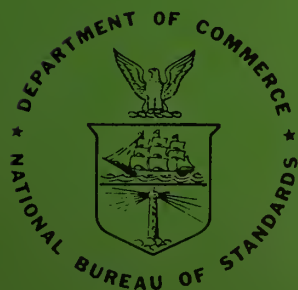**NBS** TECHNICAL NOTE

459

# Separation and Purification Section:

## Summary of Activities
## July 1967 to June 1968

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards

# NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards[1] was established by an act of Congress March 3, 1901. Today, in addition to serving as the Nation's central measurement laboratory, the Bureau is a principal focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. To this end the Bureau conducts research and provides central national services in three broad program areas and provides central national services in a fourth. These are: (1) basic measurements and standards, (2) materials measurements and standards, (3) technological measurements and standards, and (4) transfer of technology.

The Bureau comprises the Institute for Basic Standards, the Institute for Materials Research, the Institute for Applied Technology, and the Center for Radiation Research.

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> Building Research—Electronic Instrumentation — Technical Analysis — Product Evaluation—Invention and Innovation— Weights and Measures — Engineering Standards—Vehicle Systems Research.

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> Reactor Radiation—Linac Radiation—Applied Radiation—Nuclear Radiation.

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[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D. C. 20234.
[2] Located at Boulder, Colorado 80302.
[3] Located at 5285 Port Royal Road, Springfield, Virginia 22151.

# NBS ◆ TECHNICAL NOTE 459

## Separation and Purification Section:

### Summary of Activities
### July 1967 to June 1968

Edited by David H. Freeman

Separation and Purification Section
Analytical Chemistry Division
Institute for Materials Research

# 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 tech-
nical personnel encompassing some 57 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 aware-
ness 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 consider-
able 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
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 abbreviated form.

At the National Bureau of Standards publications such as these fit logically into the category of a Technical Note. In 1968 we plan to issue these summaries for all of our sections. The following is the second annual report on progress of the Separation and Purification Section.


W. Wayne Meinke, Chief
Analytical Chemistry Division

# PREFACE

The Separation and Purification Section has completed its second year of formal existence.  The lines of development have been partly in sequel to those started the first year, and partly the product of the unpredictable.  The most dramatic, and possibly the most simple, of the undertakings demonstrated that laser light scattering is elegant in its ability to provide a highly sensitive measurement of trace particle contamination.  The most extensive activity has pivoted around the fundamental development of understanding of ion exchange resin structure.  The output of practical or technological usefulness has been ample.

An important shaping factor of the Section's enthusiasms and responsibilities has been the needs of the Office of Standard Reference Materials.  The needs of materials science, which are documented by asserted requirements and proposals for standards, have grown more complicated and more difficult.  An outstanding example is the development of meaningfully characterized samples of highly purified organic chemical substances that are useful as clinical measurement standards.  Nowhere is there a satisfactory wholeness of approach to this sort of task.  The trace characterization of labile organic compounds needs fundamental and developmental work.  In a different area, it is apparent that organic matrices may have an extremely important role to play as carriers for precisely known and very small quantities of matter.  The first efforts in this direction involve single ion exchange resin beads as microstandards, and the results are promising.

The Section's facilities include a growing array of various types of gas chromatographs, an extensive assortment of analytical distillation apparatus, a low temperature laboratory, plus various measuring instruments, and hardware for electronic computation.  The microscopy laboratory has

reached a state of advanced versatility for particle examination under a wide variety of available optical conditions. An electron microscope has been added very recently. While such units may appear as disconnected bits and pieces, the individual cooperative effect can be impressive. To illustrate, the low temperature laboratory has proved to be far more helpful than when we first decided to prepare the facility. Similarly, our infrared spectrophotometer surged from routine role into one of focal importance to everything that we are doing with ion exchange materials.

The formal structure of the Section activities has developed with recognizable program lines. The largest efforts are given to the characterization of ion exchange resin, which is one important example of materials used as a discriminating phase for chemical separations. The result is that the control of resin composition and network characterization are seen to be moving on improved and valuable paths of dependability. Our capabilities for gas chromatography have evolved from a first stage of cumbersomeness into the middle ranks of efficient and flexible competence. The impact of analytical gas chromatography upon several purification efforts was encouraging. The interest in evolving competence in ultrapure reagents, stimulated by the laser study, has also attained routine dependability to those trace analysts who use this facility. Several castings about have been made in the attempt to find an area where container problems can be attacked fruitfully.

In sum, the second year of operation of the Section has been productive. There is a basis for even more optimism as new avenues of attack are made in the separation and purification fields. The organizational structure of the work is embodied in the subject outlines used in the presentation made in the following pages.

In order to specify adequately the procedures, it has been necessary occasionally to identify commercial materials

and equipment in this report.  In no case does such identi-
fication 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 Mrs. Rosemary Maddock in the prepara-
tion of this report is gratefully acknowledged.

David H. Freeman, Chief
Separation and Purification Section

# TABLE OF CONTENTS

# TABLE OF CONTENTS (Con't)

## LIST OF TABLES

## LIST OF FIGURES

ix

LIST OF FIGURES (Con't)

# SEPARATION AND PURIFICATION SECTION:   SUMMARY OF ACTIVITIES
## JULY 1967 to JUNE 1968

Edited by David H. Freeman

## ABSTRACT

The research activities of the Separation and Purification
Section are described, including their significance to the
program of the Office of Standard Reference Materials.  The
work involves basic developments to characterize ion exchange
resins using infrared spectrophotometry, stoichiometric analysis
of resin structure, and the study of chain scission.  The
availability of spherical particles of homogeneous ion exchange
resin has been exploited with the recently developed micro-
standards.  Analytical gas chromatography has been developed
with emphasis given to the specialized needs of measuring trace
contaminants in purified organic compounds including divinyl-
benzene, EDTA, and clinical standards such as uric acid and
urea.  Purification capabilities involving the use of crystalli-
zation, analytical distillation, and of the newly installed low
temperature (-30°C) laboratory are described.  The activities
of the ultra-pure reagents project, including work on the
laser light scattering measurement of traces of liquid borne
particulate matter, on reagent preparation, and methods of
reagent storage are described.


Key words:  analytical distillation, crystallization, clinical
standards, divinylbenzene, EDTA, ion exchange resins, micro-
standards, particulate matter, reagents, resin structure,
ultra-pure reagents, urea, uric acid.

# 1.  ION EXCHANGE

## A.  Introduction

Ion exchange resins are among the most versatile and use-
ful materials known to chemistry.  Their wide scope of applica-
tion includes the capability for removing salts from water,
the conversion of a compound into a different salt form by ex-
changing either a positive or a negative ion, the isolation of
electrolytes, the separation of amino acids, or of various
families of closely related elements, and their major role in
water processing, including water "softening".

In recent years, there has been little work to improve
the state of the art of understanding or controlling resin
structure.  Most efforts are aimed at improved applications,
and few are aimed at improved understanding.  In this report
we will describe our own interest in improving the means for
characterizing these materials.

Scientific research is not always expected to provide
directly useful results.  In the past year, however, we were
able to show that there is a new and exciting future role for
ion exchange resins which will be described in this report.
In essence, it has to do with the new capability of single
resin beads to perform as microstandards.  While the subject
is still in its infancy, it is already obvious that exciting
new applications of ion exchange materials are just around
the corner.

The ion exchange program at the NBS has three com-
ponents:  synthesis, structure, and metrology.  This triad
is focussed upon improved characterization, control and
application of the basic resin structure, with emphasis
given to the microstandards aspect.  While the use of ion
exchange has in the past cut across much of chemistry,
engineering, and medicine, it is now clear that the metrolog-
ical aspects of ion exchange can be expected to develop into
broad new roles that are of basic scientific significance.

## B. Ion Exchange Resin Homogeneity

Ion exchange resins in the present discussion are formed as derivatives of copolymers of styrene and divinylbenzene. The network structure of the copolymer, or of the resin, is one of statistical isotropy if the synthesis is properly carried out. To illustrate what that means, consider the contrast between the usual liquid and crystalline solid states. In the crystalline solid there is a high degree of repeated order that tends to be stationary with time. In the liquid state, there is molecular motion and a time average of uniform disorder. The resin network structure is closer to the liquid state; it is uniformly disordered, but it is also stationary with time.

The simpliest criterion for homogeneity is that the copolymer exhibit bead-to-bead constancy. Walton and Suryaraman [1] have shown that the Linderstrom-Lang technique is suitable for use with ion exchange resin. The result of using a vertical density gradient axis of glycerol solution is shown in figure 1; the narrow stratification of the copolymer beads is a direct indication of the precise constancy of the density of the beads.
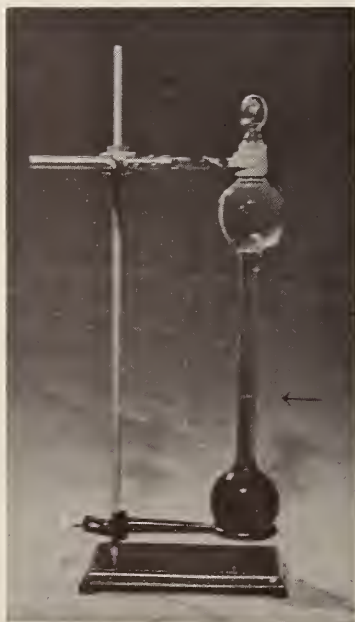


Figure 1.   Spherical copolymer beads suspended
in density gradient column.

The test for homogeneity with ion exchange beads can be done with considerable sensitivity. With relatively large beads having diameters above 300 micrometers (a micrometer equals $10^{-4}$ cm), we have previously reported procedures for measuring the ion content after neutron activation [2] where the bead diameter was measured with the bead immersed in an inert hydrocarbon fluid. These particular results are indicated at the right portion of figure 2. The rest of the measurements were done while the



$$\delta = \frac{W_{meas.} - \rho^* \pi d^3/6}{W_{meas.}}$$

MEASURED WEIGHT OF SODIUM (GRAMS)
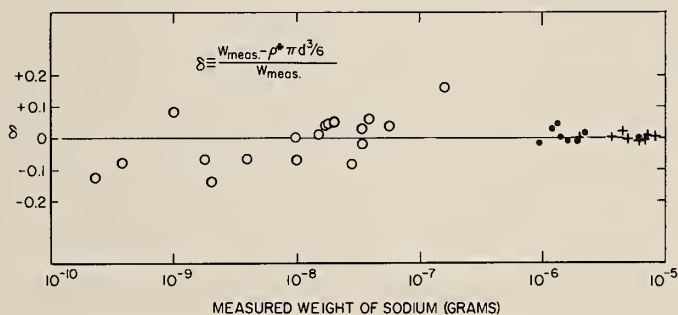
Figure 2.   Activation analysis of single ion
exchange beads plotted to show bead
capacity departures from a constant
value.  The measurements at the left
are affected by inconsistencies in
resin moisture content.

beads were exposed to the laboratory atmosphere, and there is a loss of precision. However, it is obvious that bead-to-bead exchange site concentration is approximately constant over a much wider range than has previously been recorded, and there is also considerable likelihood that marked improvement in measurement precision is possible. These latter measurements are a part of the recently reported [3] capability of ion exchange beads to act as microstandards.

C.  Molecular Structure of Ion Exchange Resin
    1.  Introduction
    Four approaches to the molecular structure of ion exchange resin are being made. The first involves the relationship between resin composition and the implied stoichiometry of the

3

resin network.  The second is a study of the precisely homo-
geneous formation of copolymer derivatives, with special atten-
tion given to sulfonation.  The third involves the use of spec-
troscopy to observe the structure; here we will discuss our
recent efforts with infrared absorption spectrophotometry.  The
fourth is the use of scission reactions which may have a funda-
mental capability of extracting structural information from a
network in which the information may not otherwise be observed.

    2.   <u>Stoichiometry</u>

    It is common practice to measure the exchange capability
of a resin sample

$$C = \text{milliequivalents/gram}$$

where the number of equivalents of exchangeable ion are
measured in one way or another by ion exchange displacement
reaction.  It is a simple matter to convert this into the ion
exchange equivalent weight

$$E = \frac{1000}{C}$$

where the subscripts refer the equivalent weight to that of
the network (N) and the counterion (C), the latter being
simply the formula weight of the ion divided by the electro-
static charge on the ion.  The former quantity can be calcu-
lated from the first principles of the network synthesis and
is therefore a fundamental guide to the resin composition.

