SECOND NIOSH SOLID SORBENTS ROUNDTABLE

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE / Public Health Service
Center For Disease Control / National Institute For Occupational Safety And Health

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Edited by

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U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health
Cincinnati, Ohio 45226
July 1976

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402

HEW Publication No. (NIOSH) 76-193

PREFACE

The Measurements Research Branch of the Division of Physical Sciences and Engineering, NIOSH, is responsible for the development and evaluation of sampling and analytical methods for toxic substances encountered in the workplace. An important technique for the collection of gases and vapors in this environment involves the use of solid sorbents. The simplicity in use and the ease of handling these sorbents in a sampling tube make them attractive for integrated personal sampling to assess chemical exposures to the American working population.

This report is a transcription of the Second NIOSH Solid Sorbents Roundtable held on December 5-6, 1973 in Cincinnati, Ohio. Thirteen papers and a general discussion are contained in the proceedings. The Roundtable was organized and sponsored by the Measurements Research Branch to bring together researchers with expertise in the field of sorbent sampling and surface chemistry, and to explore possible applications to the problems of monitoring for occupational exposure to toxic chemicals.

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*presented paper

ABSTRACT

SECOND NIOSH SOLID SORBENTS ROUNDTABLE

This volume contains the proceedings of a two-day meeting of experts on the sorption of toxic substances on solids. The primary interest of NIOSH in this area is the applicability of these solid materials to the sampling of air contaminants in the workplace in order to assess chemical exposure of the American working population. Thirteen papers and a general discussion are contained in the proceedings. Each author presents his own view of the characteristics of solid surfaces as they relate to sorption sampling. A variety of topics are discussed in the papers. These include not only the theoretical aspects of surface chemistry and sample retention performance, but also the development of monitoring hardware, the use of fluidized bed concepts, the collection of high volumes and the evaluation of a variety of sorbents for specific compounds. A roundtable discussion at the end of each presentation brings out some of the applications of the research to field sampling.

PROCEEDINGS

WELCOME TO ATTENDEES

Mr. Crable: Good morning. I am John Crable and I would like to welcome you, first of all, to Cincinnati; secondly, to the National Institute for Occupational Safety and Health; and, thirdly, to our Solid Sorbents Roundtable discussions. We had one of these a year ago last September and it was very beneficial to us; we thought we'd like to get some of the expertise from other fields not particularly associated with industrial hygiene, so we could have an exchange of ideas.

We are fortunate in having Dr. Harris with us this morning. He is the new Director of the Division of Laboratories and Criteria Development. Dr. Harris joined us in July. He comes from the Johnson Space Center in Houston.

The Physical and Chemical Analysis Branch is one of the six Branches in the Division, and Dr. Harris will welcome you and also give us a brief description of what the function of the Division is. Dr. Harris ...

OPENING REMARKS

by

Elliott S. Harris, Ph.D.
*Division of Laboratories and Criteria Development**
National Institute for Occupational Safety and Health
Cincinnati, Ohio

Thanks John. It is rather pleasing to see the turnout we have here, and, as you saw when we went around the room, we have a turnout from industry, from government, and from universities. We have tried to select people with the greatest expertise in their fields.

Now, I would like to fill you in on the background of NIOSH, and of this Division in particular. There is some confusion in the minds of some people between OSHA (the Occupational Safety and Health Administration) and NIOSH (the National Institute for Occupational Safety and Health).

**This Division is now constituted as two Divisions: Division of Biomedical and Behavioral Sciences and Division of Physical Sciences and Engineering.*

OSHA is a regulatory agency; NIOSH is not. NIOSH is a source of research information arm for the Occupational Safety and Health Administration. OSHA is in the Department of Labor; we are in DHEW. So there is quite a difference.

We provide information that OSHA uses to promulgate standards. In order to provide that information we have to develop the criteria based upon in-house and contract research; and that is the role of this division, the Division of Laboratories and Criteria Development.

The Division research encompasses everything from the description of pathological phenomena to the detection of the cause and to the control of the environment or the cause. We have the Toxicology Branch, which looks at the pathological effect of the atmospheric contaminant; we have the Physical and Chemical Analysis Branch, which looks at the detection and analysis of these contaminants; and we have the Engineering Branch, composed essentially of industrial hygiene engineers, which looks at the control of the contaminant.

In the Physical and Chemical Analysis Branch, we are concerned with the means of detecting the contaminants, and that is why you are here today. We have various techniques for trapping contaminants, such as impingers or cyclones. There are ways of detecting contaminants with "detector tubes."

We are interested in being able to use solid sorbents to collect, or trap, both groups of materials and individual compounds. We also want to be certain that we are able to elute these compounds from the sorbent, and elute them essentailly in an unchanged form.

As part of the function of the Division, we hold several symposia a year. These are not all symposia in chemistry. We had a symposium in byssinosis, which is an occupational disease, later in the year. Right now, we are interested in solid sorbents. I appreciate your coming and I wish you well in the next two days. Thank you.

Mr. Crable: Thank you, Dr. Harris.

We have asked Dr. Ballou to get things started. He has been acting as a consultant to us for the past year, and is currently at the California State Univerisity at San Jose and also at the NASA-Ames Research Center. Prior to that, he was with Lockheed Research, Gulf Research, and the Mellon Institute. He has been working with us, and we feel he has kind of an outside view of what we are doing, and also he has visited some of the contractors and is familiar with interagency agreements that we have. He is going to give us an overview of the use of solid sorbents.

AN OVERVIEW OF THE USE OF SOLID SORBENTS FOR AIR ANALYSIS

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The use of solid sorbents in air analysis has developed from requirements of the Occupational Safety and Health Act of 1970. Under this act, the National Institute for Occupational Safety and Health (NIOSH) was established. A function of NIOSH is to develop and establish recommended occupational safety and health standards. An important part of the NIOSH program is to recommend standards and sampling and analytical procedures for the concentration level of trace contaminants in the breathing zone of workers.*

Standards Lists and Definitions

Trace contaminant concentration standards are defined in the Federal Register (1), where tables list the eight-hour, time-weighted averages for 402 species. The Federal Register listing notes that the concentration levels of most contaminants are allowed to rise above the average level during the eight-hour workday. However, for 20 species, the eight-hour time-weighted average is also the ceiling value. For 22 other species, there are specific definitions of acceptable ceiling concentrations, together with specifications of time duration and concentrations for acceptable maximum peaks above the ceiling values.

These facts are pertinent to the use of solid sorbents for air analysis, since the framework and the needs of the program are set by the federal laws. The required sampling and analytical techniques must be capable of application to a large number and variety of chemical species. The allowable levels vary widely among the various contaminants. For a single species, we must be concerned with sampling both the average concentration level from a long time duration, and, in some cases, sampling a higher level allowable for a shorter period of time. For all species, the method must be capable of sampling and analysis of the maximum allowable level for a very short time period; and when ceiling values are specified, the sampling strategy should be able to verify adherence to contaminant levels below the ceiling.

The number of identified chemical species, as well as their allowable levels, is revised yearly and published by the American Conference of Governmental Industrial Hygienists (2). Revised Threshold Limit Values (TLVs) become official federal standards only after publication by OSHA in the Federal Register.

**Public Law 91-596, 91st Congress, S.2193, December 29, 1970.*

The TLV list comes in several sections. Those most pertinent to chemical species sampling and analytical development work are the list of Adopted Values and the Notice of Intended Changes. In 1973 the ACGIH published an Adopted TLV list for 466 species, 25 of which had a ceiling limit set at the level of the eight-hour time averaged exposure limit. The 1973 Notice of Intended Changes list identified 38 new species, in addition to the 466 in the Adopted Values list. Twenty-one of the 38 are noted as 1973 revisions or additions to the TLV list.

The TLV list also defines the allowable factors for excursions above the TLV, when the ceiling is not the same as the eight-hour time weighted average. These factors are listed in Table I, and are at four levels, from a factor of 3 to a factor of 1.25, depending on the TLV.

The current TLV list of the ACGIH shows that the number of species of interest for sampling and analysis is not only large, but growing each year. A number of factors enter into attempts to define and standardize sampling and analytical procedures. One factor is that TLVs may change each year for many species, and another is the different requirements for excursions and ceiling determinations.

Table II lists the 32 chemical contaminant species on the 1973 list of Adopted TLVs whose TLV differs from that in the 1972 list. This list covers aldehydes, ethers, hydrocarbons, chlorinated hydrocarbons, alcohols, glycols, and various inorganic species, with TLV's ranging from 1 to 500 ppm. Any compilation of sampling and analysis specifications, even if complete in 1972, would then have to be reconsidered, revised, or extended to account for the 32 changes introduced to the 1973 Adopted TLV list.

As seen in Table III, changes also occur in the Notice of Intended Changes, which is not surprising, as this list is designed to invite comment for the two or more years each change is listed. Any methods for species on this list must therefore be subject to the new requirements of a revised TLV.

Determination of an Unsafe Contaminant Level

Given the means of analytical detection and measurement of a certain contaminant species, there are several ways in which standards could be enforced in occupational work areas. One way would be on-site analytical determinations, with continuous recording of the contaminant level. Although this method may be necessary in selected cases, the demands for specialized equipment and skilled operating personnel are so great, that it would not be feasible for standards enforcement in a large number of occupational work areas covered by the federal law. A second method, which is being given consideration in a NIOSH interagency agreement with the Naval Research Laboratory, is direct air sampling into an evacuated vessel. For this method, one must have means of supplying, evacuating, using, and shipping vessels large enough to give suitable analytical samples; and also allow for the calculaton of eight-hour, time-weighted averages from a non-linear rate of filling.

