature. During the last year, this laboratory began a program of developing apparatus and conditions for the purification of molecular compounds. This work will eventually have an important complementary aspect to

freezing point measurements, and the initial progress in this direction is discussed as the last portion of this report.

B. Thermometric (Time-Temperature) Cryometry

The thermometric system used at NBS consists of a glass sample container with a noble metal reciprocating stirrer. The detecting and measuring portion of the system is a platinum resistance thermometer, a d-c resistance bridge, and an automatic temperature recording system made up of a high-gain direct current amplifier and a potentiometric recorder. The cryometric cell is described in detail by Glasgow and Tenenbaum [10], and the measuring system is described by Ross and Dixon [11].

The cell can be operated as a closed system, open to normal atmospheric conditions, or under controlled atmospheric conditions. Since the closed system is constructed of glass and noble metals, it is useful in determining the purity of many substances which are toxic, reactive with air, or hygroscopic. If normal atmospheric conditions can be tolerated, the open system is easier and faster to operate than the closed system. The general temperature range of the equipment will accommodate substances which freeze between 150°K and approximately 350°K. The amount of sample required for a determination is about 50ml. The time required to complete a single analysis varies from four to eight hours depending on the freezing temperature and whether open or closed system conditions are used. Figure 13 shows the time-temperature cryometer as it is normally operated.

The purity of highly purified samples of benzene, carbon tetrachloride, titanium tetrachloride, hydrogen chloride, dimethylphthalate, dichlorostyrene, isopropyl alcohol, and isomers of dichloroethylbenzene have been determined with this apparatus.

The equipment is presently being used to test the effectiveness of various purification techniques as applied to

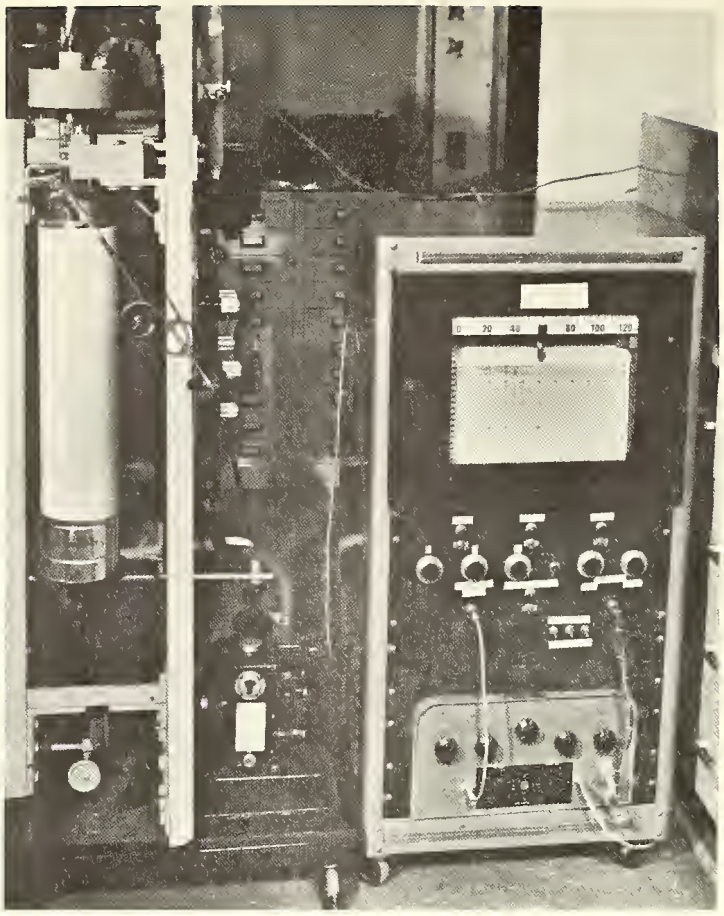


Figure 13. Thermometric Cryometer and equipment for recording time-temperature cooling and melting curves.

nitrobenzene and nitromethane. A concentrated effort has been undertaken to compare this colligative method of analysis with spectrophotometry. Nitrobenzene was chosen as one of the test materials. Six cryoscopic measurements of the starting material indicated 99.85 $\pm$ 0.08 mole per cent purity with the tolerance expressed as the standard deviation of the mean. After preliminary purification a corresponding value of 99.91 $\pm$ 0.03 mole per cent purity was measured. The purification of this material is discussed in the preceding section of this report, and the work is still in progress. The purity values of the presently available NBS standard reference materials of hydrocarbons were obtained by this method. Examples of more recent results and comparisions of this against the other cryoscopic techniques have been published [12,13].