    The combination of styrene and divinylbenzene during
copolymerization can be carried out with a known mole fraction
(X) of the latter and (1 - X) of the former.  Using brackets
to refer to formula weight, the aromatic equivalent weight
can be defined:

$$E_C = (1-x)[STY] + x[DVB] \tag{1}$$

The formation of cation exchange resin is usually followed by
sulfonation in which each aromatic ring can, in the ideal case,
receive exactly one sulfonate group:

$$\text{(2)}$$
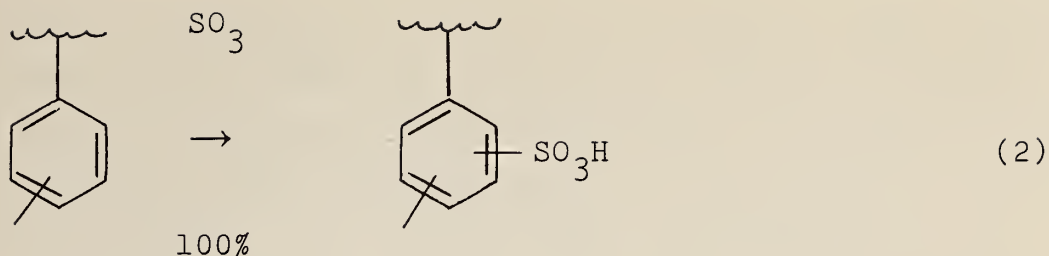
It follows for this model that monosulfonated copolymer should have a network equivalent weight

$$E_{SH} = E_C + [SO_3] \tag{3}$$

Note that $E_{SH}$ refers to the hydrogen form resin and, it follows in this instance that

$$E_N = E_{SH} - [H]$$

This provides the stoichiometric framework for evaluating the composition of any ion exchange resin. For example the weight fraction (f) of sulfur in dry sodium form cation exchange resin has the predicted value:

$$f = \frac{[S]}{E_{SH} - [H] + [Na]} \tag{4}$$

This relationship, and those like it, are readily subject to experimental test. A report on these measurements is expected to be forthcoming from work that is already in progress.

3. <u>Chemical Derivatives of the Copolymer</u>

Normally, chemical reactions are conducted in the gas or in the liquid phase so that there is ample opportunity for mixing. The chemistry of the copolymer network is complicated by the requirement that any reactant or diffusible product is involved in two processes: diffusion and reaction. The situation can be very complicated.

One test for adequacy of a structural reaction in the net-work is to search for the possible birefringence of the product. If marked birefringence is observed, that indicates mechanical

strain.  While studying the use of nitrobenzene as a solvent for sulfonation, we recorded a finding of unusually poor conditions for this reaction.  The results of the agony of a single bead which has been exposed to bad synthetic conditions are depicted by the photomicrographs shown in figure 3.  The results are



Figure 3.    Solvent stressed ion exchange bead (a) disgorging its interior during sulfonation, (b) after disgorgement and (c) a piece of the expelled interior.

explained as follows.  The procedure calls for preswelling by the solvent, but this has been incomplete.  As the sulfonating agent penetrates the network, the process of sulfonation causes network contraction and apparently enormous forces are exerted at the interface between swollen exterior and unswollen copolymer core.  The result of the contractive shearing action is the expulsion of the core, as shown in the photomicrograph.

Experiments are now in progress to determine the implications of various possible swelling conditions.  The results to date include the use of methylene chloride as a network expanding solvent, and the addition of nitromethane because of its ability to swell the resin.  In a 1:1 mixture of these two solvents, the addition of oleum leads to 90% of complete sulfonation within one hour of exposure for a network with $X = 0.08$.  These conditions are not as good as we had hoped. It appears that sulfonation with oleum may tend to be accompanied by sulfone bridging.  However, the point remains that

the relationship between the solvent and the nature of the
reaction is an important aspect of network chemistry and the
attempts to exert improved solvent control are being continued.

4.   Infrared Spectrophotometry

When irradiated with infrared light it is possible for
an organic matrix to absorb some of the radiant energy which
is then converted into increased vibrational energy. The
observation of IR absorption at particular frequencies can
often be interpreted in terms of a particular structure whose
vibrational modes become known.

The present uses of infrared spectrophotometry are illus-
trated as follows.  In figure 4 is shown the absorption spec-
trum for styrene, and in figure 5 is shown for meta divinyl-
benzene.  Both molecules have vinyl groups.  In figure 6 is
shown the spectrum for a copolymer formed with 0.08 mole
fraction of commercial divinylbenzene.  It should be noted
that the vinylic character is absent.  This is, of course,
expected, since the copolymerization involves the formation of
a hydrocarbon backbone.  This occurs with a corresponding loss
of vinylic character of the reactants.

In the copolymer, we find that disubstituted benzene
compounds exhibit strong ring C-H out-of-plane vibrations in
the region between 720 $cm^{-1}$ and 850 $cm^{-1}$.  In figure 6, for
example, the meta isomer vibration for divinylbenzene is
evident at 805 $cm^{-1}$, and the corresponding para vibration is
obscured at 845 $cm^{-1}$.  It is apparent that infrared spectros-
copy provides a convenient and sensitive approach to determine
isomeric purity for either position isomer.  To illustrate,
the polymerization of the vinyl group (to form a substituted
hydrocarbon matrix is detectable using the -$CH_2$- deformation
vibration at 1450 $cm^{-1}$.  This wavelength is notable because it
tends to be vacant with a sample of pure monomer.

The infrared spectrum of ion exchange resin beads has
been implied in a related study by Zundel [4] on sulfonated
membrane films.  With small ion exchange resin beads there

7
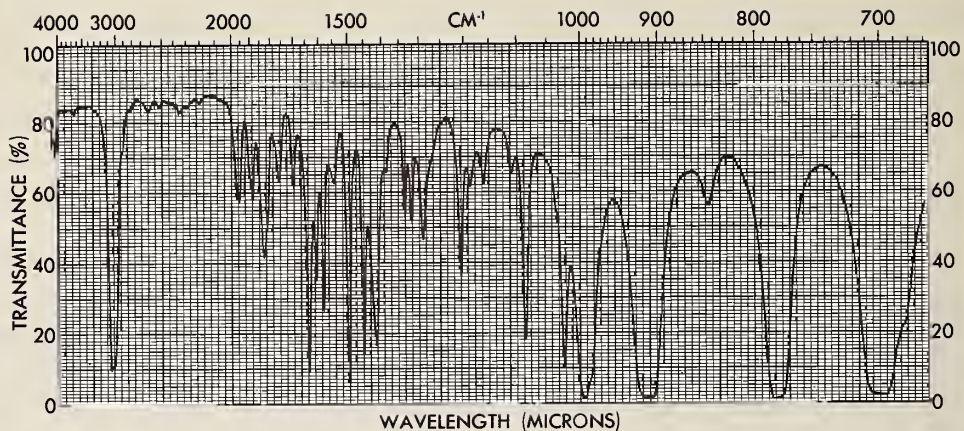
Figure 4.   Infrared spectrum of styrene monomer liquid.
Vinyl group absorptions are specifically
indicated at 910 and 990 cm$^{-1}$.
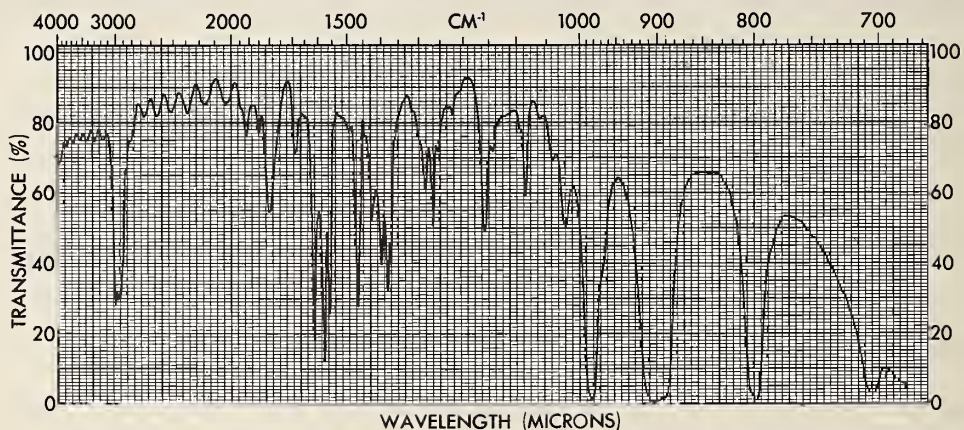


Figure 5.   Infrared spectrum of meta-divinylbenzene showing
vinylic character at 905 and 980 cm$^{-1}$.
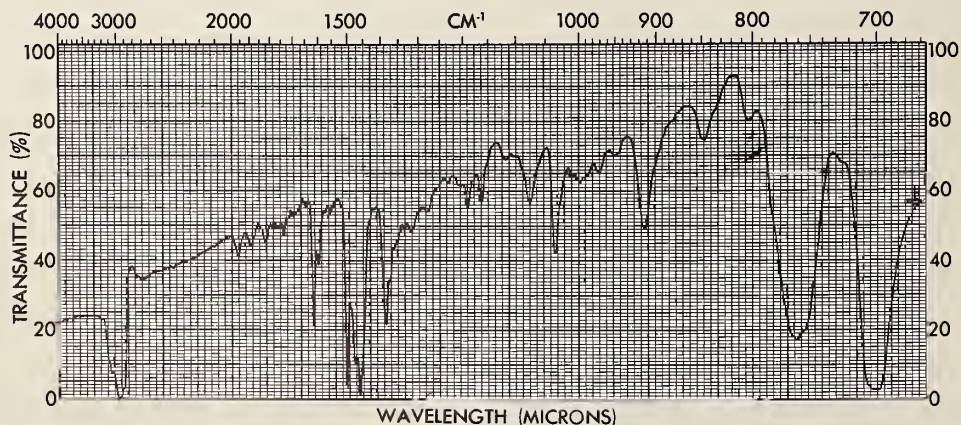


Figure 6.   Infrared spectrum of commercial copolymer of
styrene and divinylbenzene (nominal 8%).

8

is no difficulty in preparing samples for IR analysis. An
example of the resin spectrum is shown in figures 7 and 8.
The band assignments are shown in table 1.

While this work is being continued, we have been encour-
aged by the potential of these methods for describing local-
ized molecular structure in a copolymer, or in an ion exchange
resin. One of the problems in improving the synthesis of co-
polymer is the controlled use of pure divinylbenzene. In this
instance, we were able to find that para divinylbenzene is
readily distinguished from two types of contaminants; meta
divinylbenzene and polymerized meta or para divinylbenzene.
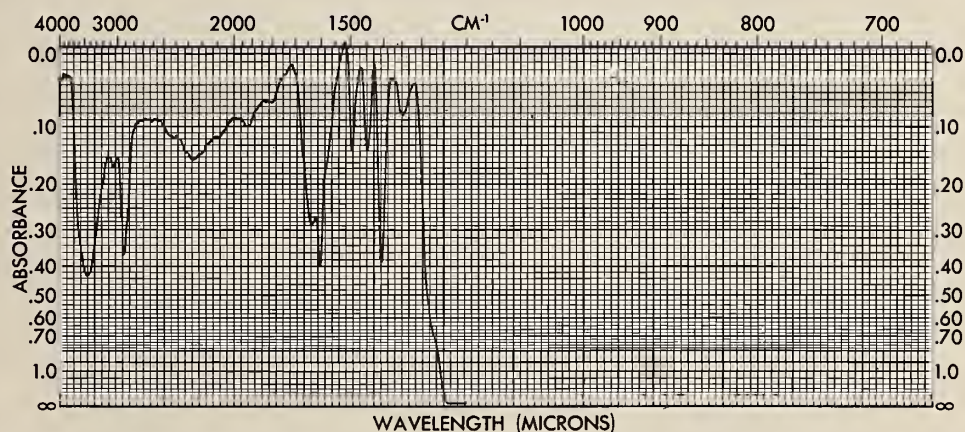
Figure 7. Infrared spectrum of cesium form of sulfonated
8% DVB, nominal, copolymer (Halocarbonoil).
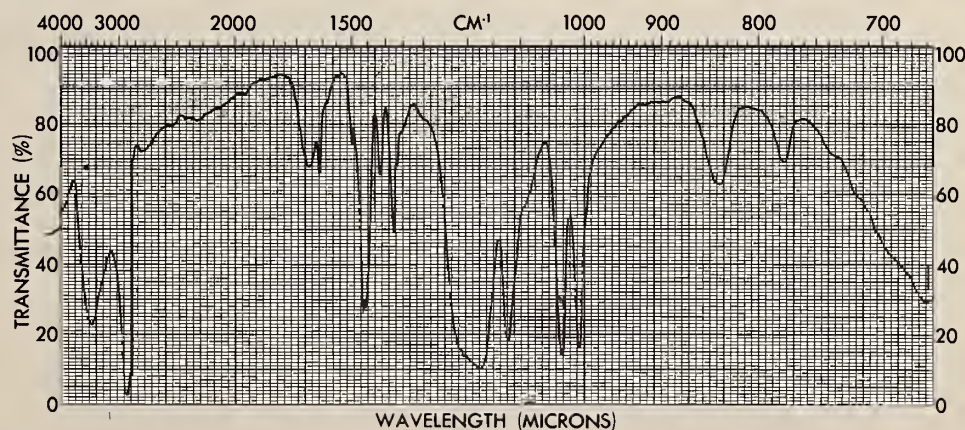
Figure 8. Infrared spectrum of cesium form of sulfonated
8% DVB, nominal, copolymer (Nujol).