Table I

Allowable Factors for Excursions above TLV[a]

	Factor
TLV from 0 to 1 ppm or mg/m^3	*3*
TLV from 1 to 10 ppm or mg/m^3	*2*
TLV from 10 to 100 ppm or mg/m^3	*1.5*
TLV from 100 to 1000 ppm or mg/m^3	*1.25*

[a] *Unless TLV = Ceiling (C notation on ACGIH list of TLVs)*

Table II

Changes in ACGIH Adopted TLVs, 1972 to 1973

	1972		1973	
Species	ppm	mg/m^3	ppm	mg/m^3
Acetaldehyde	(200)[a]	(360)	100	180
Acetic Anhydride	(5)	(20)	C-5[b]	C-20
Allyl Glycidyl Ether	C-(10)	C-(45)	5	22
Ammonia	(50)	(35)	25	18
Bismuth Telluride	unlisted		–	10
Se-doped Bismuth Telluride	"		–	5
Butane	"		500	1200
Chloroform	C-(50)	C-(240)	50	240
Copper fumes	–	0.1	–	(1)
1,2-Dibromo ethane	C-(25)	C-(190)	20	145
1,1-Dichloroethane	(100)	(400)	200	820
Dichloroethyl Ether	C-(15)	C-(90)	5	30
Diisobutyl Ketone	(50)	(290)	25	150
Diquat	unlisted		–	5
2-Ethoxyethanol	(200)	(740)	100	370
Ethylene Glycol (particulate)	unlisted		–	10
Ethylene Glycol (vapor)	"		100	260
Fluorine	(0.1)	(0.2)	1	2
Furfuryl Alcohol	(50)	(200)	(5)	(20)
Germanium Tetrahydride	unlisted		0.2	0.6
Hexafluoroacetone	"		0.1	0.7
Isophorone	no values		(25)	(140)
Isopropyl Ether	" "		250	1050
Lead, Inorg. fumes & dusts	" "		–	0.15
Methylacrylonitrile	unlisted		1	3
Methyl Bromide	no values		15	60
Methylcyclohexanone	(100)	(470)	50	235
o-Methylcyclohexanone	(100)	(460)	50	230
Phenylphosphine	no values		C-0.05	C-0.25
Silicon	unlisted		–	10
Sulfur Tetrafluoride	"		0.1	0.4
Toluene	no values		100	375

[a] TLVs in parenthesis indicate species is in Notice of Intended Changes for that year

[b] C indicates TLV is also ceiling value

Table III

Changes in ACGIH Notice of Intended Changes, 1972 to 1973

	1972		1973	
Species	*ppm*	*mg/m^3*	*ppm*	*mg/m^3*
Ethylidene Norbornene	*0.2*	*0.6*	*C-5*[a]	*C-25*
Methyl Ethyl Ketone Peroxide	-	*C-1*	*C-0.2*	*C-1.5*
Paraffin Wax Fumes	-	*1*	-	*2*
Subtilisins	-	*0.003*	-	*0.0006*

[a] *C indicates TLV is also ceiling value.*

A third method of determination of contaminant concentration, and the one of concern for this discussion, is the collection of the contaminant species in an adsorber, followed by analysis of the adsorbed species at a remote analytical facility. The use of solid sorbents, in particular, is attractive for sampling trace contaminants. Some of the possible advantages of a solid sorbent as a sampling mechanism are:

1. *Sorbents with large surface areas and large pore volumes may have very high capacities for contaminant species, so that a small mass of sorbent can contain either excursion samples or long-time samples.*

2. *The solid sorbent, presumably in granular form in a tube, can be stored and shipped without any special precaution beyond sealing the tube.*

3. *The adsorbed species can be recovered in a concentrated form so that the sensitivity required of the analytical technique is considerably less than that for whole air sampling.*

4. *The trace contaminant can be recovered as the original species for analysis, so that positive identification can be made. The recovered species should also be present in quantitative representation of the amount collected.*

5. *A sampling system using solid sorbents can be compact and light in weight, and sorbents are not fragile or hazardous. This is important for personal sampling, where a sampling device is worn on the person of the worker, so that samples will truly represent his breathing space.*

6. *The solid sorbent approach requires technical skills in regard to the mechanics of the sampling, but no skill in chemical analysis is required outside of the remote laboratory.*

7. *With proper sorbent selection, it should be possible to sample a species of interest in the presence of other chemical species, and to complete the recovery and analysis with a minimum of interference.*

8. *A variety of solid sorbents, such as activated carbon, silica, alumina, zeolites, various metal oxides, and clays are available on the market; and many of these can be obtained in reproducible quality for the properties which affect their characteristics as trace contaminant adsorbents.*

Potential Sampling Problems

Several technical areas may pose problems in the development of solid sorbent sampling systems for a variety of contaminant species. Properties of the toxic species which determine its adsorbability and releasability from the sorbent are the molecular weight, molar volume, vapor pressure, polarizability, as well as the structure of chemical groups. The several hundred species of interest offer a wide variation in these properties, and it is likely that a multiple selection of sorbents would be needed to fulfil all demands for sampling. The problem is emphasized by the wide range of TLV's for various species and the necessity to sample excursions above the time-weighted allowable levels.

Once it is found that the sorbent has adequate capacity, it is still necessary to devise a means to desorb the adsorbed toxic species, and the desorption must either be quantitative, or a fixed proportion of that adsorbed. It is also necessary to insure that other species entering the "sorber" during the sampling period do not block the surface for further adsorption. At the very low partial pressures characteristic of TLV levels, adsorbed species often cover only a small portion of the total available surface area of the adsorbent. Although the extent of total surface area may seem to indicate a number of species could co-exist on the surface at concentrations consistent with the amount collected at TLV concentration levels, the site-energy distribution of the surface prohibits this. The less strongly adsorbed species can only occupy adsorption sites at the high energy end of the distribution. Therefore, when displaced by a more strongly adsorbed species, the less strongly adsorbed species desorb rather than move to lower energy sites on the surface. This was the case when, for example, adsorbed vinylidene chloride was displaced from charcoal by toluene (3).

Further constraints, which may occur in solid sorbent sampling, are that the sorbent capacity for the species of interest must be large enough to completely adsorb this material during the test period; the desorption method should yield all, or a constant proportion, of the adsorbate; and the adsorbed species should not be chemically changed by either adsorption or desorption. It is evident that a large enough adsorbent bed would provide sufficient capacity, but it will, at some point, be unacceptable in terms of the weight or volume of the sampling apparatus. A backup section in the sampling tube is useful to insure a valid test, when nothing is recovered from the backup. However, when the backup section also desorbs the species of interest, some doubt will exist concerning the maximum amount of contaminant in the sampled air stream.

Desorption of the adsorbed contaminant species is achieved by displacement with another, more strongly adsorbed, species or by raising the temperature. Examples of displacement are the desorption of solvent-type hydrocarbon species from charcoal by extracting in liquid carbon disulfide (4) and the desorption of aromatic amines from silica gel by extraction in liquid ethanol (5). An example of elevated temperature desorption is the "heat gun" technique for removal of formaldehyde from alumina sorbent (6). In liquid displacement the displacing species is not only more strongly adsorbed, but is also in extremely high volume concentration. The method yields a liquid extract which can be used for multiple analytical determinations. Disadvantages of liquid extraction are the dilution of the sample by the extracting material, and the fact that desorption efficiencies are not always 100% (Table IV). When the desorption efficiency is not 100%, the method is still useful and valid if the desorption efficiency has been established for the species of interest on the sorbents in use. The reason for less than complete desorption is not self-evident, as the displacing species is in overwhelming concentration and is strongly adsorbed. It can be presumed that some portion of the sample molecules are adsorbed at sites which have long exchange times compared to the time allowed for the experiment. These could be either high energy adsorption sites, or geometrically remote adsorption sites, i.e. small pores and cracks.

Table IV

*Desorption Efficiencies from Coconut Charcoal**

Compound	*% Recovered*
Benzene	*100*
Trichloroethylene	*100*
Cyclohexanone	*47*
1,1,2,2-Tetrachloroethane	*68*
Methyl Isobutyl Ketone	*89*
Methyl Ethyl Ketone	*62*
Toluene	*98*
Styrene	*80*
Cyclohexane	*100*

**NIOSH in-house data on Barneby-Chaney charcoals received 1-28-72 to 6-28-72 Addendum to Los Alamos Scientific Laboratory communication of 12-8-72 characterizing charcoals tested by NIOSH.*

When a solid sorbent is used in trace contaminant sampling, it is assumed that the species adsorbed is the same one that is identified and determined quantitatively in the subsequent analytical procedure. Therefore, the interaction of the adsorbed contaminant species with the sorbent, and with the displacing agent, cannot be so strong that irreversible chemical bonding occurs. When desorbed by heat, the adsorbate cannot be decomposed, or undergo any other reaction at the temperature necessary for desorption. The impact of these constraints is that a compromise must be found in the energy of interaction between the species of interest, the solid sorbent, and the displacing species. A possible exception is the case when the contaminant may be sampled and treated by a method which converts it in a known and reproducible manner for analysis. For example, trace CO can be determined after passing through a Sabatier reactor in which it is reduced quantitatively to methane (7).

All the problems associated with finding suitable sorbents, screening tests, sorbent modification, conformation of sorbent capacity, desorption efficiency and resistance to interference involve some kind of technical effort in the laboratory. When several hundred species are considered, on a list which is expanding and changing each year, it is evident that the funds, available manpower and facilities to develop finished methods must be allocated carefully.

Priority of Technical Efforts

The issue of technical priorities in methods development involves not only what species to work on, but also the relative effort devoted to screening new sorbents and analytical methods, modifying or developing new sampling systems and analytical methods, and verifying the reliability and precision of existing sampling systems and analytical methods.

From the list of toxic species, the following factors must be considered:

1. *the known or estimated toxicity of the species,*
2. *the frequency of occupational exposures to the species,*
3. *the frequency of requests by NIOSH or Department of Labor field personnel for determinations of whether a certain species exceeds the allowable level in occupational situations,*
4. *the impact of priorities of efforts on certain species on allowable levels in occupational situations and*
5. *the associated pressures from political motivations and public concern for various occupational hazards.*

One indication of the toxicity of a species is the TLV, since the more toxic species have lower TLV's. However, the TLV is the concentration allowable during work time without any harmful effects and the magnitude of the effect when concentrations greater than TLV are present is not part of the value. For example, carcinogens may be deadly around TLV limits, whereas solvent vapors may cause functional disorders above TLV limits. Also, a low TLV may not reflect a grave occupational toxicity problem if the species of interest is rarely found at that level in work areas. Some estimate of the frequency of human exposures to any particular contaminant has to be considered in its priority, and the frequency of requests for sampling and analysis reflects this factor.

From the point of view of the efficiency and productivity of laboratory development programs, we might ignore all factors except the "chemical continuity" of the species investigated under a given program. The term chemical continuity is used here to designate species with either similar chemical groups (such as amines, alcohols, etc.), similar vapor pressures, similar molecular sizes, similar retentivities in sorbent beds or columns, or similar responses to an analytical technique. It does not matter what criteria are used, as long as the chosen species are convenient to the investigations of the experimenter, and the techniques and knowledge learned in the methods development for one species can be applied to the others in the same program.