C. Calorimetry

In order to meet modern demands, increasingly more sensitive methods must be applied to obtain precise and accurate estimations of the purity of materials. Adiabatic calorimetry is the most sophisticated method for determining total purity of a substance by physical analysis. In addition to being a powerful analytical tool, the calorimeter plays an important role in the assimilation of physical constants and properties of the measured research materials. Since apparatus of this type is normally not commercially available, a program was initiated to design and construct a high-precision adiabatic calorimeter with special emphasis directed to extending the capabilities of the Division in evaluating the purity of materials. In general, the reliability of this type of apparatus is determined by its ability to ascertain true equilibrium temperatures and maintain precise adiabatic conditions. Accordingly, much effort has been devoted to the design and the construction of a sample container to achieve thermal equilibrium conditions. Fully automatic temperature control units are employed to obtain precise adiabatic control.

Figure 14 is a cross-section sketch of the calorimeter construction. The sample container, valves and filling assembly are made of platinum, iridium, and gold to minimize heat transfer problems and to provide a surface which is inert to a broad range of materials. Perforated disc-type vanes of platinum are horizontally attached to a central re-entrant well to help prevent segregation of impurity during analysis. The sample container is suspended in the calorimeter by a thin-walled platinum tube containing a needle valve to allow sealing of the sample container. This prevents vaporization of material into the filling tube during analysis. The central re-entrant well contains a platinum resistance thermometer and a non-inductive wire heater.

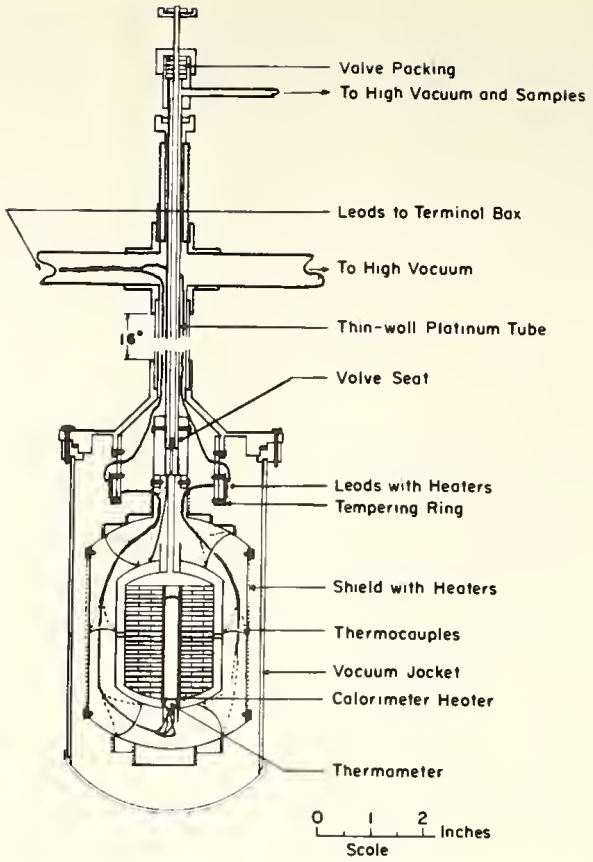


Figure 14. Adiabatic calorimeter for volatile materials.

A copper shield surrounds the sample container. Electronic equipment controls the shield heaters so that the temperature can be automatically maintained the same as that of the sample container. Thermocouples between the shield and the sample container control operations of the electronic equipment. The space surrounding the shield and sample container is maintained at a pressure of approximately 10^{-6} torr.

The temperature control units operate from an amplified signal to an indication potentiometric recorder with a control setting device. A control unit which automatically produces an output current proportional to the input requirements of the precess completes the system. Direct current is used to avoid electronic interference that is normally associated with the use of alternating current. The temperature of the sample

is measured with a platinum resistance thermometer and a Mueller G-3 bridge. Electrical input energy is determined from measurements taken with a six-dial, triple range potentiometer which provides precise measurements of voltages between the limits of zero and 1.6 volts. The time interval of heating is obtained by using NBS standard time frequencies and a gated electronic counter. The rise of the electrical input signal at the beginning of the heating interval starts the counter and the fall of the signal at the end of the interval stops the counter. A highly sensitive microvoltmeter is used as the detector for the bridge and potentiometer. A low pass filter is used to eliminate line interference to the detector from rectified d-c sources used to supply power to the main and shield heaters.