9

Table 1. Band assignments ($cm^{-1}$) of sulphonated copolymer.

| | |
|---|---|
| 3450 | OH – valence vibration of $H_2O$ in resin phase |
| 3040 | C–H – valence vibration of aromatic hydrogen |
| 2930 | Symmetric and antisymmetric valence vibration of the $C-H_2$ group |
| 1640 | $H_2O$ deformation |
| 1610 | Aromatic ring quadrant stretch |
| 1490 | Semicircle stretch |
| 1450 | $C-H_2$ deformation |
| 1408 | Semicircle stretch |
| 1333 | $SO_2$ antisymmetric vibration |
| 1175 | Antisymmetric valence vibration of $O\!\!-\!\!S\!\!-\!\!O$ group (O above and below) |
| 1111 | In-plane aromatic hydrogen bend |
| 1030 | Symmetric valence vibration of $O\!\!-\!\!S\!\!-\!\!O$ group (O above and below) |
| 1005 | In-plane aromatic hydrogen bend |
| 833 | Out-of-plane aromatic hydrogen bending for para substitution |
| 775 | Out-of-plane aromatic hydrogen bending for ortho substitution |
| 671 | C–S valence vibration |

## 5. Peroxide Scission of Ion Exchange Resin

In 1957, Hookway and Shelton [5] described the degradation of cation exchange resin by 3% hydrogen peroxide. We have established that the peroxide attack depends upon the presence of a catalyst, and ring opening may or may not occur depending upon chemical conditions. In 3% hydrogen peroxide with catalyst and with temperature in excess of 65°C we find:



$$\xrightarrow[\text{cat.}]{H_2O_2} \quad CO_2 + HSO_4^- + H_2O \tag{5}$$
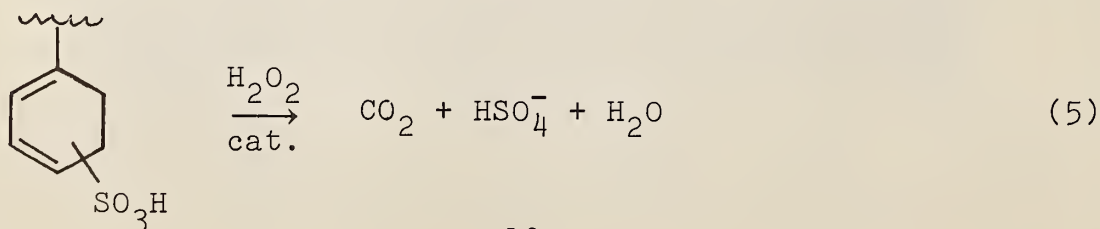
The reaction is altered by threefold dilution of the hydrogen peroxide: in that case, no sulfate is formed before complete dissolution of the resin has taken place, and it may be that aromatic ring opening is impeded up to, and possibly beyond, that point.

The progress of the scission reaction may be followed through observation of increased resin swelling. The swollen volume of a sample of ion exchange resin is a measure of the limiting steric extendability and if scission occurs, this limit is necessarily increased. Following an empirical tactic stated by Boyd and Soldano [6] we have the relationship:

$$q-1 = \frac{k}{X} \tag{6}$$

where q is swelling ratio (q = V(swollen/V(unswollen))), and X is the molar crosslinking. On this basis we have measured the variation in "X" with time of exposure of resin to 2% hydrogen peroxide solution. The results are shown in figure 9.
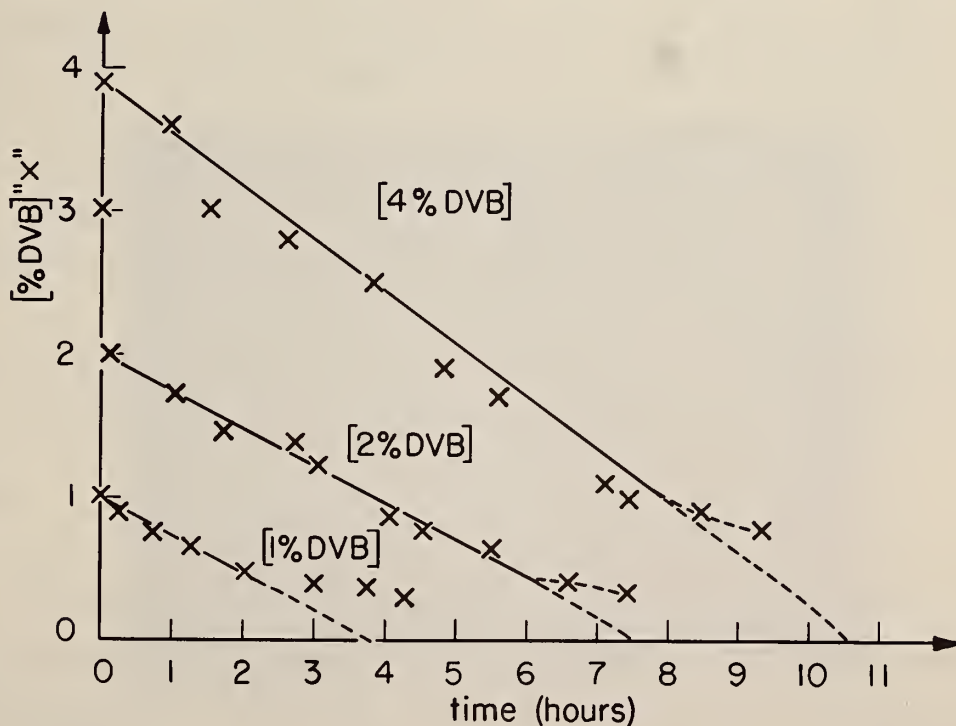


Figure 9. Decrease of "X" during exposure of sulphonated copolymers to 2% of $H_2O_2$ at 65 °C.

11

At the point of dissolution of the resin, network segments may exist in varying degrees of complexity. When random scission continues to occur, their molecular weights must decrease.

The scission reaction offers several opportunities for interest. The controlled chemical dissection of this kind of network, if properly done, should carry information to reflect upon the original network structure. To illustrate, the effective change $\Delta X/X = 0.2$, implying loss of 20% of the apparent crosslinking, is evidently just sufficient to cause total network dissolution. That quantity must be a product of the mechanism of the scission, and the structure that is being cut; it is obvious that an understanding of the former should have an important bearing upon the nature of the latter.

D.   Chemical Microstandards

1.   Introduction

Ion exchange resin beads have an important capability for holding an exact quantity of matter [3] as dictated by the law of electroneutrality. The amount of matter that is calculated to be present on a single bead depends upon two assumptions, both of which are subject to precise test. First, the concentration of the exchange sites is taken to be a physical constant of the material; that depends upon the exact achievement of homogeneous site distribution during the resin synthesis. Second, because the beads are extremely spherical, the amount of matter is related to the bead diameter.

Consider that all of the exchange sites on a single resin bead are saturated with a single type of chemical element. Then:

$$m = \rho f v \tag{7}$$

where $\rho$ is density, $f$ is weight fraction of the particular element, and $v$ is $\pi d^3/6$, the bead volume. Since diameter can be measured accurately under the microscope, it is possible to use microscopy as a weighing tool. In this way, extremely small quantities of matter are fixed into a round container, and their amount is related to the measured container diameter.

12

The range of single ion exchange bead capacity is indicated in figure 14 by a nomograph which varies the bead diameter from one to one thousandth of one millimeter. The fractional loading is taken as the product $\rho f$ and this is usually somewhat less than unity. The range of counterion mass is thus seen to extend to quantities much smaller than a nanogram ($10^{-9}$ gram).

One aspect of ion exchange resins that is not widely known to the casual user is the remarkable sphericity of these beads. This is a result of the conditions of synthesis in which the formation of copolymer is carried out as a droplet suspended in a liquid in which the droplet is immiscible. A surface free energy minimum is required and the corresponding minimum surface geometry is that of a sphere. We have recently obtained an electron microscope to perform a variety of tasks, and one of the first of these was to show that this sphericity extends to even the smallest of resin particles that can be made synthetically. This is shown by the electron micrograph shown in figure 10, where it is fully evident that this micrometer resin bead is indistinguishable from a spherical shape and, hence, can be measured meaningfully for its diameter.
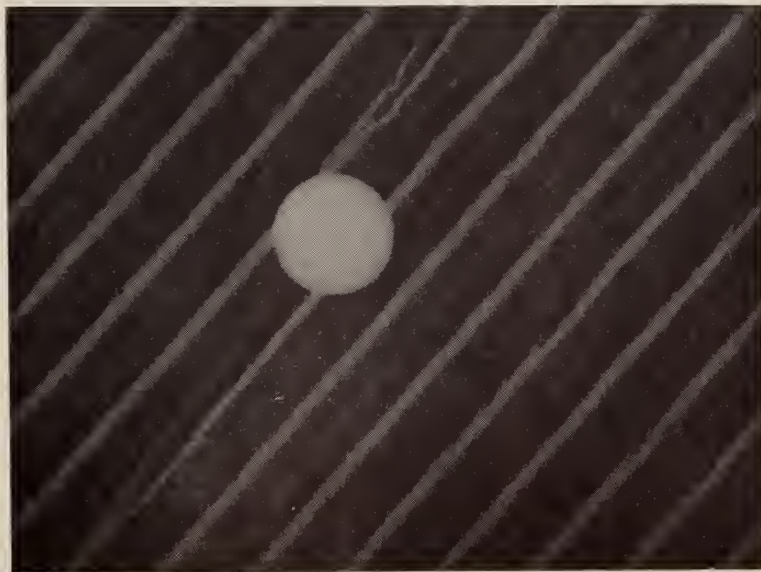


Figure 10. Electron micrograph of 1.3 micrometer copolymer bead indicates high degree of sphericity of very small resin particles.

13

## 2. Preparation

The usefulness of the foregoing concepts is of direct
significance to the growing needs of science to operate effec-
tively with smaller and smaller quantities of matter.  Highly
sensitive analytical instrumentation is dependent upon standards
which can be used effectively to set detection limits, and to
perform calibration.  There are vast areas in which the avail-
ability of microchemical standards will become useful.

The methods of preparing ion exchange beads saturated with a
particular element are well known.  Then, for microstandards,
it should be obvious that ion exchange must be rigorously
prevented.  Careful washing, rinsing and drying procedure is
needed, and highly purified solvents are essential.  After
drying, bead clusters are broken up and, in the presence of
a pure inert solvent, the beads can be cast onto a slide, as
shown in figure 11.  One difficulty is that the larger beads
tend to fall off.  For the electron microprobe we have found it
useful to embed the beads in a film of polyisobutylene; in this
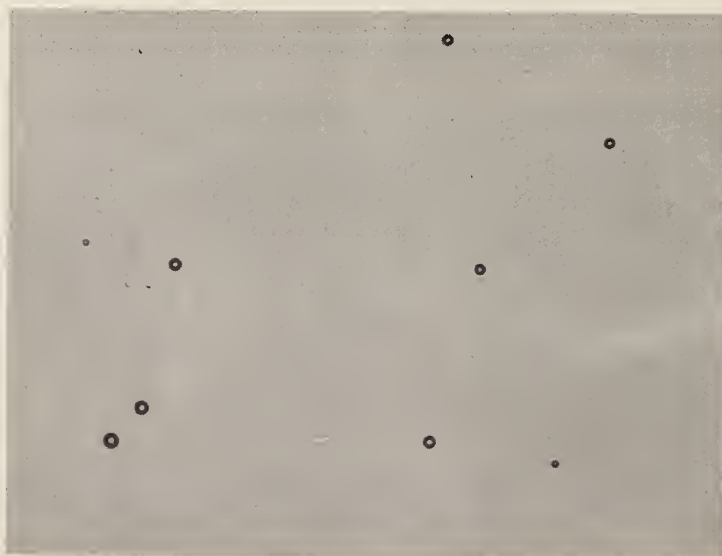


Figure 11.   A two-dimensional dispersion technique
is used to isolate single microstandard
ion exchange beads:  nine such beads
are visible in this photomicrograph.
(125 X)

way the beads do not move appreciably, even when they are extensively irradiated with the electron beam.