In defining programs and species priorities, a balance of the aforementioned factors should be considered. The task of developing and testing sampling and analytical methods for all possible contaminant species is very large, and the convenience and efficiency of experiments on a series with chemical continuity, in a given program, must be considered if a considerable portion of the task is to be accomplished.

Current Methods Status

One approach to the need for a large number of sampling and analytical methods that has been taken by NIOSH, is the classification of currently available methods. Table V gives five classifications and the number of contaminant species in each. Recommended methods are those which have been through a collaborative test program. It is expected that the methods for seven species now in this program* will become recommended when collaborative test results are evaluated. Tentative methods are those in wide use or recommended by other government agencies** or professional societies. The 133 operational methods are used by professional analysts but have not been thoroughly evaluated by NIOSH or professional societies. The 179 proposed methods have not been tested, but appear to be reasonable approaches to the sampling or analysis of particular species. They are based on literature background and similarity to methods in use for chemically similar species. The total of 371 species for all methods leaves some additional contaminants for which TLV limits have been set, but no methods considered.

Table VI shows proposed groupings of contaminants with similar experimental approaches to sampling and analysis. The first group, which is essentially the in-house development work, anticipates continued research on the use of charcoal tubes as sampling devices. Species whose vapor pressure and

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*The seven species currently in a collaborative test program are benzene, carbon tetrachloride, chloroform, methylene chloride, dioxane, trichlorethylene, and *m*-xylene.

**A tentative method has been submitted by Los Alamos Scientific Laboratory, under NIOSH Project R-059, for the aromatic amines (aniline; *o*-toluidine; N, N'-dimethyl aniline; *o* and *p*-anilidine; *o*, *m*, and *p*-xylidine; *o*-chloroaniline; and *p*-nitroaniline).

Table V

Current Methods Status

Class A	*Recommended*	*0 Species*
Class B	*Accepted*	*6 Species*
Class C	*Tentative*	*53 Species*
Class D	*Operational*	*133 Species*
Class E	*Proposed*	*179 Species*

Table VI

Proposed Groups of Contaminant Species for Methods Development

Group 1 -- Solvent hydrocarbons, CS_2, ethers, chlorinated aliphatics, volatile monomers, alcohols, nitriles, phenols

Group 2 -- Ketones, aldehydes, aromatic and aliphatic amines, some volatile inorganic species

Group 3 -- Various inorganic gases - NH_3, SO_2, NO, NO_2, HCl, HNO_3, CO, $COCl_2$, Cl_2, F_2, HF

Group 4 -- CO, O_3, H_2S, AsH_3, HCN, MDI, TDI

Group 5 -- Carcinogens (coal tar pitch, Ni carbonyl, 4-amino diphenyl, benzidine, bischloromethyl ether, beta-naphthylamine, etc.)

Group 6 -- Pesticides (organic phosphorous compounds, chlorinated diphenyl, parathion, etc.)

adsorptivity are in the same range as that of the common solvent hydrocarbons would be most amenable to extension of this program. In many cases, experimental work should be preceeded by some estimate of the suitability of charcoal tube adsorbents for the particular species at the required TLV levels. This problem is treated in more detail in a subsequent section.

A second proposed group of species includes butanes, aldehydes, amines, and some inorganics such as hydrazine. These are in a similar vapor pressure range to the sorbent hydrocarbons and are more polar due to substituent groups. Screening of a variety of sorbents may be necessary to find materials of suitable retentivity and desorption characteristics.

The inorganic gases such as ammonia, sulfur dioxide, carbon monoxide, the halogen gases, and oxides of nitrogen are a group which can be studied together and, due to their high vapor pressure, may require specialized adsorbents. The most suitable analytical technique is mass spectrometry, or mass spectrometry combined with gas chromatography. Since the sensitivity and versatility of this type of instrumentation is applicable to all the species of group 3, they make a suitable project for simultaneous study. The group 4 species includes inorganic gases which could be part of the aforementioned study. However, the possibility of solid sorbent detector tubes was considered for these species -- that is, sorbent tubes containing a reagent which reacts with the adsorbate and produces a spectral, or other, change which can be measured directly on the tube, or on an extract from the tube.

The fifth group includes chemical species defined as carcinogens, which have emergency standard TLV's at the lowest detectable level. A number of these species are multiple benzenoid ring structures with amino or imino functional groups, and relatively high molecular weights and low vapor pressures. Methods should be developed for these species in one program, due to chemical similarities as well as the low detection levels necessary, and the precautions needed in handling these species in the laboratory. A sixth group is the pesticides, because they have been in widespread use, and it should be possible to find a development laboratory with special experience in their collection and detection. As a low level detection may be necessary, the sampling techniques for pesticides may involve a higher atmospheric throughput in the sorbent device, than is the case for species to be detected at higher TLV levels. The tentative species groupings (Table VI) do not have a common rationale of chemical differentiation, or required adsorption or detection equipment. They are, however, grouped by technical considerations of the methods development.

The current programs in methods development by NIOSH, and associated government laboratories and contractors, are listed in Table VII. The group of species under investigation at the Los Alamos Scientific Laboratory (LASL) emphasizes organic amines. The group under investigation at the Aeronautical Research Laboratory (ARL) is suitable for mass spectrometric studies, while NIOSH in-house work continues to emphasize charcoal adsorbent tubes, desorption in CS_2 *eluate, and gas chromatographic analysis.*

Table VII

Current Assigned Methods Development

1. *Southern Research Institute* - Acrylonitrile, nitrogylcerine, ethylene glycol dinitrate, phosgene, methyl chloride.*

2. *National Bureau of Standards** - Cl_2, F_2, HF, HCN, PH_3, O_3, TDI, CO.*

3. *Aeronautical Research Lab USAF** - NH_3, SO_2, NO, NO_2, N_2O, HCl, HNO_3.*

4. *Los Alamos Scientific Lab AEC** - Formaldehyde; acrolein; methyl, ethyl, isopropyl, butyl, cyclohexyl, dimethyl, diethyl, and triethyl amine; ethylenediamine; ethanolamine; diethylenetriamine; diisopropylamine; morpholine; ethylene and propylene imine; N-ethyl morpholine; 2-diethyl and 2-dibutyl aminoethanol; methyl and 1,1-dimethylhydrazine.*

5. *NIOSH In-house - Various solvent hydrocarbons, ethers, chlorinated aliphatics, volatile monomers, coke oven emissions, etc.*

**Contract with NIOSH*
***Interagency Agreement*

Solid Sorbent Qualification and Selection

In research carried out to date at NIOSH and associated laboratories, a number of solid sorbent materials have been tested for their capacity and desorption characteristics. The most useful is activated carbon, which is recommended, or in use, by NIOSH for sampling solvent hydrocarbons, dioxane, chlorinated alphatics, styrene, vinyl chloride, carbon disulfide and other species totaling over 180 compounds. The activated carbon currently in use is a cocoanut shell charcoal manufactured to NIOSH specifications.*

Other solid sorbents in current use in the occupational safety and health program are:

1. *silica gel - recommended for aromatic amines in tentative method submitted by LASL,*
2. *alumina - recommended for formaldehyde adsorption by LASL, and*
3. *molecular sieve 5A zeolite - recommended for* SO_2 *adsorption by ARL.*

The choice of sorbent may hinge on the type of interaction needed for the sampling system. In general, the type of adsorption may be characterized as physical adsorption or chemisorption. There is overlap, however, in the magnitude of heat effects for physical adsorption and chemisorption. Criteria such as electron transfer (8) and surface mobility (9) are more clear-cut in concept but not as straightforward in measurement. Table VIII lists some generally observed criteria for differentiating physical adsorption and chemisorption. For the purpose of sampling trace contaminant species on solid sorbents, physical adsorption is generally preferred. However, for cases in which specificity for a given species is desired, as well as a high capacity using the total surface, chemisorption is desirable, providing desorption reversibility is maintained. Therefore, a compromise in physical adsorption and chemisorption characteristics is needed for the atmospheric sampling of contaminant species at TLV levels.

Prediction of Adsorption

Due to the wide range of chemical species, and of TLV levels, it would be of some value to correlate the physical adsorption data obtained in tests with various conditions and species. This would allow prediction of the applicability of a sorbent to any new species for which a sampling test was being developed.

A method which has proved useful for predicting the adsorption of trace contaminants in manned spacecraft contaminant control systems (10) is the application of the Polanyi-Dubinin potential plot. The procedure for this approach is as follows:

1. Physical adsorption data are obtained on the sorbent over a range of partial pressure, equilibrium saturated vapor pressure, temperature, and molar volume values.

**Mine Safety Appliances Co., Pittsburgh, Pa.*

Table VIII

Adsorption on Solid Sorbents

Physical	*Chemical*
Generalized - all species at high P/Po	*Specific chemical interactions*
No electron transfer	*Electron transfer*
Rate of adsorption often fast	*Rate of adsorption often slow*
Mobile adsorbed film	*Immobile adsorbed film*
Adsorbate desorbed by lower P or higher T or displacement *e.g. butane on carbon,* N_2 *on carbon*	*Adsorption may or may not be reversible with P and T* *e.g.* H_2 *on nickel,* O_2 *on tungsten,* SO_2 *on* Cu_2O

2. The data is plotted as log volume adsorbed vs. T/V log p_o/p, where T is the experimental temperature, V is the molar volume of the adsorbate, p_o is the saturation vapor pressure of the adsorbate, and p is the partial pressure of the adsorbate in the experiment.

3. The plot then shows physical adsorption for all vapors over a wide range of temperature and pressure conditions, and allows prediction of the adsorption capacity of the sorbate for any species for which the saturation vapor pressure and the molar volume are known. Such predictions have been made for the adsorption of trace contaminants anticipated in manned spacecraft, and incorporated into the recommended design for the atmospheric control system (11).

Sorbent Choice, Specificity, Modification, and Characterization

A wide variety of natural and synthetic materials may be considered for solid sorbent sampling. Some major types are: the activated charcoals and carbons, including carbonized polymers; silicas, including gels, aerosols, flame-formed silica, and porous glass; other metal oxides, including alumina and most heavy metal oxides; "molecular sieve" type synthetic zeolites; other combinations of silica and alumina either found naturally (e.g. clays), or formed synthetically (e.g., either silica or alumina catalysts); and porous polymer beads.

Although physical adsorption is generally non-specific, it is possible to consider some degree of specificity in adsorption on the higher energy sites of a given adsorbent. Such specificity may be a function of ions at the surface, the chemical groups at the surface, the pore size distribution of the solid sorbent, dispersed metals or other additives, or non-volatile surface coatings which have been added to the sorbent.