The calorimeter is mounted in a stationary position and is limited to the assaying of materials which can be introduced and removed by distillation. The temperature range of the system was designed for determining purity of materials which melt from 90°K to approximately 375°K.

Three days to one week are required for the completion of a single analysis. Approximately 50ml of sample is required, but the method is non-destructive and the material can be reclaimed. All the data needed for a purity determination can be obtained from one experiment.

Construction of the apparatus has been completed and some preliminary tests have been made. Modifications and adjustments are being made as indicated by the performance and calibration tests.

Since actual analyses have not yet been made with this equipment, the precision and accuracy limits are not yet known. However, it is anticipated that subsequent work will show improvement in methods for estimating impurities in the parts per million range.

D. Purification by Zone Refining

Since the invention of the transistor, zone melting techniques have been employed in the preparation of extremely pure semiconductor and metallurgical materials. More recently, this technique has been applied as a purification process for organic chemicals. The number of publications on this subject are numerous, and for complete coverage of the subject one should consult the works of Pfann [14], Schildknecht [15], and Herington [16]. Basically, zone refining involves the passing of a series of molten zones in one direction through a frozen segment of material. Depending on whether the impurities lower or raise the melting point of the material, they will be rejected by the freezing solid and concentrated in the liquid or they will be rejected by the liquid and concentrate in the solid. In either case, they will usually tend to concentrate at one end of the segment.

Our major interest in zone refining is aimed at the study of extreme purification as a controllable process. The method is equally important as a pre-concentration step for determining trace impurities.

During the last year we have begun to establish a capability for the zone refining of fragile compounds, including substances whose melting points are between room temperature and -50°C. Our approach to low temperature zone refining has been to apply conventional methods and reduce the temperature of the atmosphere around the apparatus. In this modern age of refrigeration equipment, low temperature lubricants, and machines, no major difficulty has been experienced so far.

Some early and very crude experiments were undertaken to determine feasibility and to gain some insight in the problems expected. The first work was done on the purification of nitrobenzene (M.P. 5.9°C.). The apparatus was assembled from spare laboratory parts using one motor to rotate the tube at about 30 RPM and a clock motor to pull a resistance heating wire at

the rate of 2.5 cm per hour. The diameter of the glass tube was 1.2 cm and the melted zone was kept at approximately the same width. The complete apparatus was placed in a freezer chest at -20°C. The chart (figure 15) shows the results of chromatographic analysis for traces of benzene as a function of tube length after 50 zone passes. Even though the conditions were very crude for this experiment the results have been especially instructive in planning our future purification efforts.

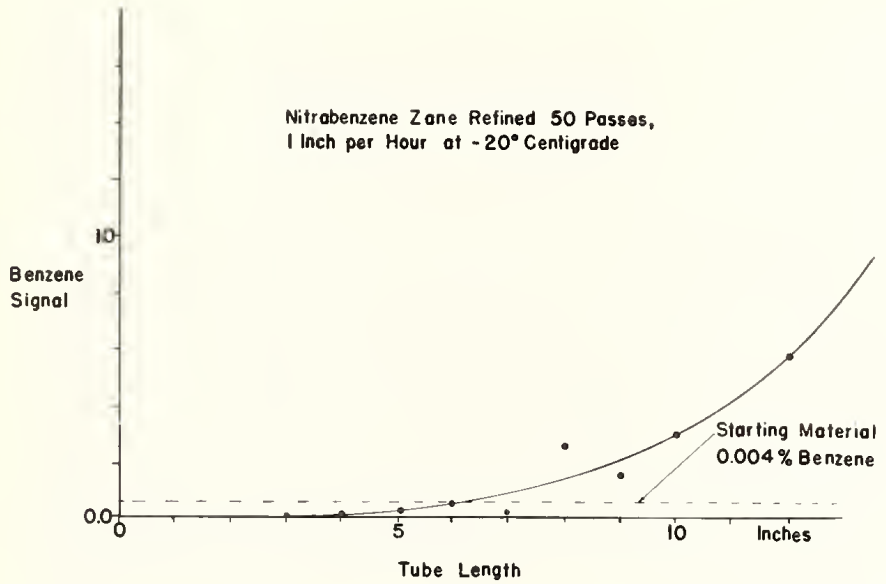


Figure 15. Concentration of benzene in nitrobenzene after 50 passes of a single zone.