The use of a microstandard for calibration depends upon suitable technique. The measurement of diameter and the transfer of a single bead to a desired location can be done with the illustrated in figure 12. The results of activation analysis experiments provide a test of equation (7), as shown earlier in figure 2. It is evident that the results exhibit scatter in the vicinity of ten percent. There is good reason to expect that the precision can be improved, and efforts are now underway to provide sharpened control.



Figure 12. Microscope and micromanipulator are used in the processes of measurement of individual microstandard beads, and for transpositioning to the apparatus requiring calibration.

15

### 3. Range of Usefulness

Ion exchange resins can be saturated with any ion that is suitably stable in an appropriate polar solvent. That applies to most of the periodic table, as shown in figure 13. Positively charged ions (cations) must be placed onto the negatively charged sites that exist on a cation exchange resin. Conversely, negatively charged ions (anions) must be placed onto anion exchange beads with their fixed positive charge sites. Counterion loading is not limited to inorganic chemistry, however. There are many organic structures that may be placed onto the resin sites carrying the opposite charge.

Figure 13.   A periodic table shows the broad range
             of possibilities for loading elements
             onto anion or cation exchange resin
             beads for subsequent use as micro-
             standards.

The microstandard capability can be carried into broad usefulness. To illustrate, consider available bead sizes which may range from about one millimeter down to one micrometer. The corresponding volumes extend over nine magnitudes. Assume saturated ion exchange sites have a value of of as

roughly 0.2 (it varies for different counterions).  Using the
nomograph in figure 14 of equation (7) given on page 12, it
is seen that this corresponds to a counterion content reaching
from over $10^{-4}$ to less than $10^{-13}$ grams.  If the conditions of
mixed elemental leading can be brought under good control, it
should be possible to use these beads to carry just a few atoms
of a required element or isotope.



Figure 14.   Nomogram for determining mass of counter-
ion as a function of particle size and of
specific counterion density (grams/millimeter).

17

## 2.  GAS CHROMATOGRAPHY

### A.  Introduction

Gas liquid chromatography (GLC) is an interesting subject in its own right, and it is frequently useful for following chemical purification.  Our activities in this area have been pointed at two objectives.  First, we have sought experience with trace volatile constituents that may be present in widely different types of sample materials.  Second, we have made a series of efforts to apply these techniques to the characterization of materials that are being tested for certification as Standard Reference Materials.  Notable in this regard are the relatively recent undertakings to develop biomedical and clinical Standard Reference Materials.

### B.  Dimethylsylfoxide (DMSO)

The Section on Molecular Biophysics of the National Institutes of Health (under the supervision of Dr. Edwin D. Becker) communicated to us the need for anhydrous hexadeuterated DMSO as a reference standard in NMR studies. Ordinarily, the drying of a stable organic liquid would be a minor problem, but this material is not easily dried by any of the obvious methods.  For example, it is believed that sodium metal is apt to react with it explosively. It is a costly material so that conventional water determination by Karl Fischer titration, which wastes relatively large samples required for trace water analysis.  GLC offers the obvious advantage of requiring very small samples for analysis (0.001 ml) and the results of our calibration are reported in the following.

The water measurements involved the use of a 3.5 mm diameter (i.d.) stainless steel column 40 cm in length packed with Porapak-Q, a chromatographic material that forms a particularly sharp water peak.  With temperature programming from 100 to 250 °C at a rate of 30 °/min, the following relative retention times for fully resolved peaks were obtained:  air,

0.024; water, 0.062; and DMSO, 1.000. Under these conditions, a determination is completed within one minute.

One of the typical problems here is a need to have analytical capability without having a completely dried sample. This calibration was carried out using the method of standard addition. Known amounts of water were added to the DMSO which also contained an unknown amount of water. The resulting peak heights h(water) and h(DMSO) are assumed to obey the relation:

$$\frac{h(water)}{h(DMSO)} = k(C_W^o + C_W) \tag{8}$$

where $C_W^o$ = conc. of residual water, and

$C_W$ = known conc. of water.

The test of this equation was carried out by adding water to a constant stock solution of DMSO. The results are shown in figure 15. From the parameters obtained using linear least squares analysis, we have $C_W^o$ = 0.3% and k = 1/4.07. This gives the analytical equation for subsequent analysis:

$$C_W = 4.07 \; \frac{h_{water}}{h_{DMSO}} \tag{9}$$

On this basis, it was possible to establish a series of reference solutions of known water content to be used for subsequent calibration purposes. It was eventually determined that hexadeuterated DMSO, containing approximately 0.04% water, or less, would not exhibit the exchange reaction that interferes with its use for nuclear magnetic spectroscopy.

C. Divinylbenzene

This material is widely used as a polymer crosslinking agent. It is used to prepare copolymers with styrene, and these are among the intermediates described earlier for the synthesis of ion exchange resins. The crude commercial material is a mixture of diethylbenzenes, ethylvinylbenzenes,
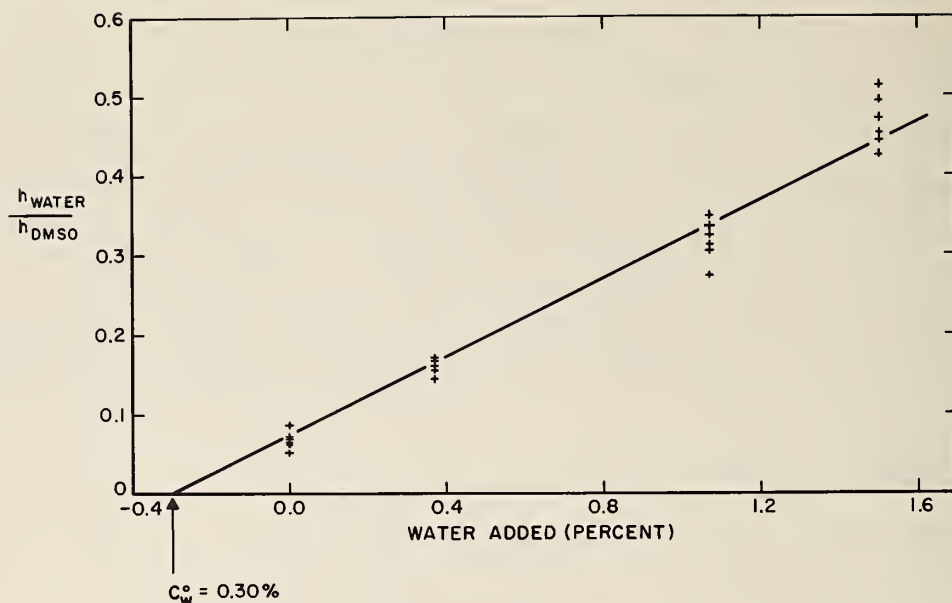
Figure 15.   Gas chromatographic calibration of trace water in dimethylsufoxide.

and divinylbenzenes.   Generally, these occur as the mixed meta and para isomers, where the total divinylbenzene content is about one half of the total.   Naphthalene may also be present since:
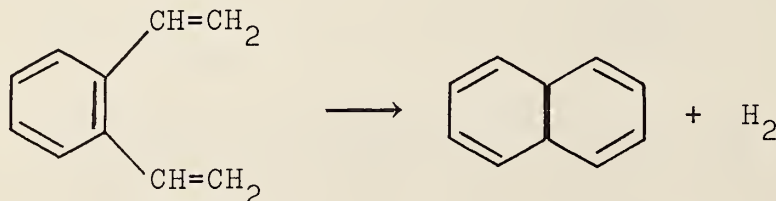


These materials have been studied extensively by Wiley, Allen, Chang, Musselman, and Venkatachalam [7].   We have used his gas chromatographic analytical methods to provide a basis for measurement of the composition of various samples of divinylbenzene.

For the analyses of mixtures of para- and meta- divinyl-benzenes, a 305 cm by 3.5 mm stainless steel column packed with a mixture of 85% by wt. of chromasorb W, 15% Bentone-34, and 5% Ucon oil was used.   Small samples of about 0.0002 ml

20

were injected and, for the estimation of constituents other
than the divinylbenzenes, the temperature was programmed from
135°C to 200°C at 6°C/min.  Under these conditions the para-
isomer elutes before the meta-isomer.  It has been found
inadequate resolution if the mixture contains a high concen-
tration of p-dvb (>95%) so that the first peak is relative-
ly large.  Columns packed with FFAP (Varian Associates, free
fatty acid analytical phase) elute the isomers in the reverse
order and may also be effective for such mixtures.

Development quantities of divinylbenzene were procured
from the recently formed Petrochemicals Division of the Shell
Chemical Company of New York, N.Y.  The commonly available
crude divinylbenzene has a gas chromatogram shown in figure
16, in which the peaks due to the mixed ethylvinylbenzenes,
and the mixed DVB isomers are evident along with the least
volatile naphthalene.  The corresponding analytical chromato-



Gas chromatogram of crude divinylbenzene

Figure 16.  Gas chromatogram of crude divinylbenzene mixture.

21

grams of concentrated para and meta isomers are shown in
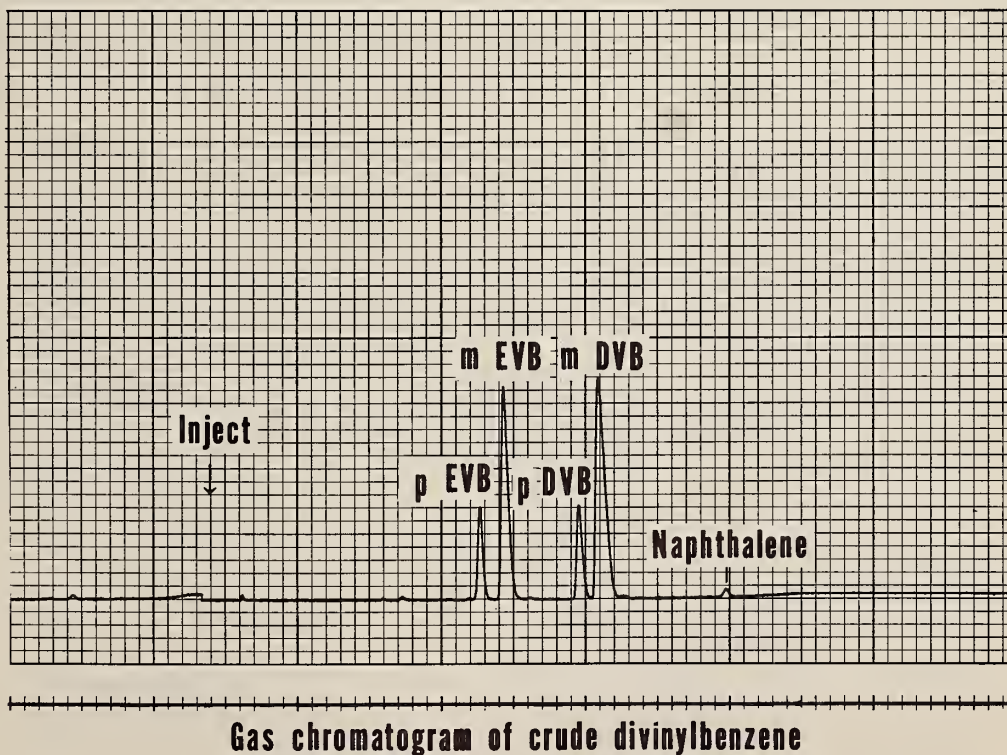figures 17 and 18. This analytical effort has provided us
with a basis for continuing our purification efforts leading
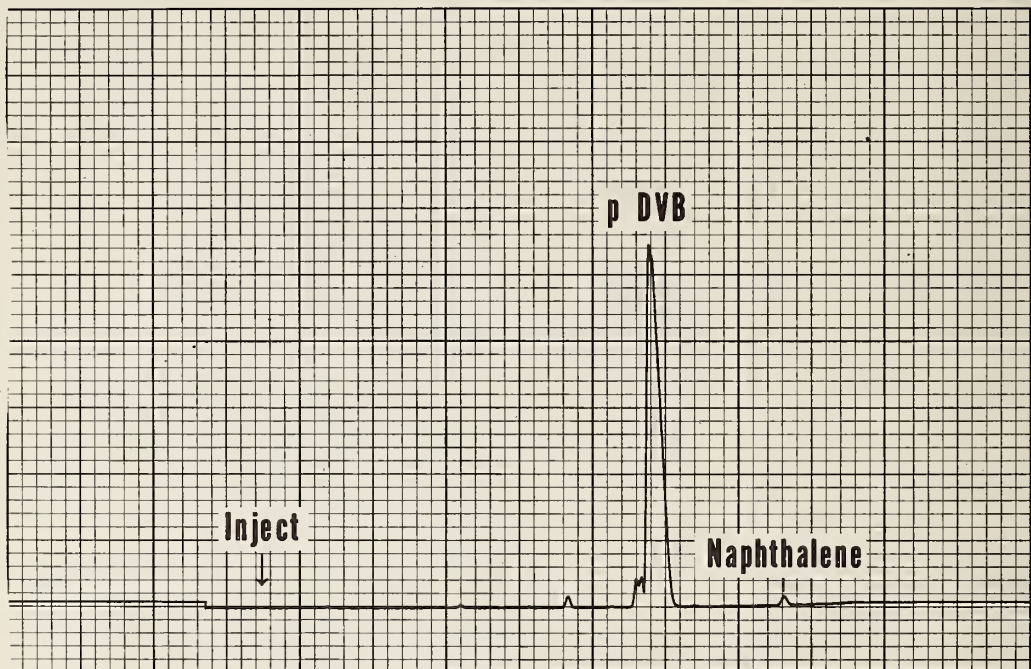