Modifications can be made in the adsorptivity of a given adsorbent material by:

(a) changing the pore size distribution by sintering, oxidation, reduction, or reacting the surface with other species,

(b) impregnation of the adsorbent by metal salts or solutions containing reactive chemicals, or

(c) changing the chemistry of the surface by attachment of other groups (e.g. silane reacting with silica OH surface groups), or surface oxidation or reduction, or coating the surface with a non-volatile film.

These modifications may also introduce specificity to the adsorbent surface by the introduction of higher energy adsorption sites to react with the species of interest. Increasing specificity of adsorption may then conflict with the thermodynamic reversibility of the process, and inhibit the quantitative desorption of the selected contaminant species.

Since adsorbents with different properties are desirable for sampling different species, it would be valuable to be able to characterize the *adsorbents by tests other than the actual sampling procedure. This would insure the consistency of batches and guide the screening of new adsorbents to determine what fundamental properties are desirable in a given sampling situation.*

Various tests have been traditionally used in the characterization of adsorbents and porous catalysts. These are:

(a) Surface area - that is, total extent of surface on the same scale as the molecular size of the interacting species. This is often equated to the monolayer capacity of the porous material for some adsorbate, such as nitrogen, which enters the pore structure and adsorbs on the solid surface.

(b) Pore size distribution - given as the volume and area of pores in a number of discrete pore size ranges. The area within pores from about 10-300 Å radius is the greatest contribution to total adsorbent surface area. This parameter is obtained from analysis of vapor adsorption data or non-wetting liquid (e.g., mercury) intrustion data.

(c) Surface acidity or basicity - a chemical characterization of the porous solid surface, which, in the case of catalysts, can be determined and defined in terms of acidic or basic site concentrations in discrete pK_a *ranges. The situation is less clear in the case of activated charcoal, but it is well known that so-called "H-chars" or "L-chars" (12) can be made by treatment of the carbon in either reducing or oxidizing atmospheres.*

(d) Surface polarity - another chemical characterization, primarily related to the concentration of hydroxyl, oxide, or other polar surface groups. The state of the surface can be determined quantitatively by analysis of adsorption isotherms of water and hydrocarbon on the adsorbent (13).

(e) Adsorption site energy distribution - this may be ascertained by analytical treatment of calorimetric and isotherm data (14). It is not a straightforward measurement for porous materials due to molecular sieve and capillary condensation effects.

(f) Adsorption tests with the contaminant species of interest such as complete isotherms, breakthrough curves, and retention time of injected volumes.

All these tests are directly related to adsorbent properties of interest to contaminant sampling. However, none of them has unique significance in the monitoring of adsorbent batch consistency, or the prediction of adsorbent suitability for a given sampling procedure. The routine test that appears to have the most potential in relation to the sampling of contaminant species is the retention time test on the injected species. This technique is being tested at LASL and is the subject of an associated paper by Dr. Wood (15). Breakthrough curves and adsorption isotherms of the contaminant species of interest are very valuable, but more tedious to obtain. A more thorough discussion of breakthrough curves is given in the associated paper by Dr. Teass et al. (16). Direct characterization of *vapor species-adsorbent interactions seems to be a more fruitful use of a limited research and development effort than indirect characterizations of the adsorbent. However, in some sampling problems, a better understanding of the efficacy of a given adsorbent is of primary interest, and sorbent characterizations such as pore structure and adsorption energies may be helpful.*

Steps for Development of a Sampling and Analysis Procedure for a New Species

For each new species considered for solid sorbent sampling techniques, a series of steps should be taken prior to the formulation of a tentative method. These steps are:

1. *Choose the prospective sorbent or sorbents to be used by whatever background investigation and tests are appropriate.*
2. *Set up a contaminant generation system for the generation of the desired species at TLV levels.*
3. *Obtain breakthrough data on the contaminant species with the chosen sorbent or sorbents at simulated operational conditions.*
4. *Investigate the method required for desorption of the contaminant species from the sampling tube and obtain enough retentivity data for statistical analysis of the reliability of the sampling and desorption methods.*
5. *Obtain so-called "bleed-out data" showing whether the sampling in the adsorption tube is displaced by carrier gas or by other species likely to be present in the sampling environment.*
6. *Obtain storage data on the sampling tubes both before and after contaminant sampling to make sure the sorbent is stable and that migration to the back-up adsorbent bed is not so rapid that the analysis of the beds fails to differentiate adequate retentivity from sample breakthrough.*

These steps are delineated to show that each new contaminant to be sampled at TLV levels represents a sizable project in terms of the efforts demanded of laboratory personnel. Balanced priority should allow timely development of the methods required for trace contaminant sampling in occupational work areas.

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Discussion

Dr. Dravnicks: *May I make a remark regarding this adsorption plot, in terms of a so-called "potential plot". In some cases where the pore size is very small, do you have to use the square of log p_O/p?*

Dr. Ballou: *You are quite correct.*

Dr. Klier: *I thought there was room for the square on the slide, or was that just a typing error?*

Dr. Ballou: *The way I have used the potential plot is with the abscissa T/V log p_O/p, but also there is another correlation, which may be more suitable for adsorbents with micropores, in which the log of the pressure ratio is squared. I proposed the use of log p_O/p as there is extensive experimental background in the use of this correlation for the prediction of adsorption of contaminants at TLV levels on activated carbon beds.*

Dr. Dravnicks: *I think where the pores are small, the plot of the square of the pressure ratio tends to be more linear.*

Dr. Ballou: *I think you are right. In my plot, high molecular weight adsorbates would be in the upper left, and that is nonlinear and the square plot would be better.*

RESEARCH AND USE OF SOLID SORBENTS BY THE U.S. ENVIRONMENTAL PROTECTION AGENCY FOR OZONE, NITROGEN OXIDES, AND SULFUR DIOXIDE

by Andrew O'Keeffe

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Responsibility and Objectives

The group within EPA that I speak for is the Chemistry and Physics Laboratory in the Environmental Research Center, North Carolina, where I have a Branch called the Air Quality Measurement Methods Branch, whose responsibility is the provision of methods for measuring air pollutants in the ambient air. This is in contrast to the measurement of pollutants in stacks or sources, which is the specific responsibility of another Branch.

Our principal development program over the few years that we have been in existence has concentrated on reliability, using the term in a broad sense. We have considered that feature more important for the time being than any other consideration, such as cost, size, or color.

We believe that we have accomplished at least a first approximation of the objective of providing reliable methods for the most common pollutants. Now we can indulge in what would have been the luxury of turning to two other needs, both of which can be satisfied by a single development effort.

One is the need for simple yet reliable methods that are financially within the reach of smaller governmental and industrial units; in other words, less costly means of measuring air pollutants in the ambient air. It is just plain common sense that they must come.

The other is the need for methods capable of providing information regarding pollutant concentration integrated over periods of time in the range, say, from hours to days, just the type of things Dr. Ballou has discussed - the need for a time-integrated measurement of pollutant concentration.

The many difficulties that we experienced in the years prior to the existence of this program lay in trying to apply classical analytical schemes involving solution chemistry, in the precise metering of the liquid reagents which are often corrosive, and in the instability of reagents or of the reagent-pollutant adducts.

The Use of Solid Sorbents

The inconsistent performance of gas-liquid scrubbers depending on bubble size (for instance), column height and many other variables, suggested advantages to be found in systems in which the pollutant is collected (that is, sorbed without saying whether it's ad- or ab-) on a solid reagent for transport to the laboratory and eventually for analysis at that point. This is exactly the overview that Dr. Ballou gave.

The extended surface of such a sorbent is more readily reproducible and more constant in its appetite for the pollutant than is a solution. I'd like you to follow that through in your own mind, and I think most of you will agree with me.

The reasoning I have just gone through puts me approximately at the place where Dr. Tswett was in about 1895 when the lightning struck, and he had invented chromatography. I believe he was trying to isolate the chlorophylls or some plant pigments, and he had been doing it in separatory funnels, doing liquid-liquid extraction. He had a bathtub and gallon buckets and paint cans and everything else filled with liquid, and he still hadn't gotten anywhere. Then the lightning struck and he came up with the thought that sorption on a solid for analytical purposes is far superior to liquid-liquid or gas-liquid extraction.

As I implied early in my introductory remarks, our developmental effort on use of solid sorbents is presently in an extremely early stage, so much so, that very little of what I have to say is going to be experimental fact. Rather, it's fact with a large amount of prediction mixed in, and I am not going to attempt to untangle the two. I will try to run through for the three gases named in the title of my paper what we have going, what we hope to do and perhaps what the solid sorbent device of a few years from now might look like.

Detection of SO_2

Considering the several pollutants in the order of their known health effects, let's start with SO_2. In that case we can go way back in history. I must admit I don't know how far. Sulfur dioxide has long been collected on the lead oxide candle.

Perhaps if somebody were to take the lead candle and reconstitute it with some simple sample-metering device so that it's not totally dependent upon convection to get that which is measured to the storage device, it might take over.

Other sorbents studies (and about-to-be studies) for SO_2 include triethanolamine. This does pick up SO_2 quantitatively at tens of parts per billion, at least, and it certainly releases it on simple heating. We don't yet know whether this release is quantitative, but hope to soon find out.

A potential sorbent that has intrigued me for several years since I just simply stumbled on it in reading is camphor. There are several articles way back in the literature, showing that camphor is an excellent solvent for SO_2, one mole of camphor dissolving more than 2 moles of SO_2. Evidently, camphor has a tremendous thirst for SO_2. This indicates that it may well serve to collect SO_2 from the air. Once collected, SO_2 can easily be quantified by releasing it (as by heating) and passing it into a flame photometric sulfur detector. It is immaterial whether the dissolved SO_2 is released as SO_2 or is converted into some other volatile sulfur compound, as the FPD can measure either with equal facility.

Further work on SO_2 sorbents is being carried out by Dr. Lambert of Kansas State University, who has synthesized some thiadiazole derivatives that exhibit a high degree of specificity in their ability to abstract SO_2 specifically from gas mixtures. This work may, in the long term, lead to a practical analytical sorbent.

Detection of NO and NO_2

Triethanolamine has been much publicized within the past several years as a sorbent for NO_2. (Parenthetically, my definition of a solid sorbent, admittedly a very loose definition, includes gas chromatographic column packing materials such as, for example, diatomaceous earth coated with liquid triethanolamine.)