We have also acquired equipment for purifying by multiple zone refining. This unit employs alternate heating and cooling. Second, a piece of equipment (figure 16) of our own design will accommodate three tubes simultaneously, each with approximately 100cc initial charge. A third commercially available piece of equipment will take an initial charge of at least 300cc and is designed to operate at -25°C.

Zone refining for the purification of organic material is well established in the literature and preliminary tests have convinced us that the techniques deserve much more attention and adaptation to the problems of modern analytical chemistry.

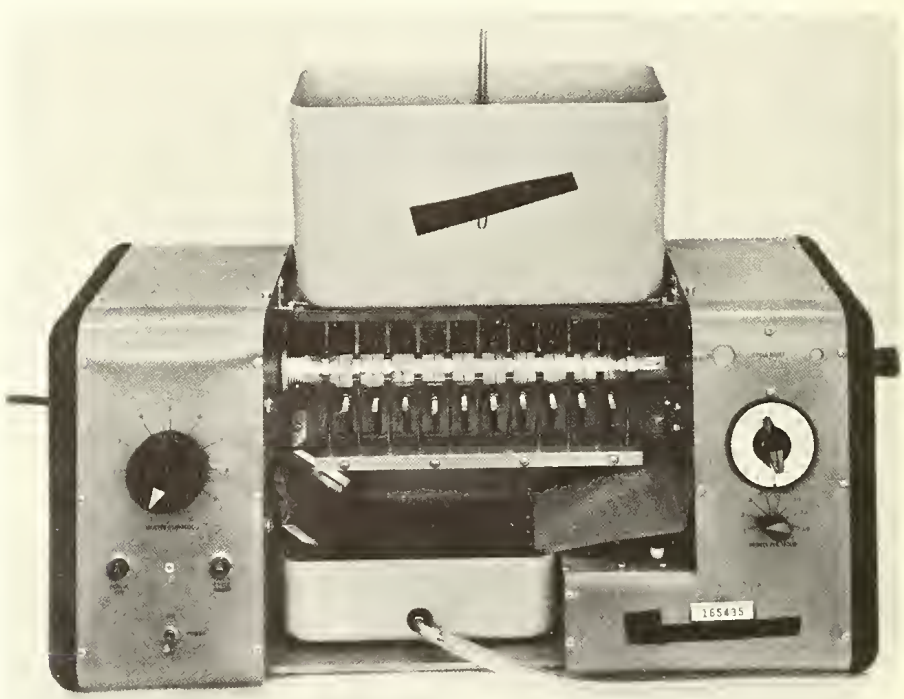


Figure 16. Multiple zone apparatus used for the purification of organic materials.

7. PERSONNEL AND ACTIVITIES

A. Personnel Listing

Separation and Purification Section

David H. Freeman, Section Chief
Ellen L. Matthews, Secretary

Ion Exchange

William C. McCauley - Summer student, 1967
Walter F. Rittner
Gabriella Schmuckler - On Sabbatical leave from the Technion - Israel Institute of Technology, Haifa, Israel

Ultra Pure Reagents

Delmo P. Enagonio
Edwin C. Kuehner

Pure Materials

Robert T. Leslie
Charles B. Romain

Crystallization

Herbert D. Dixon

B. Publications

1. D. H. Freeman, Precise Studies of Ion-Exchange Systems Using Microscopy, (Chapter 5) in "Ion Exchange", Volume I, J. A. Marinsky, Editor, Marcel Dekker, Inc., (New York, 1966).

2. D. H. Freeman, A. S. Aiyar, Studies of Ion Exchange Materials: Homogeneous Fractional Sulfonation of Copolymers of Styrene and Divinylbenzene, Anal. Chem. 39, 1141-1144 (August 1967).

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C. Talks

1. D. H. Freeman, "Studies of Ion Exchange Materials: Homogeneous Fractional Sulfonation of Copolymers of Styrene and Divinylbenzene", Division of Analytical Chemistry of the American Chemical Society, Miami Beach, Florida. April 10, 1967.

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