Figure 17.   Gas chromatogram of 98+% pure para divinylbenzene.
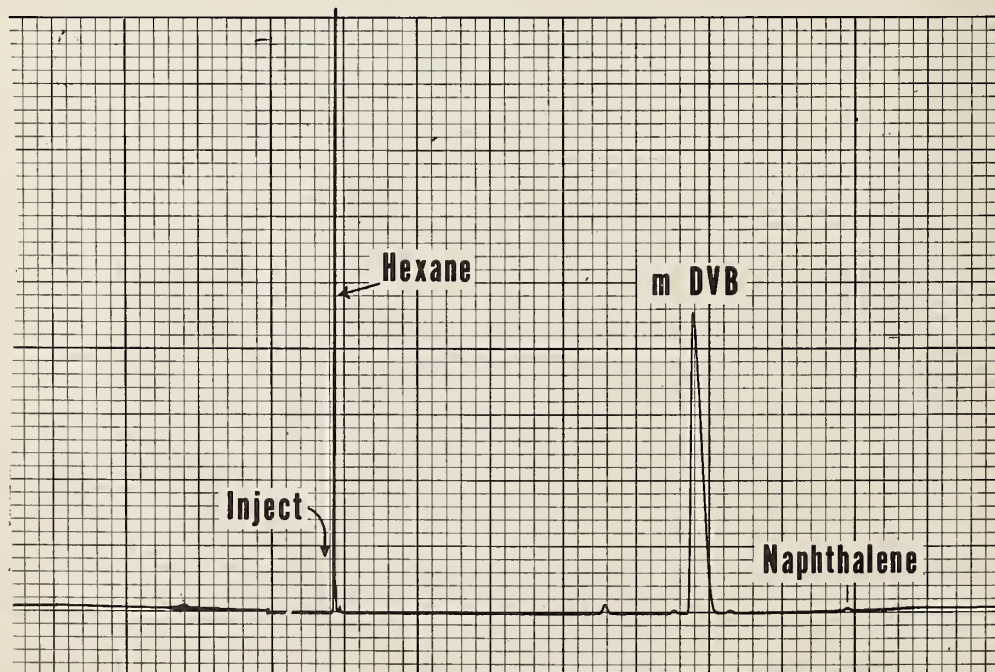


Figure 18.   Gas chromatogram of 90% pure meta divinylbenzene.

toward the preparation of hopefully 99+% pure isomers, and for potential for issuance of samples for investigative use. That aspect of the work is being coordinated through the NBS Office of Standard Reference Materials.

D. GLC Study of Trimethylsilyl Derivatives of Organic Compounds

   1. Introduction

   Because of its speed, accuracy and sensitivity, gas chromatography can offer an advantage over conventional methods of detecting or measuring impurities. In the application of this technique it may be necessary to prepare volatile derivatives of compounds with otherwise low volatility. A suitable derivative must provide enhanced volatility and adequate stability.

   Among the derivatives used in gas chromatography, considerable versatility is provided by trimethylsilyl ethers. The silylation of various functional groups has been known for some time [8-10]. The trimethylsilyl group can be substituted into many organic compounds containing active hydrogens. This method may be applicable to a wide variety of organic compounds which include alcohols, amines, amides, amino acids, carbohydrates, carboxylic acids, phenols, sterols and steroids Among the commercially available reagents used for preparing trimethylsilyl ether derivatives are trimethyl chlorosilane (TMCS), hexamethyldisilazane (HMDS) and Bis(trimethylsilyl) acetamide (BSA). Representative reactions are indicated by the following equations.

$$(CH_3)_3SiCl + ROH \longrightarrow (CH_3)_3SiOR + HCl$$

$$(CH_3)_3SiNHSI(CH_3)_3 + 2ROH \longrightarrow 2(CH_3)_3SiOR + NH_3$$

$$\text{C}_6\text{H}_5-\text{N}(\text{H})-\overset{\displaystyle O}{\overset{\|}{\text{C}}}-\text{CH}_3 \;+\; \text{CH}_3-\overset{\displaystyle O-\text{Si}(\text{CH}_3)_3}{\underset{}{\text{C}}}=\text{N}-\text{Si}(\text{CH}_3)_3 \longrightarrow$$

$$\text{C}_6\text{H}_5-\underset{\underset{\displaystyle \text{Si}(\text{CH}_3)_3}{|}}{\text{N}}-\overset{\displaystyle O}{\overset{\|}{\text{C}}}-\text{CH}_3 \;+\; \text{CH}_3-\overset{\displaystyle O}{\overset{\|}{\text{C}}}-\text{NH}-\text{Si}(\text{CH}_3)_3$$
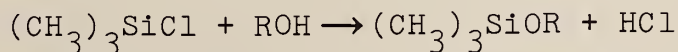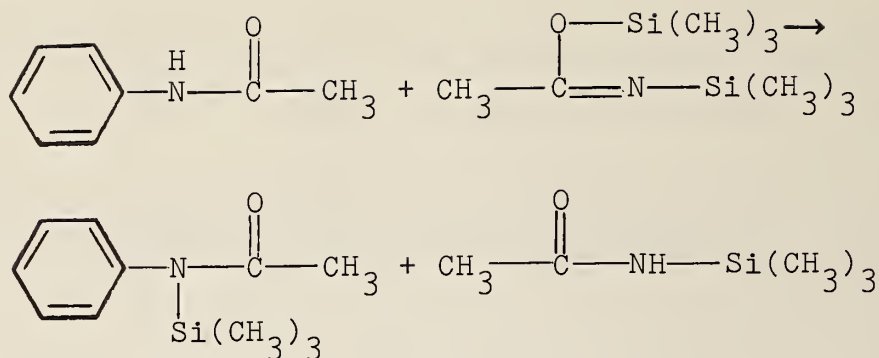
## 2.  Experimental Methods

The ease of formation of the silyl derivative varies widely.
Frequently, organic compounds will establish reaction satura-
tion after a few minutes at room temperature.  With other com-
pounds, several hours of reflux in an appropriate solvent may be
needed.  Exact conditions are established by following the
reaction progress as a function of time.

In general, it is important that air be excluded during
reaction.  In this regard we have used septum vials as shown
in figure 19.  The separated components show the vial, septum,
and aluminum cap.  The cap crimper is used to tighten the septum
against the vial.  We have seen that the ampoulation technique
is suitable for repeated withdrawal of samples using a hypo-
dermic needle to penetrate the septum.  However, punctured
vials do not provide protection for more than an hour or so
against contamination from the atmosphere.  By contrast,
unpunctured vials have been stored for several weeks at -20 °C
with no noticeable deterioration.  A disadvantage that can
have serious analytical consequences is that organic liquids
may leach impurities from the rubber septa.  This is especially
important if the liquid swells the rubber.

The conditions for GLC analysis after silylation were to
improve as a result of quite rapid temperature p.  ᴄᵐ  .

24

Figure 19.    Photograph of rubber septum vials that have
              been used to assist silylation gas chromato-
              graphy.

The chromatographic column was 3.5 (i.d.) by 180 cm in length.
Temperature programming was used from 100 to 300 °C at a rate
of 30°/min.   The packing was 10% (w/w) of silicone gum rubber
(UCW-98) on Chromosorb W (80-100 mesh).   Helium carrier gas was
used with a flame ionization detector.   It was necessary to
clean the flame chimneys after every 100 hours of use in order
to improve the sensitivity, and to sharpen the peaks which
otherwise tended to become irregular and jagged.

        The results of using the foregoing conditions is illus-
trated with the chromatography of a series of hydrocarbons,
as shown in figure 20.   The chromatography of all compounds
studied was found to be subject to contamination peaks that
were identified by running a blank, as shown in figure 21.
Some of the various impurities are in the silylating reagents,
some appear to be formed by reaction of the reagents with
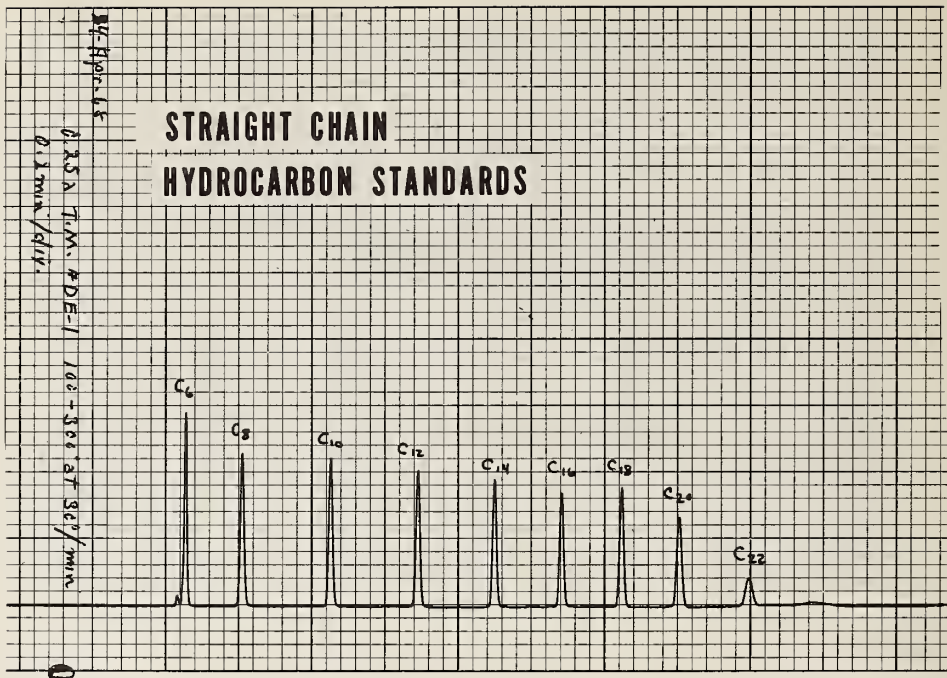impurities in the rubber septa, and none are attributed to the
solvent.

Figure 20.  Gas chromatogram of $C_6$ to $C_{22}$ normal
hydrocarbons as they appear from temper-
ature programming procedure followed in
silylation gas chromatography.
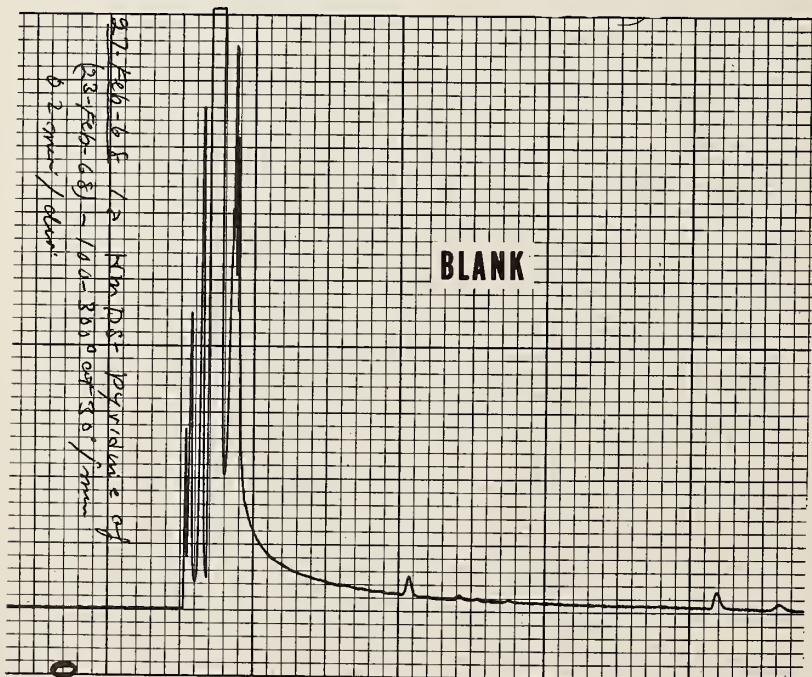


Figure 21.  Reagent blank as obtained during silyla-
tion gas chromatography.  Impurities in
the reagents, from the septum and from
atmospheric contamination are apparent.