The Mishmash reaction uses lead oxide, which reacts with either NO or NO_2 to produce lead nitrate. This can be measured by means of a nitrate-specific electrode, or by other convenient means.

A related reaction that has met with a small degree of success is the use of cobaltic oxide in an analogous manner. However, cobaltic oxide is much more amenable to recovery of the NO_x by simple heating than is the lead oxide. This suggests a much simpler overall system.

Metallic copper has been studied by Dr. B. E. Saltzman. He reports that he can sorb NO_x, either nitric oxide or nitrogen dioxide, on copper metal. He first started out using copper shot and soon realized that, by exposing a larger surface, he could have a more efficient operation. Recovery of NO_2 for measurement is accomplished thermally.

Detection of Ozone

Ozone poses a difficult problem when the task is one of collecting and holding ozone, then transporting it to the laboratory for analysis later. However, a group in NASA interested in the most academic type of photochemistry, the kinetics of certain ozone reactions, came to us within the past few months with a scheme that is certainly intriguing and offers the possibility of effectively collecting and transporting ozone. It's done in this way: Their compound of choice presently for solid sorbent is rubrene, a tetraphenylnaphthacene which reacts with ozone *to produce a metastable adduct. Let's call it an ozonide, for lack of a better term. This ozonide remains stable in storage and during transport. Once it's in the laboratory the measurement step consists of heating this ozonide to about 50 degrees Centigrade, at which point the ozonide emits large numbers of photons which can be counted and can be directly related to the ozone exposure of that sample.*

It's not quite as simple as that. There is some difficulty in that the rubrene must be protected from light, because when it's exposed to ozone, you get a perturbation of the ozonide formation due to atmospheric molecular oxygen. I do not mean that the molecular oxygen-to-ozone conversion actually takes place, but as far as the reaction with rubrene is concerned, it might just as well have taken place.

We are on the verge of funding an interagency agreement with NASA, largely to support this work and to carry it further along. They are interested in bringing this to a workable stage and then extending that type of thinking to possible application to other bothersome pollutants, like NO_2*.*

Idealized Solid Sorbent

Now I'd like to back off a little bit and indulge in a bit of conjecture on what our ideal solid sorbent should look like. I don't mean the cartridge containing the solvent, but the individual particles of the sorbent. Let's assume that that is -- we will take the simplest example, the first example that comes to mind, lead oxide, that is going to be used to sorb SO_2*. The adduct form presumably is lead sulphate which has zero vapor pressure. In other works, the reaction of* SO_2 *with lead oxide is a one-way nonequilibrium reaction. To determine the concentration of* SO_2 *in air, knowing the amount of* SO_2 *sorbed, it is necessary that we also know the volume of air from which it was extracted. In other words, it is necessary to have a reasonably accurate metering device.*

There has been a great deal of interest, gradually increasing over the last two years, in the strategy of placing a permeable membrane barrier between the lead oxide (or other sorbent) and the air being sampled. The rate of SO_2 *permeation through the membrane will be in proportion to the* SO_2 *partial presure, not to the absolute quantity of* SO_2*. Therefore, in such a system it is not necessary to meter the air sample.*

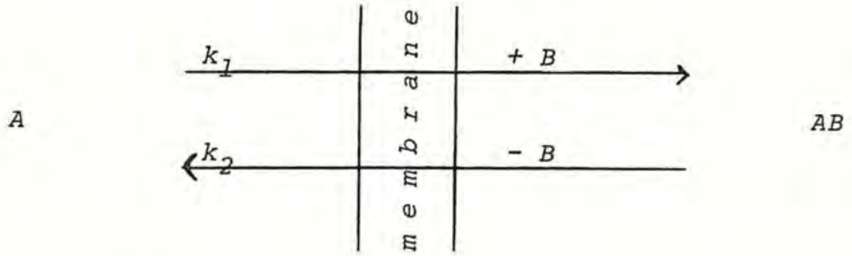
Dr. Philip West of Louisiana State has recently published a simple scheme wherein he has used West-Gaecke solution and a silicone membrane to collect SO_2 *in a manner exactly analogous to that just outlined. Quantification involves only the measurement of the color developed in the West-Gaecke reagent.*

We should certainly give serious consideration to the advantages that lie in using a solid sorbent, as discussed earlier, and at the same time providing a barrier between that sorbent and the atmosphere which is to be sampled. The combined effect is one of greatly simplifying the tasks of collecting a pollutant gas for transmission to the laboratory, and eventual analysis.

Discussion

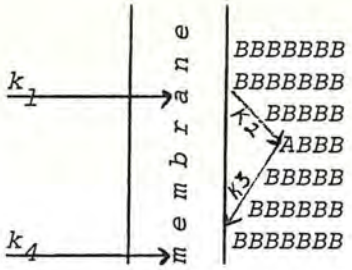
DR. KLIER: I was wondering if this system does not really need a reversible rather than irreversible sorbent.

MR. O'KEEFFE: Consider first the collection of pollutant A by permeation through a membrane, followed by its irreversible combination with reagent B to form AB:



Permeation in the forward direction is at a rate, k_1*, proportional to partial pressure of A. Since formation of AB is irreversible, than the rate of permeation in the reverse direction* $k_2 = 0$*. The accumulation of A on the right will accurately represent the integrated product of concentration and time of exposure.*

Next, consider the collection of A by permeation, followed by solution in solid sorbent B.



As in the previous case, k_1 *is proportional to partial pressure of A. After dissolving in B, A must diffuse into the bulk of B else capacity will be limited to a monolayer of A at the interface of the membrane and B. That is, the rate of diffusion* $k_2 > 0$*. Reverse diffusion and escape of A from B will be at a rate* $k_3 << k_2$*. Further, because B is a solid, both* k_2 *and* k_3 *will be small. The reverse permeation rate* k_4*, being dependent on* k_3*, will approach zero. Overall, accumulation of A in B will approximate the integrated product of concentration and time. The accuracy of this approximation will have to be determined in one or more real cases in order - hopefully - to establish the general validity of the method.*

The chief advantage of the second (reversible) case over the first lies in the analysis step. Assuming that heating gives quantitative release of A from its solution, existing (instrumental) methods of measuring A can be applied, whereas the irreversible-combination case may necessitate the evolution of new methodology for measuring AB. It should be noted that this advantage is largely fortuitous, and that it exists to a greater degree with respect to problems of EPA than to those of NIOSH.

SURFACE CHEMISTRY OF TRANSITION ION-DOPED SOLID SORBENTS

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Characteristics of Surface Complexes

Transition metal ions placed in solid surfaces are known to function as selective adsorption centers for various molecules. Surface complexes thus formed resemble in some respects the organometallic coordination complexes but in other respects have characteristic features of their own. The energy of formation of their surface complexes can often be controlled by the characteristics of the solid surface and the metal ion. Among the analytical applications are color indicators for various molecules based on the spectral changes induced by binding of molecules onto the metal ions. Fluorescence studies of transition metal complexes with trapped molecules are just beginning. Chromatography on aluminosilicate sorbents such as zeolites is a well established discipline but its potential may be enhanced by introducing selective adsorption centers for certain molecules by ion exchange.

Selectivity of the transition ion sorption complexes exhibits itself in characteristic shapes of adsorption isotherms, in adsorption energies, and in changes of physical properties such as optical spectra, magnetic moment, quadrupole moment at the nucleus, and various spin characteristics such as NMR hyperfine splitting and spin relaxation times. I shall give a few examples demonstrating the properties of sorption complexes between Type A molecular sieve zeolite, and ions such as Ni^{2+}, Co^{2+}, Fe^{3+}, Cr^{2+}, Cr^{3+}, *and inorganic as well as organic sorbates. Type A zeolite is superior to Types X, Y, mordenites, and sheet silicates in that it sustains the metal ions in well defined surface sites of uniform properties.*

Adsorption on A Zeolites

An example of olefin sorption complexes is the Co(II) A-ethylene system. The properties of this system are illustrated in Figures 1-4. Figure 1 shows adsorption isotherms of ethylene in Co(II) A zeolite with two distinct regions, a cobalt-specific adsorption at pressures less than 1 torr, and a non-specific adsorption at higher pressures. Figure 2 demonstrates the changes in adsorption energy in these two adsorption regions. The bare Co(II)A site has a structure shown in Figure 3. Cobalt is placed in a trigonal position in an oxygen six-ring of the aluminosilicate skeleton. Similar sites exist in the surfaces of sheet silicates (Figure 4) such as micas or montmorillonites.

X-ray crystallography has shown conclusively that the olefins and acetylenes are bonded by a π-bond and that acetylene (and probably also ethylene) freely rotate about the axis of this bond. This was also concluded earlier from optical studies. The next few figures demonstrate the spectacular spectral changes on adsorption. Figure 5 shows the electronic spectra of Co(II)A zeolite without any ligands (curve 1) and the presence of gases that cause relatively minor changes in the optical spectra (curves 2-4). Figure 6 demonstrates the differences among the spectra of CO(II)A with adsorbed N_2O, cyclopropane, and water, all of which are axial ligands of different strengths, and Figure 7 shows the spectral changes of CO(II)A on adsorption of the π-ligands ethylene, propylene, and acetylene.

All these changes are accompanied by visible color changes of the zeolite samples. For strongly adsorbing species such as water, the color changes proceed zonally in a zeolite bed; for weakly adsorbing species the whole sample changes color at once (N_2O). Optical spectra show greater detail, such as the small shift of frequency between propylene and ethylene. It is even possible to distinguish between cis- and trans- but-2-ene; cis-butene has spectrum shifted by -580 cm^{-1} from ethylene and trans-butene by -800 cm^{-1}. These changes are well understood within the framework of ligand field theory from the varying ligand field strengths of the above olefins. A simplified model for an olefin on Co(II) site is one in which the olefin plus the three base oxygens form a tetrahedral component of the ligand field and the "rest" of the olefin molecule a low-symmetry component.

A corresponding ligand-field term splitting diagram is in Figure 8 in which the left-hand side demonstrates the effect of the tetrahedral component of the ligand field, and the right-hand side the effect of the low symmetry component due to the linear nature of the double bond. The earlier described shifts can be explained as steric effects; ethylene is sterically unhindered and therefore represents the strongest ligand, trans-but-2-ene is most sterically hindered and represents the weakest ligand.

Similar complexes are formed with ions other than Co(II), and a pictorial representation of electron jumps in Ni(II)A with adsorbed molecules is given in Figure 9. The spectral changes are easily understood; the adsorbed molecule is a perturbation on the electronic system of the metal ion such that it repels the electrons in out-of-plane orbitals (e.g. d_{z^2}), shifts their energies closer to those of the in-plane orbitals ($d_{x^2-y^2}$, d_{xy}) and thereby causes bathochromic shifts on all spectra. The details of the band splitting are then determined by the symmetry of the adsorbed molecules. The symmetries in question are summarized in Figure 10. Within each of these symmetry groups, the individual molecules exert different ligand field strengths giving rise to the earlier mentioned spectral shifts.

Interaction of Transition Ions with Water

On hydrophilic surfaces such as those of the zeolites, the sorbing molecules always compete with water when present in the system. Therefore, I shall give some information on the interactions of the transition ions with water. The water sorption and reactions can be followed conveniently in the near-infrared region by monitoring the molecular water bands $(\nu + \delta)$ *and* 2ν *illustrated in Figures 11 and 12. The surface hydroxyls that are sometimes formed from water can be followed by monitoring the silanol* 2ν *band at 7300* cm^{-1}*. Detailed analysis of these NIR spectra permits the determination of the structure of water and OH containing complexes with the metal ions. Apart from the monoaquo-complexes described earlier, intermediate hydrates have been identified such as the Cu(II) tetrahydrate in montmorillonite depicted in Figure 13; eventually hexahydrates are formed. The orientation of these hydrates has been determined from the anisotropies of the g-tensor in ESR. Evidence for Ni(II) hexahydrates in zeolites comes from the similarity of the optical spectra of the water-Ni(II)A complexes with spectra of the* $Ni(H_2O)_6^{2+}$ *ions in solutions, shown in Figure 14. Water is a strong ligand, however, and in zeolite beds is usually separated from the mixture with other gases in the top most layer. The more weakly adsorbing gases then proceed ahead in the column in a dry state and form sorption complexes of their own which can be identified separately.*

Complexes with Organic Molecules

An important trend in the chemistry of transition metal ion-doped surfaces is the investigation of complexes with larger organic molecules which can develop into the synthesis of surface chelates, some of which may be of value in analysis for selectively sorbed molecules. Although not analytical in nature, a few examples are given of imidazole complexes synthesized and characterized in our laboratory. The complex of imidazole iron is represented in Figure 15. We have followed the reactions of such complexes as model enzyme reactions.

One of the reactions of interest to us is the proton abstraction which occurs according to the scheme in Figure 16. Figure 16 shows that the zeolite sorption complex can accommodate further imidazole molecules, up to 6 per cobalt ion, which on desorption returns to the 1:1 imidazole-cobalt complex.

Adsorption of Open-Shell Ligands

So far the complexes described are ones in which the adsorbed molecule is a closed shell system and does not undergo reactions with breaking of the closed shell. There is a substantial group of ligands, however, that are radicals or decompose with the formation of open-shell ligands. Such molecules are, for example, O_2*, NO, and* N_2O*. These ligands give rise to charge transfer complexes with some of the transition metal ions. For example, the oxygen molecule is not adsorbed on most of the normal valency* *metal ions of the first transition series but does undergo interesting reactions with the Cr(II) ions in Type A zeolite. The O_2-Cr(II)A isotherm is shown in Figure 17, and the corresponding spectra in Figure 18. The features of the N_2O-Cr(II)A and O_2-Cr(II)A spectra are (a) reversibility, (b) similarity of the two spectra, and (c) high intensity of the bands. Although an interpretation of these charge transfer spectra is presently unavailable, it is clear that the optical transitions must be due to electron jumps between molecular orbitals shared by the adsorbed molecule and the central ion Cr(II). Such a situation is particularly conducive to long lifetimes of excited luminescent states, as documentated for example by the recent work of Harrigan and Crosby (1) on the luminescence in ruthenium complexes.*

The luminescence in such complexes originates from jumps of the system from one spin multiplicity state to another, and its wavelength is determined by the energy difference between the excited low multiplicity states and the ground state which regularly is the highest multiplicity state. Such a situation is illustrated on the complete energy term diagram of the Ni(II) ions in trigonal fields where the ground state is a triplet and the excited states are singlets (Figure 19). An interesting observation has been made recently that nitric oxide (NO) forms a charge transfer complex with the Co(II) ions which are otherwise inert toward oxygen. Because of the great sensitivity of the measurements of fluorescence, it is likely that surface charge transfer complexes of the type described will be of analytical significance.

Conclusions

In conclusion, we discussed phenomena which result in selective identification of various molecules through physiochemical properties of their sorption complexes with transition metal ions in aluminosilicate surfaces and we propose that fluorescence of these sorption complexes be investigated both from theoretical point of view and from the viewpoint of analytical applications.

Reference

1. *Harrigan, R. W., and Crosby, G. A., J. Chem. Phys. 59, 3468 (1973).*

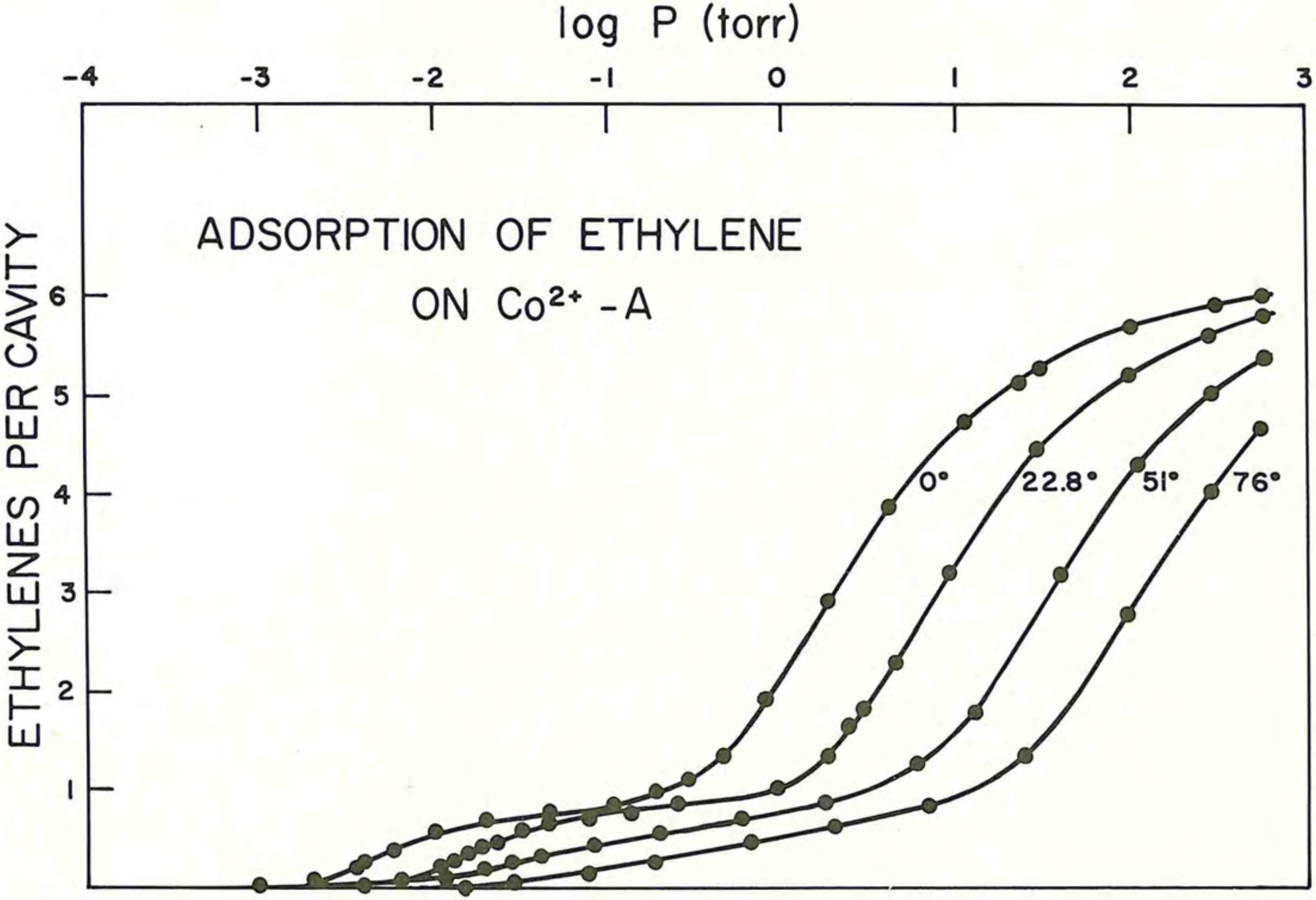


Figure 1. The Co(II)A-Ethylene Isotherms at 0°-76°C.