26

In all cases, the formation of a well resolved peak was
followed up to identify the mass of the derivative using mass
spectroscopy.  We are happy to acknowledge the cooperative
assistance given to our efforts by Dr. Ray Pittman and
Dr. Robert Milne at the National Institutes of Health.

### 3.   Ethylenediaminetetraacetic Acid

As noted by Farrow and Hill [11] it is common for ethyl-
enediaminetetraacetic acid (EDTA) to be contaminated with
small quantities of nitrilotriacetic acid (NTA).  This has been
useful in screening to find a material of sufficient purity for
issuance as a Standard Reference Material.  We have found
commercial samples of EDTA do tend to be contaminated by vary-
ing quantities of NTA.  As shown in figures 22 and 23, the NTA
peak which corresponds to the trisilyated derivative, and the
EDTA peak which corresponds to the tetrasilylated derivative
are obtained after refluxing with the silylating reagents in
pyridine for a period of approximately twenty hours.  Subse-
quently, it was found that "BSA" reacts much more rapidly.
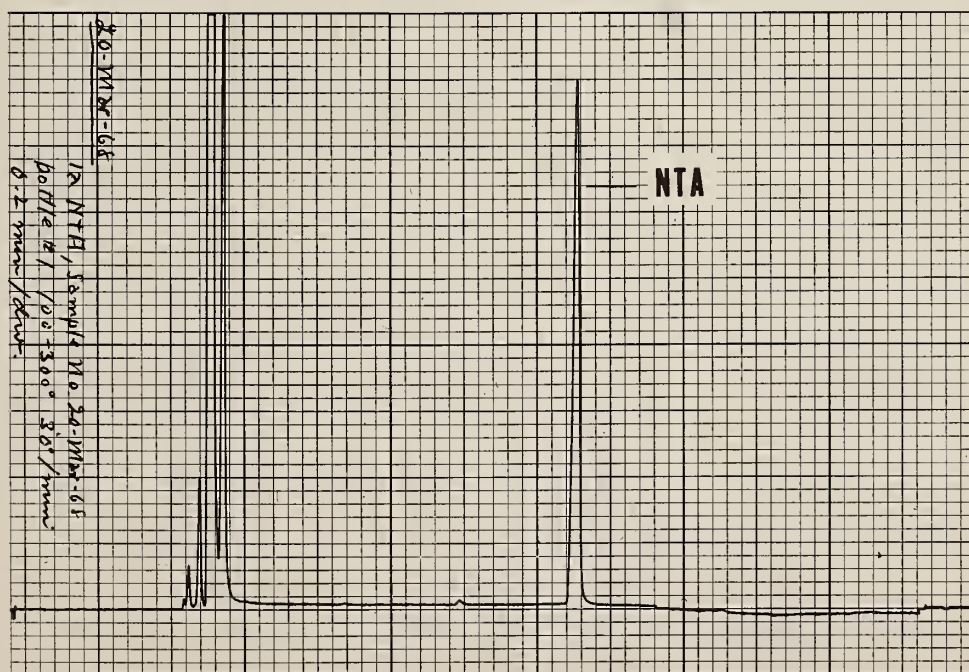


Figure 22.   Nitrilotriacetic acid is obtained as a well formed
peak after silylating and use of gas chromatography.

27
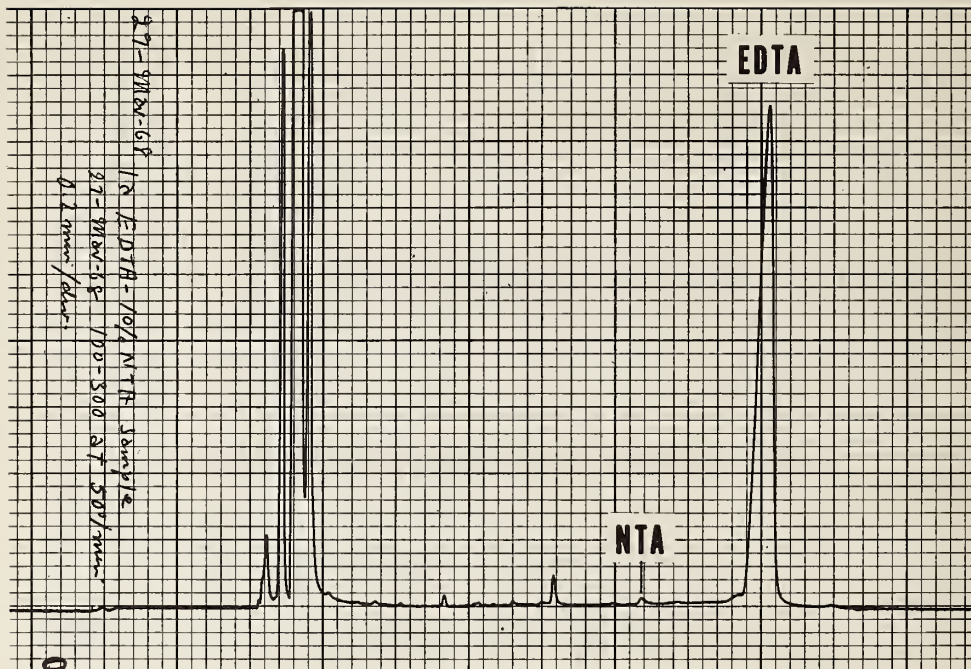
Figure 23.   Silylation chromatogram of EDTA containing a small quantity of NTA contaminant.


## 4.   Clinical Standard Reference Materials

The NBS Office of Standard Reference Materials has spurred the development of purified and carefully character- ized chemicals to serve as standards for biomedical and clini- cal analysis.  Without silylation, the gas chromatography of some of these materials is practically useless.  The silyla- tion reaction has been helpful in the formation of derivatives of urea (disubstitution) as shown in figure 24, and uric acid as shown in figure 25.

Although this work is still incomplete, we have formed several conclusions concerning the use of silylation in the investigation of these clinical materials.  First, volatile derivatives can be formed in good yield.  Second, it is necessary to unscramble trace contamination from the reagent blank and from that which may be present in the compound under investigation.  In general, the highly purified materials show relatively few contaminants compared with the many that
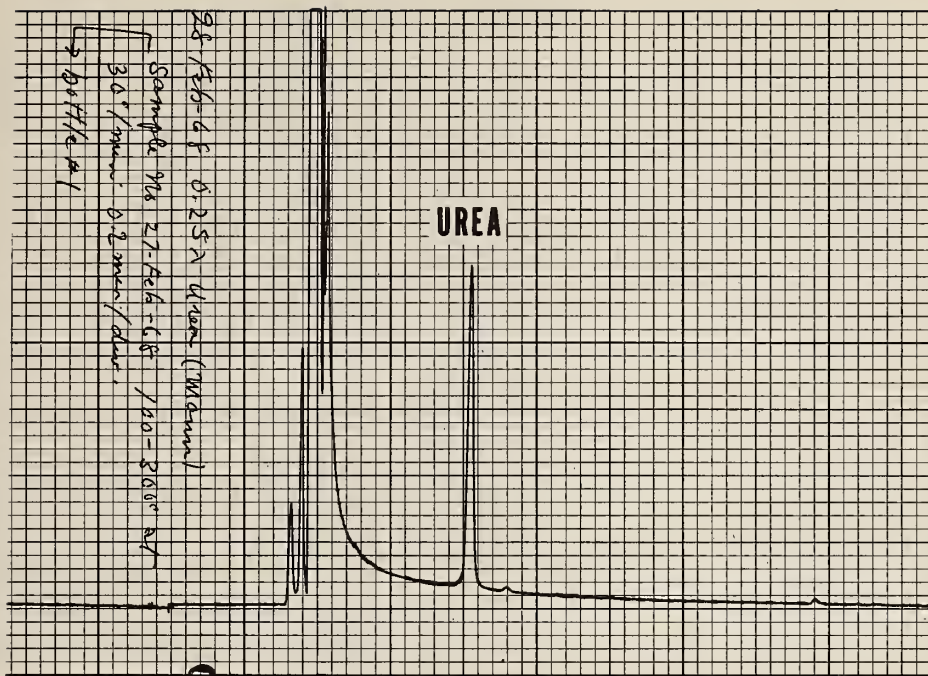
Figure 24. Gas chromatogram of silylated high purity urea.
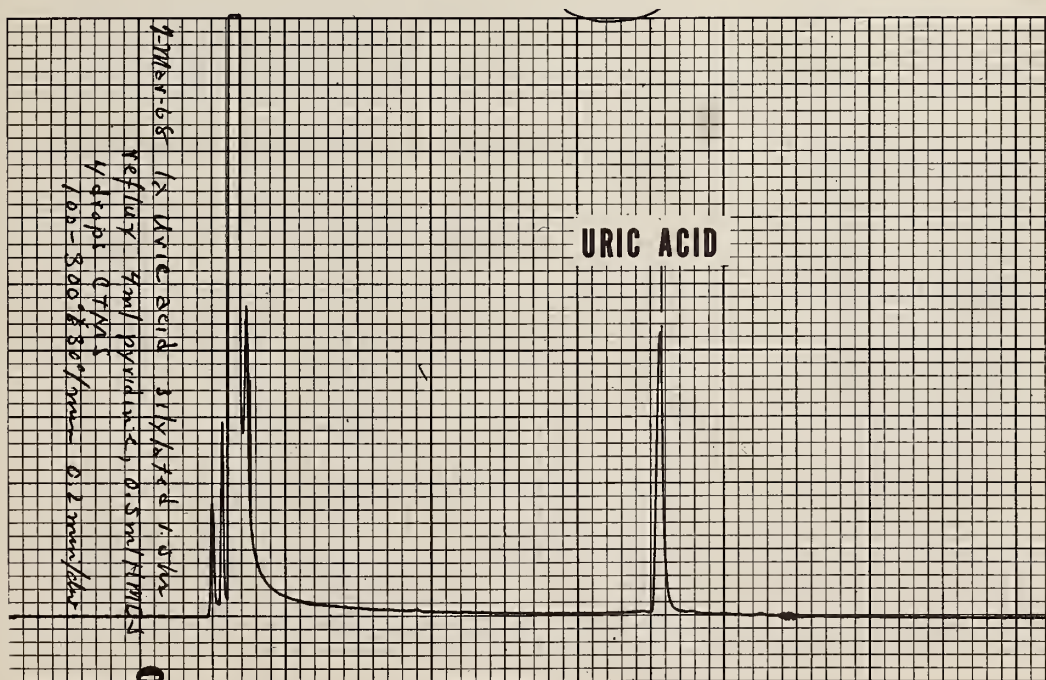


Figure 25. Gas chromatogram of silylated high purity uric
acid, a material being characterized prior to
issuance as a clinical Standard Reference Material.

may occur in the blank. However, systematic unscrambling is
possible and, especially with the use of mass spectroscopy,
it is clear that silylation does permit identification of
impurities, providing that the impurities actually form a
volatile silylate adduct. Third, not all impurities will form
such adducts. As shown in figure 26, allantoin, which is a
suspected contaminant in uric acid, does not silylate.
Similarly, with urea, we were able to show that the biuret
peak tends to coincide with the urea peak. Finally, we have
found several preliminary indications that the quantitative
calibration of GLC for measurement of silylated components
in a mixture may be feasible, that precise work may require
the use of an internal standard, and that precise control of
reaction conditions is necessary in order to obtain reproducible
chemical reaction yields.
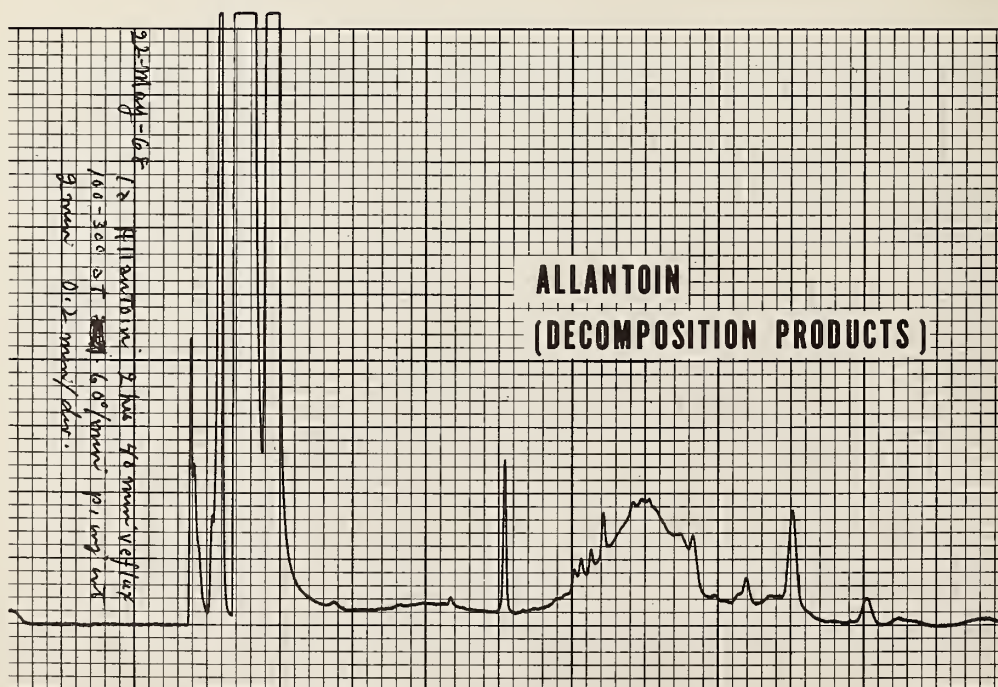
Figure 26. Gas chromatogram of silyated allantoin shows
evidence for poor feasibility of detecting this
substance as a contaminant of uric acid.