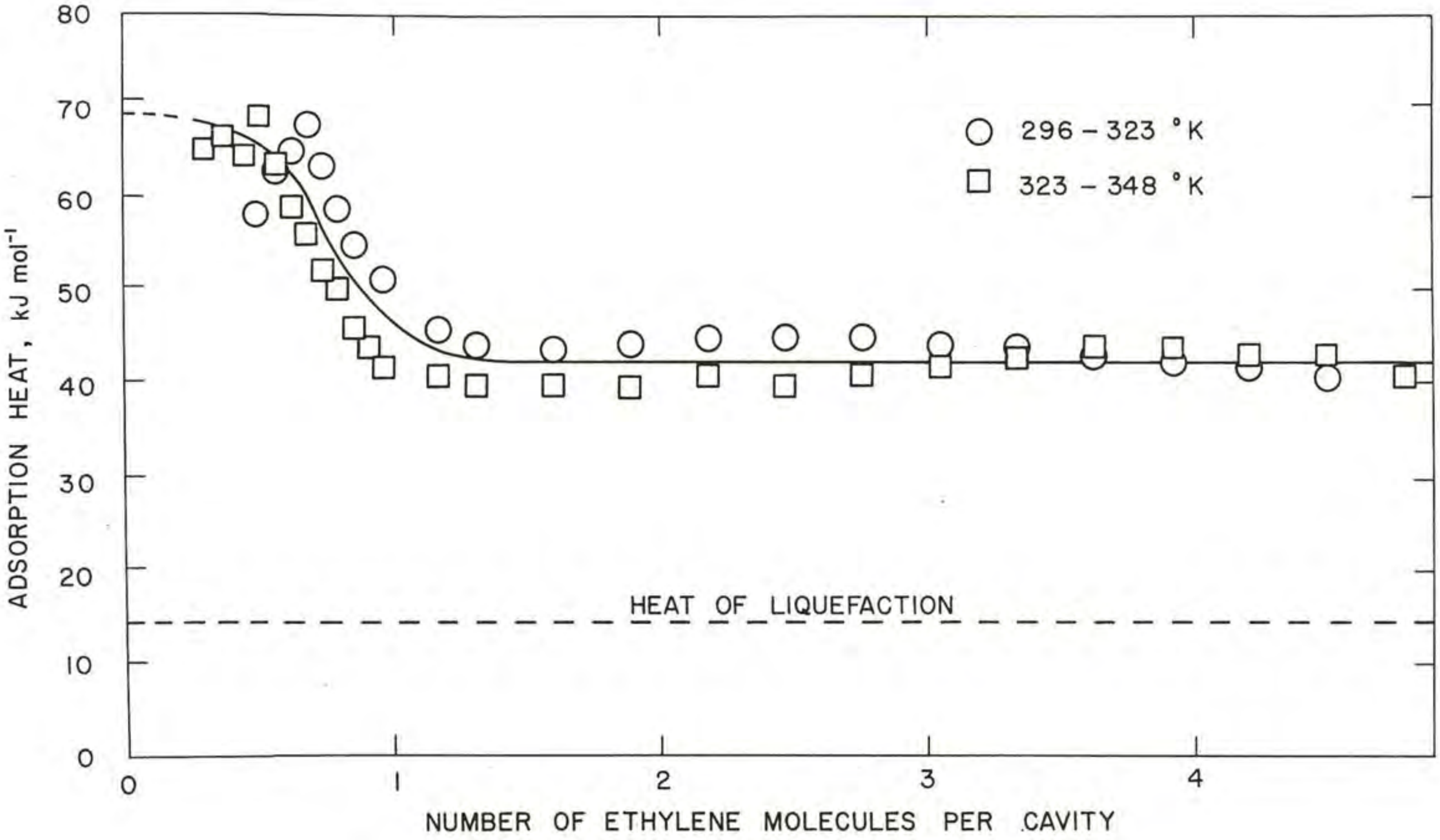


Figure 2. Heats of Adsorption of Ethylene in Co(II)A.

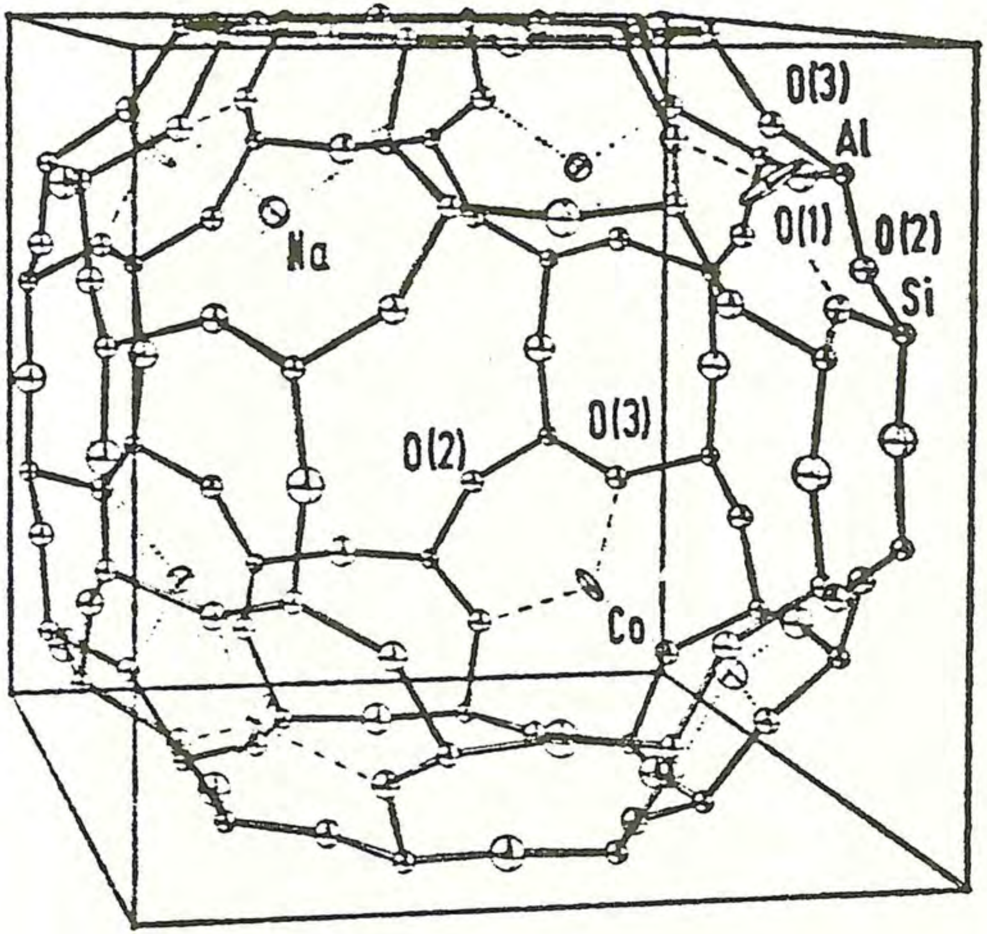


Figure 3. The Unit Cell of Partially Co(II)-Exchanged Fully Dehydrated Zeolite A.

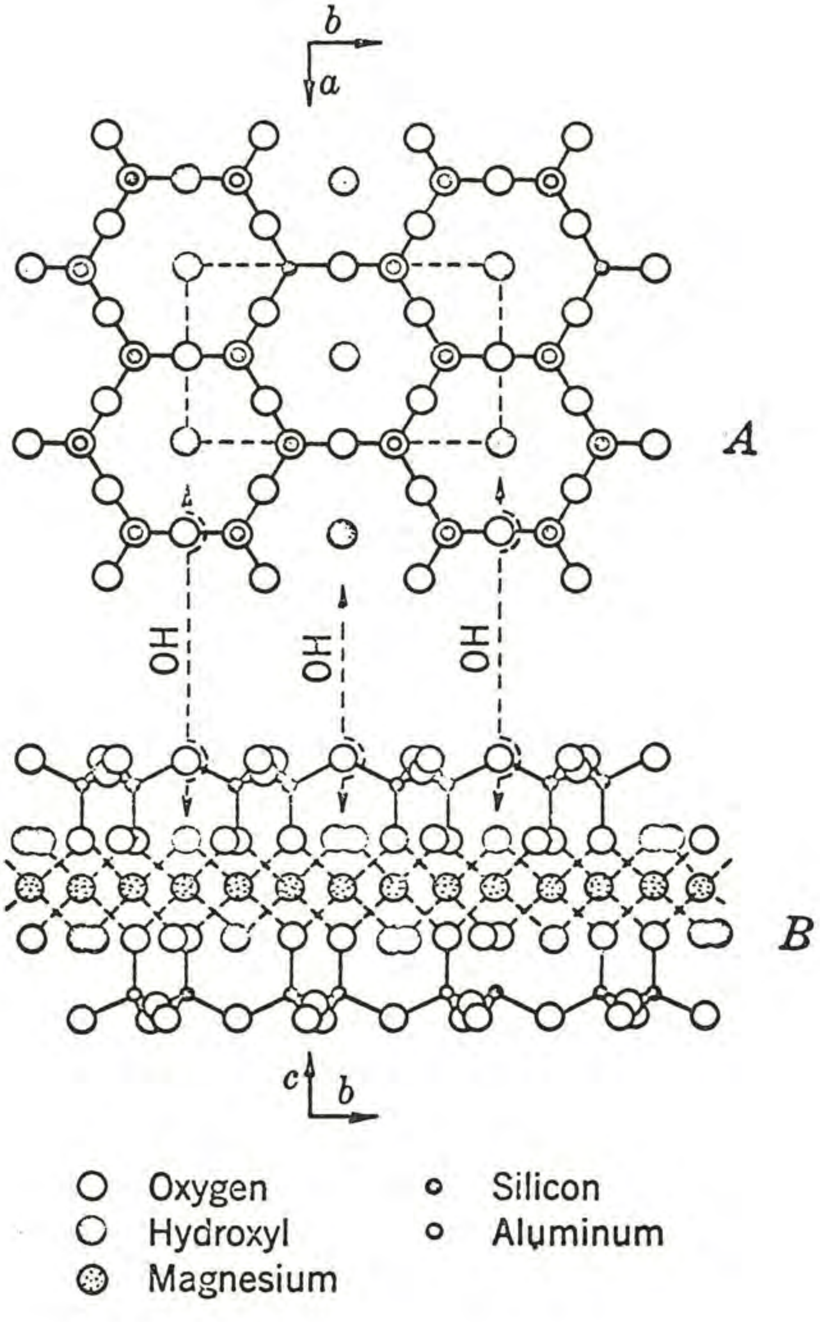


Figure 4. Crystal Structure of Phlogopite Mica.