# 3. CRYSTALLIZATION

The purification of chemical compounds is often possible by using crystallization techniques, including crystallization from a solvent or from the melt. The first procedure is practiced in virtually all organic chemistry laboratories. The latter has achieved considerable importance as a result of work done in the metallurgical and solid state physics laboratories. Unfortunately, the adaptation of zone melting by chemists has not been rapid in this country. The principles and techniques are described in the works of Pfann [12], Schildknecht [13], and Herington [14]. The first of a two volume series in the general area has been published under the editorship of Zief and Wilcox [15].

One of the major advantages of crystallization from the melt is its potential for repetition that leads to extreme purification and, indeed, spectacular accomplishments have been made. The method is not always applicable, however. A major problem with chemical compounds is the possibility of decomposition. We found, for example, that zone crystallization of urea was an excellent method for removing sulfate contamination, but the simultaneous generation of ammonia limited the operation to just two passes. This gave ample indication that the urea was undergoing rapid decomposition at its melting point.

Zone refining is a particularly effective purification technique when it is applicable. Contraindications include glass formation, instability at the melting point, and breakage problems caused by volume expansion upon crystallization. Apparatus capable of accommodating three samples tubes, while operating at temperatures down to -50°C is shown in figure 27. In addition to this, we have obtained the heavier duty commercial instrument shown in figure 28. This is suited to larger scale operation for horizontal or vertical operation. Both devices are scheduled for future testing, with emphasis upon their use of temperatures below 0°C.

31
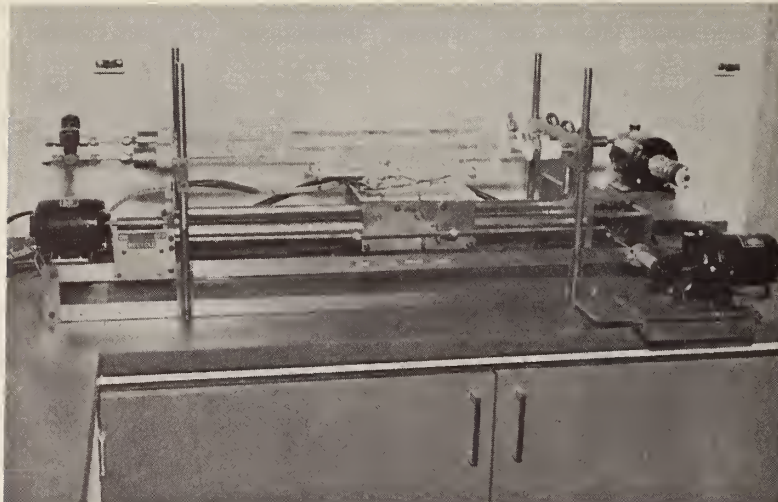
Figure 27.   Three tube zone crystallization apparatus equipped
with three heaters per tube.
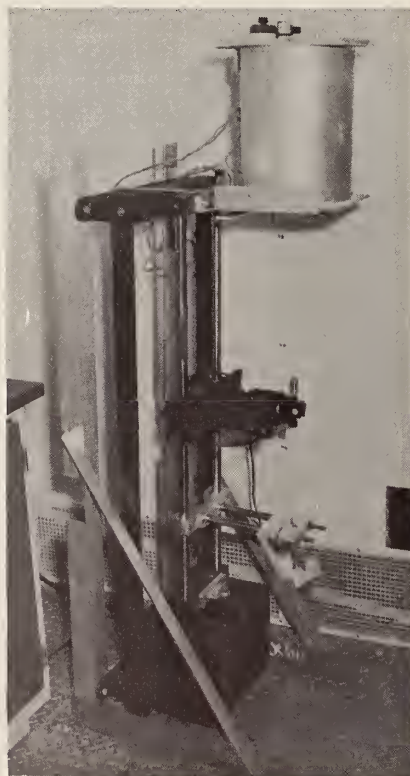


Figure 28.   Heavy duty gear drive apparatus used for normal
freezing.

# 4. DISTILLATION

During the past two years, the use of precision laboratory distillation in the Analytical Chemistry Division has been held in abeyance. This is partly because of need for greater emphasis on other methods of separation, and partly for lack of facilities at the new NBS location. Specially designed facilities in the newly constructed Hazards Laboratory have now become available. The newly constructed Hazards Laboratory is shown in figure 29. The inside of this laboratory is shown in figure 30 which displays the facilities which were especially designed for a variety of tall-column experiments, including high efficiency distillation.
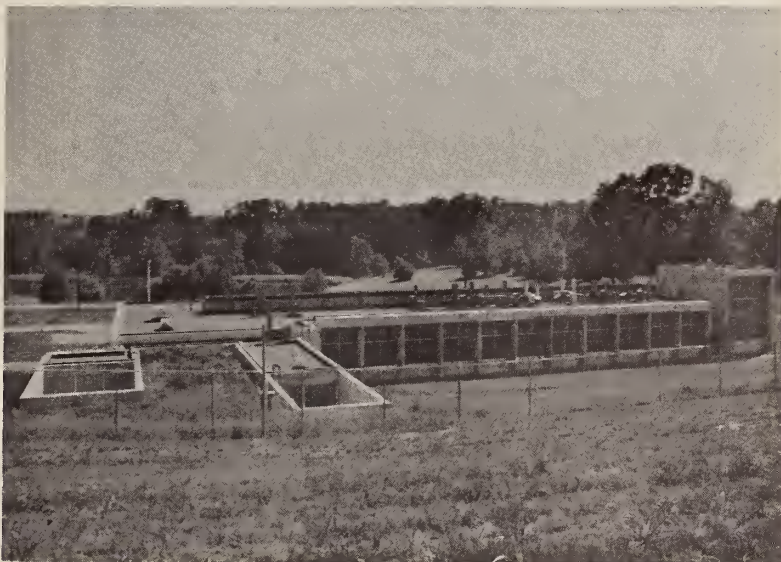


Figure 29.  Photograph of recently constructed Hazards Laboratory.

The Purification Section has in storage a number of types of stills the more important characteristics of which are summarized in table 2. Efforts are being made to return the distillation laboratory into operation. Originally, the laboratory was quite active because of the scarcity of other sources of distillation capability. Today, there are several sources of purified organic solvents. The present status of

33

distillation has been described [16]. It is essential that
one knows when to use distillation, or when to choose the more
complicated alternative of preparative scale gas chromatography
It is already evident that distillation from quartz apparatus
is appropriate in the purification of mineral acids, and such
apparatus is being readied for use in the areas more fully
described in the next section.
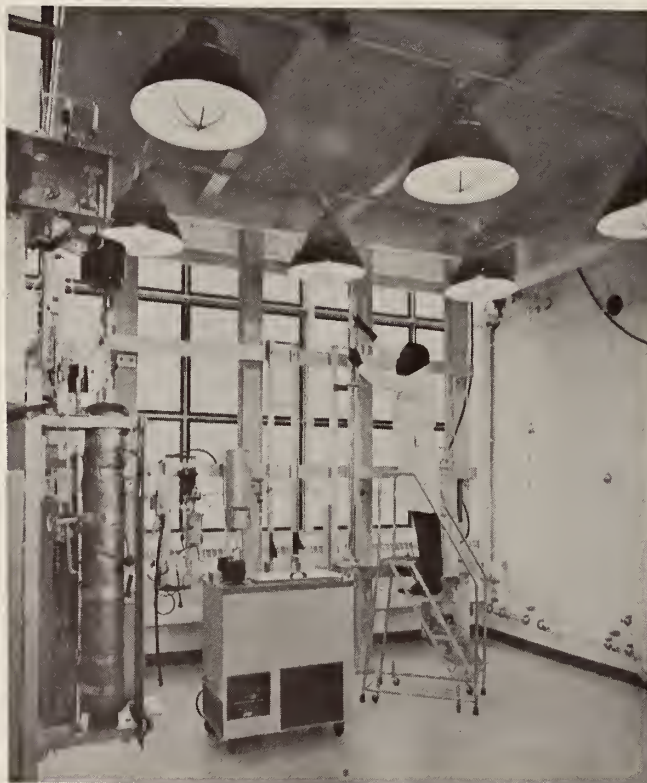


Figure 30. New high ceiling laboratory for planned use as
distillation facility in Hazards Laboratory.

Table 2. Description of laboratory stills.

| Type of still | Quantity per batch | Pressure of distillation | Rate of distillation for good results | Number of theoretical plates | Operating temperature |
|---|---|---|---|---|---|
| | ml | mm Hg | ml/hr | Optimum condition | °C |
| Micro-concentric tube | 1-4 | 760-1 | 0.1 | 40 | +250 to -190 |
| Macro-concentric tube[a] | 5-50 | 760-1 | 1-2 | 70-90 | +150 to -190 |
| Micro-spinning band (2 stills)[a] | 5-100 | 760-1 | 1-2 | 70-90 | +250 to -150 |
| 1-meter precision packed[a] | 500-1500 | | | | +150 to +10 |
| 3-meter random packed[a] | 1500-4000 | 760-90 | 15-20 | 200-260 | +130 to +30 |
| Oldershaw perforated-plate (30 stages)[a] | 1500-20,000 | 760-300 | 1000 | 10-25 | +130 to +30 |
| 3-meter packed Monel[b] | 500-1500 | 760-90 | 5-20 | 200 | +250 to -190 |
| Fused silica 1-meter packed[c] | 200-1500 | 760-40 | 5-50 | 10 | +1000 to -190 |
| Molecular single stage | 1-5 | $1-10^{-5}$ | 0.1-1.0 | 1 | +400 to -190 |
| Molecular falling film | 25-50 | $1-10^{-5}$ | 5-15 | 1 | +100 to +30 |
| Molecular falling film with scraping blades | 50-200 | $1-10^{-3}$ | 10-3 | 1 | +150 to +30 |

[a] Reflux ratio controlled by timing mechanism.
[b] Reflux ratio controlled by throttling.
[c] Reflux ratio controlled by partial condensation.

# 5. REAGENTS

## A. Introduction

The study of chemical reagents impinges upon broad areas of chemistry. The purity of solvents or reagents is often a direct limitation to the sensitivity that can be reached with wet chemical methods of analytical chemical measurements. Past studies of chemical reagents have been relatively rare and unenlightening. A recent article by Robertson [17], however, sets a good example. There is a growing interest in highly purified reagents, and there is indication that some of the needs for such materials can be satisfied as a result of recent industrial investments in this area.

Recent advances in chemical reagents have taken directions that could not have been forecast a few years ago. This can be illustrated. First is the concern for the measurement of particulate impurities at the trace level; this is indicated in the following discussion of laser light scattering techniques Second is the bottleneck problem in which purification is counteracted by the limiting processes of contamination. Thus, container methods and materials have a way of eventually dominating any discussion of the limiting benefit of trying to improve chemical purity. It is important that the reagent composition be time independent so that inadvertent contamination, either by exposure to the atmosphere, by degradation, or by dissolution of the container, is somehow avoided.

## B. Facilities

The construction of a low temperature laboratory was completed during the early part of 1968, and the facility has been tested since that time. A plan of the facility is shown in figure 31. The design provides for a core laboratory that can reach to -30°C and be sustained for long periods. An anteroom is used to give a temperature buffer, or it can provide a second independently operated laboratory at temperatures to 0°C. Crystallization apparatus is being developed, as

Figure 31.   Low temperature (to -30°C) laboratory.

described on page 32, and it will be used in the facility.
The experimental capability includes electrical and liquid
conduits.   Finally, there is a large window for viewing of
experiments in progress.

The reagents project maintains quartz distillation
apparatus; two units that are suited to mineral acid distilla-
tion are shown in figure 32; this will have an efficiency of
approximately 14 theoretical plates.

C.   Particle Detection

The concern for particulate impurities in reagents has
given impetus to the construction of a new type of light scat-
tering apparatus.   This is shown in figure 33.   It is used for
detecting traces of fluid-borne contamination by laser beam
scattering.   A detailed description of the apparatus and its
applicability in determining suspended particles in solutions
of various reagents, water, and air is to be published [18].
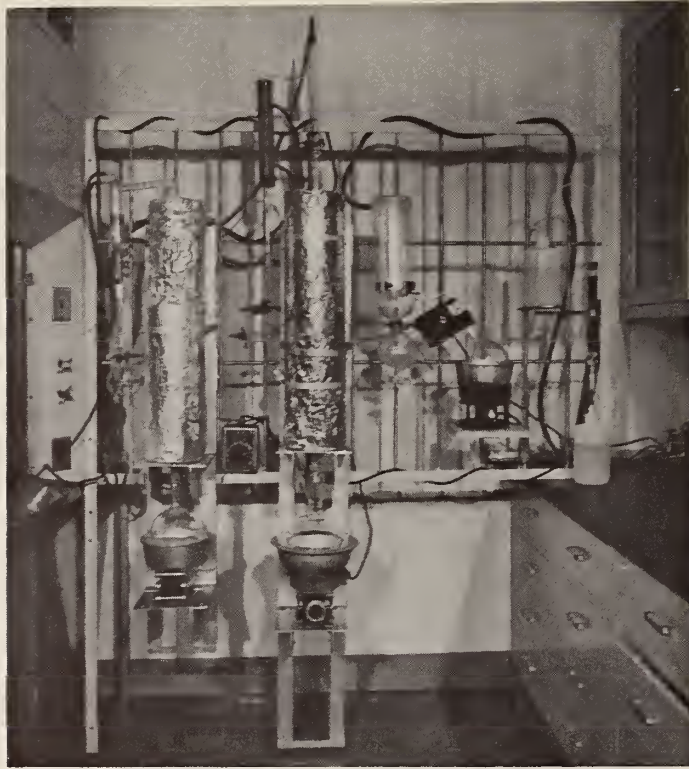
Figure 32.    Quartz distillation apparatus.
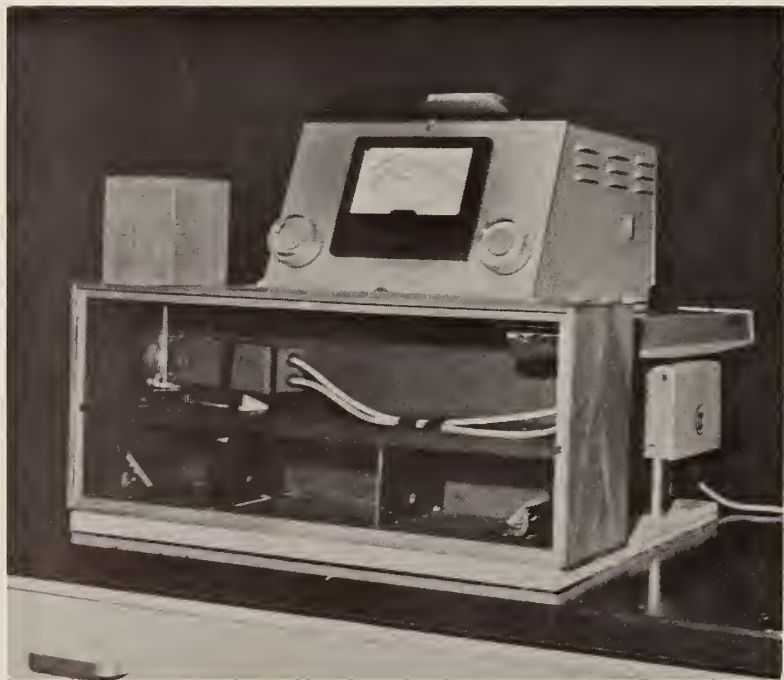


Figure 33.    Photograph of laser light scattering apparatus.

Briefly, the cylindrical cell containing the liquid sample is placed vertically in the cell holder and the amount of scattered light is measured with a photomultiplier. With different concentrations of suspended polystyrene latex spheres of known diameters a calibration curve is obtained for estimating concentration. Light scattering measurements were made of water obtained from different sources, organic solvents, organic compounds dissolved in distilled water. A few of the solutions were filtered through a 0.01 micrometer (as indicated by manufacturer) porosity filter to study the effect of filtration. The results of some of these measurements are shown in Table 3.

The laser detection of particles was also adapted to monitoring particle contamination in the air. In one test, the solids in air were estimated at 0.014 ppm when 115 liters of air were scrubbed by slowly bubbling through distilled water. The apparatus is shown in figure 34.



Figure 34. Apparatus for scrubbing dust from measured volumes of laboratory air.

Table 3.  Measurements of water insoluble particles in
         solid chemical reagents.

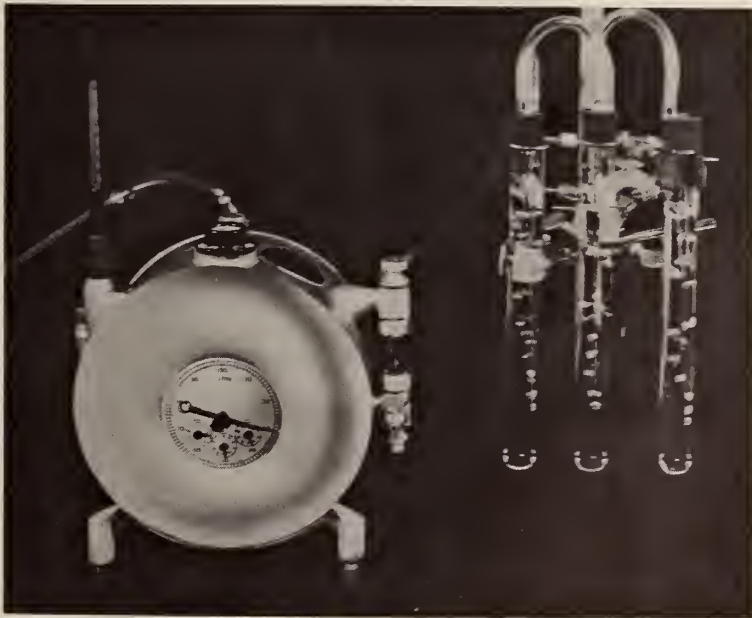| Solute | Wt.(%) | Estimated particle concentration (ppm) | Filtered[a] $(I-I_W)/I_W$ | Estimated particle concentration (ppm) in solute |
|---|---|---|---|---|
| cadmium nitrate | 10 | 10. | 8.4 | 0.40 |
| silver nitrate | 10 | 0.74 | 2.9 | 0.030 |
| sodium nitrate | 10 | 0.76 | | |
| sodium chloride | 10 | 0.63 | | |
| sodium sulfate | 10 | 0.72 | | |
| potassium iodide | 10 | 1.6 | | |
| glycine | 10 | 5.0 | | |
| sodium benzoate | 10 | 0.45 | | |
| agar | 0.1 | 132. | 2.0 | 1.0 |
| sulfonated polystyrene | 0.1 | 160. | 4.7[b] | 13 |
| disodium ethylene-diaminetetraacetate | 2 | 6.6 | 1.4 | 20 |

[a]Through 0.01 micron millipore filter, except for poly-
styrene sulfonated sample.
[b]Filtered through 0.22 micron millipore filter.

D.  Containers

     The purification of reagents can be hindered by improper
containment.  A program of monitoring container materials is
being carried out with attention given to purity, durability,
solubility, permeability and other aspects of container use.
Microscopic examination has shown the presence of many fine
particles embedded in polyfluorocarbon materials.  Figure 35
illustrates this.  Laser probe spectroscopic analysis of
these particles in one instance showed Fe, Mg, Si, Zn, Al,
Ni, Cu and Mn among the constituents.  Methods of cleaning
and removing these particles are being investigated.
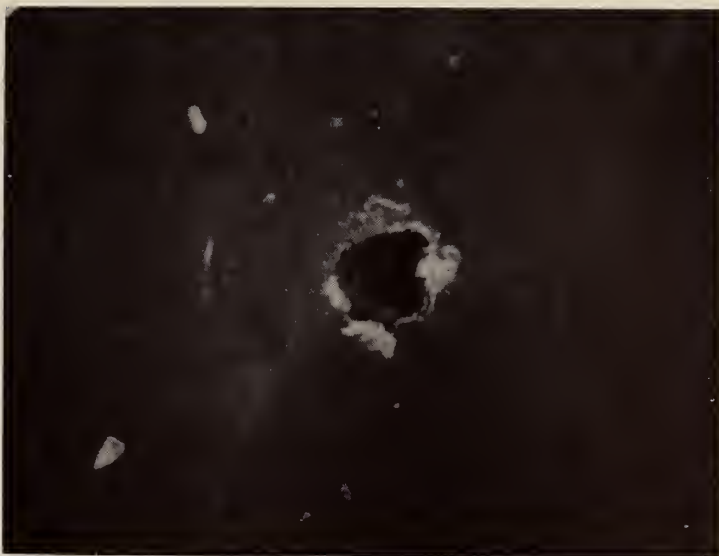
Figure 35.   Photomicrograph of solid particle embedded in
             a polyethylene container.

E.   Purified Reagents

The present project was designed with the idea of antici-
pating the future needs at NBS for high purity reagents in
trace chemical analysis.  In order to anticipate these needs,
a materials bank has been made of the purest reagents that
can be obtained commercially.  These are kept refrigerated
and ready for prompt use.  (Cold storage has the important
benefit of drastically retarding the various deterioration
processes.) The response to these efforts has been favorable.
During the past year 56 of the reagents were issued to various
chemists at the Bureau.  All but three of the approximately
28 different types of reagents, listed in Table 4, have been
dispensed within the past year.  The completion of a low
temperature (-30 °C) laboratory, shown in figure 31, has
permitted refinements in the practice of storage and dispens-
ing of the reagents.

Table 4.   List of highly purified chemical reagents.

Acids

| | |
|---|---|
| $CH_3COOH$ | (*) |
| HBr | (**) |
| HCl | (**********) |
| Hf | (**) |
| HI | |
| $HNO_3$ | (*********) |
| $HClO_4$ | (***) |
| $H_2SO_4$ | (*) |

Salts

| | |
|---|---|
| $CaCl_2$ | (**) |
| LiBr | (**) |
| KCl | (**) |
| NaCl | (**) |
| BaCl | (**) |
| BaF | (*) |
| Mg | (*) |
| NaF | (**) |

Bases

| | |
|---|---|
| $NH_4OH$ | (***) |
| NaOH | (*) |

Redox

| | |
|---|---|
| Br | |
| $I_2$ | |
| LiF | (*) |
| KI | (*) |
| $Na_2S_2O_3$ | (**) |
| CsI | (**) |
| NaI | (*) |

Buffer Salts

| | |
|---|---|
| $NH_4Cl$ | (*) |
| $CH_3COONa$ | (*) |
| $Na_2SO_4$ | (*) |

* Indicates request for one or more units for a specific
  application during FY 1968.

| Micro filters material type | Pore sizes (micro meters) | Diameter size millimeters) |
|---|---|---|
| Cellulose | 0.45 | 47, +142 |
| " | 0.22 | 13, 25, 47, +142 |
| " | 0.10 | 47, +142 |
| " | 0.05 | 47 |
| " | 0.01 | 13, 25, 47, +142 |
| Solvinert | 1.5 | 47 |
| " | 0.5 | 25, +47 |
| " | 0.25 | 25, +47 |
| Nylon | 1.0 | 47 |
| Polytetrafluoroethylene | 5.0 | 25, +47 |
| Polycarbanate | 8.0 | 25, +47 |
| " | 5.0 | 25 |
| " | 2.0 | 25, +47 |
| " | 1.0 | 25, +47 |
| " | 0.8 | 25, 47 |
| " | 0.5 | 25, 47 |

# 6. 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, 1968
> 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. Talks and Publications

D. H. Freeman, W. F. Rittner, "Structure and Its Relation to Selectivity," Gordon Research Conference, New London, New Hampshire. August 22, 1967.

D. H. Freeman, "Chemical Microstandards," Massachusetts Institute of Technology, Cambridge, Massachusetts. November 30, 1967.

D. H. Freeman, "Chemistry of Ion Exchange," Science Club, Winston Churchill High School, Potomac, Maryland. January 11, 1968.

D. H. Freeman, "Laser Detection of Small Particles in Liquids," New York Academy of Sciences, New York, New York. February 2, 1968.  (Same as ref [18], p. 45)

D. H. Freeman, "Chemical Microstandards," Division Colloquium, National Bureau of Standards. February 13, 1968.

D. H. Freeman, "Modern Reagents for Future Chemical Standards," 19th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio.  March 6, 1968.

D. H. Freeman, "Microstandards for Analytical Chemistry," 155th National Meeting of the American Chemical Society, San Francisco, California.  April 3, 1968.

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