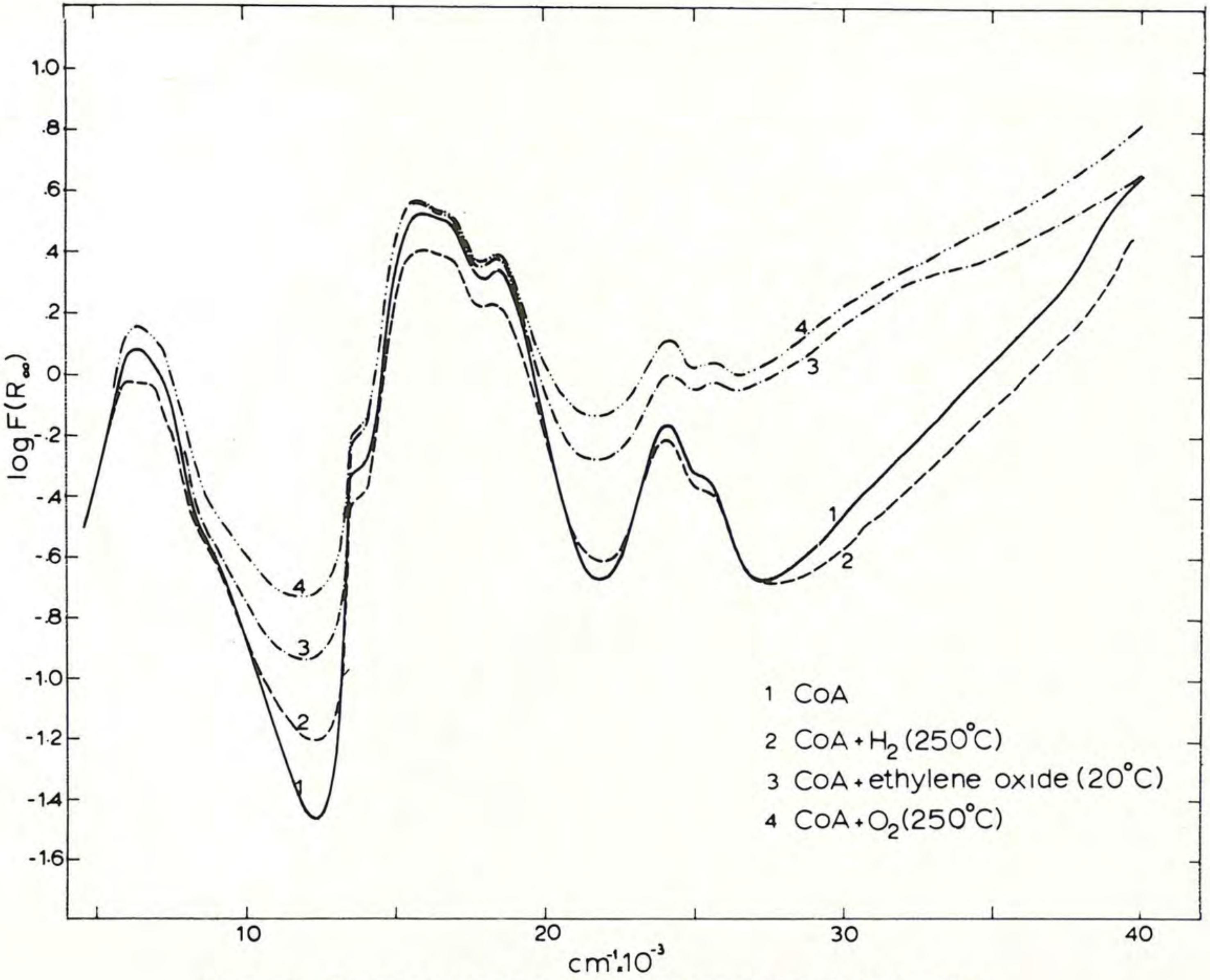


Figure 5. Spectra of Anhydrous Co(II)A Molecular Sieve Zeolite - Pure, and after Exposure to Hydrogen, Ethylene Oxide, and Oxygen.

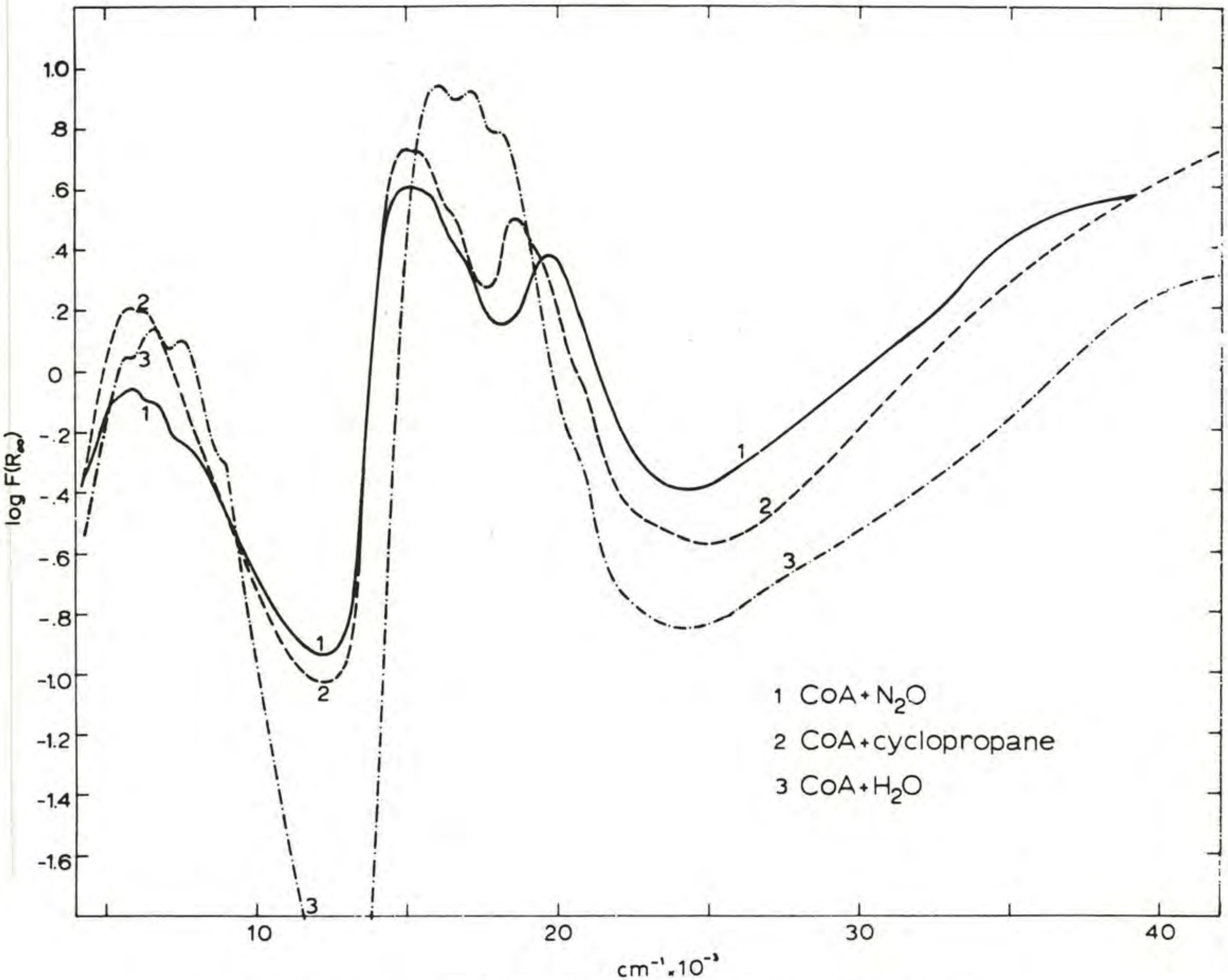


Figure 6. Spectra of Anhydrous Co(II)A Molecular Sieve Zeolite with Adsorbed Nitrous Oxide, Cyclopropane, and Water.

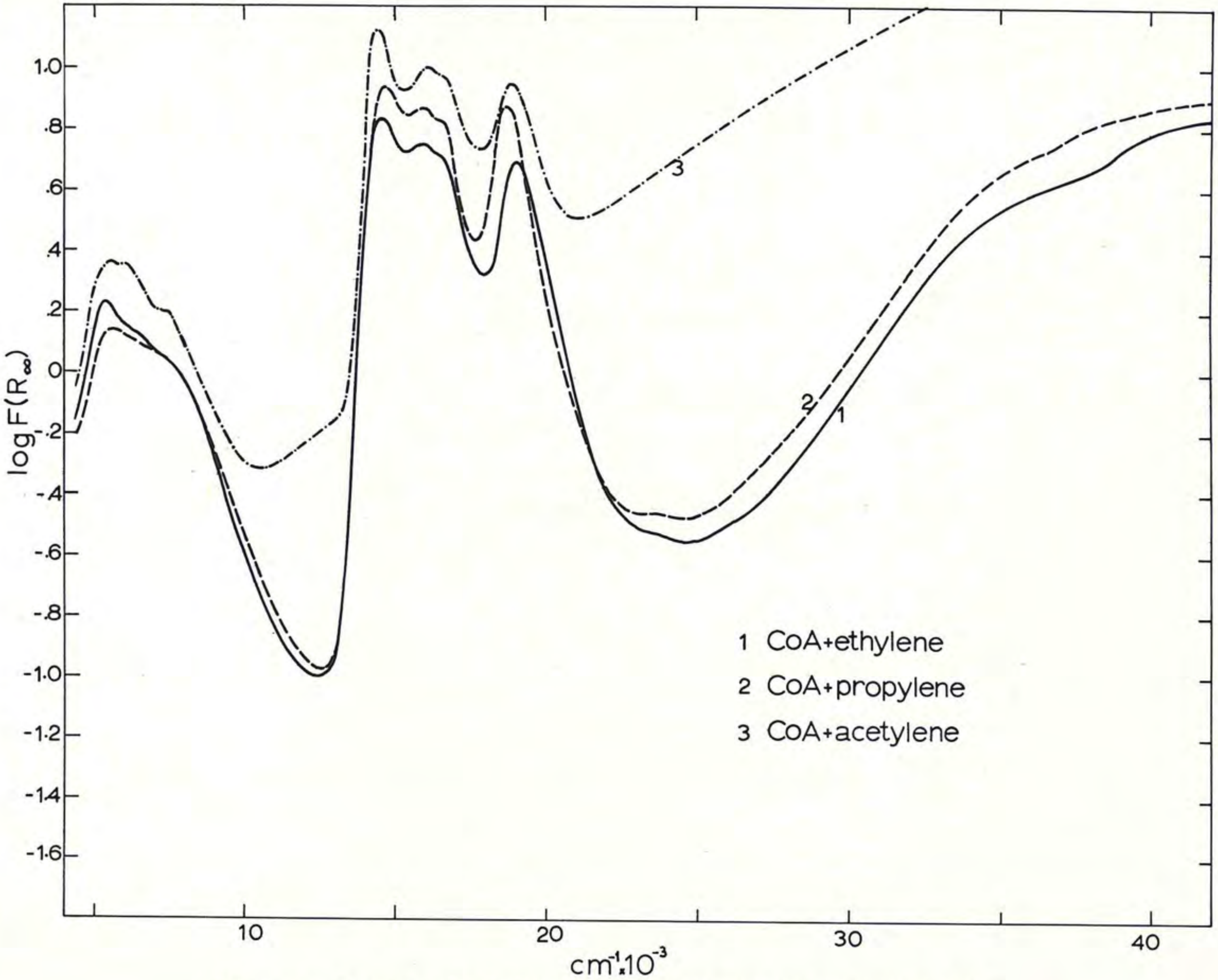


Figure 7. Spectra of Anhydrous Co(II)A Molecular Sieve Zeolite with Adsorbed Ethylene, Propylene, and Acetylene.

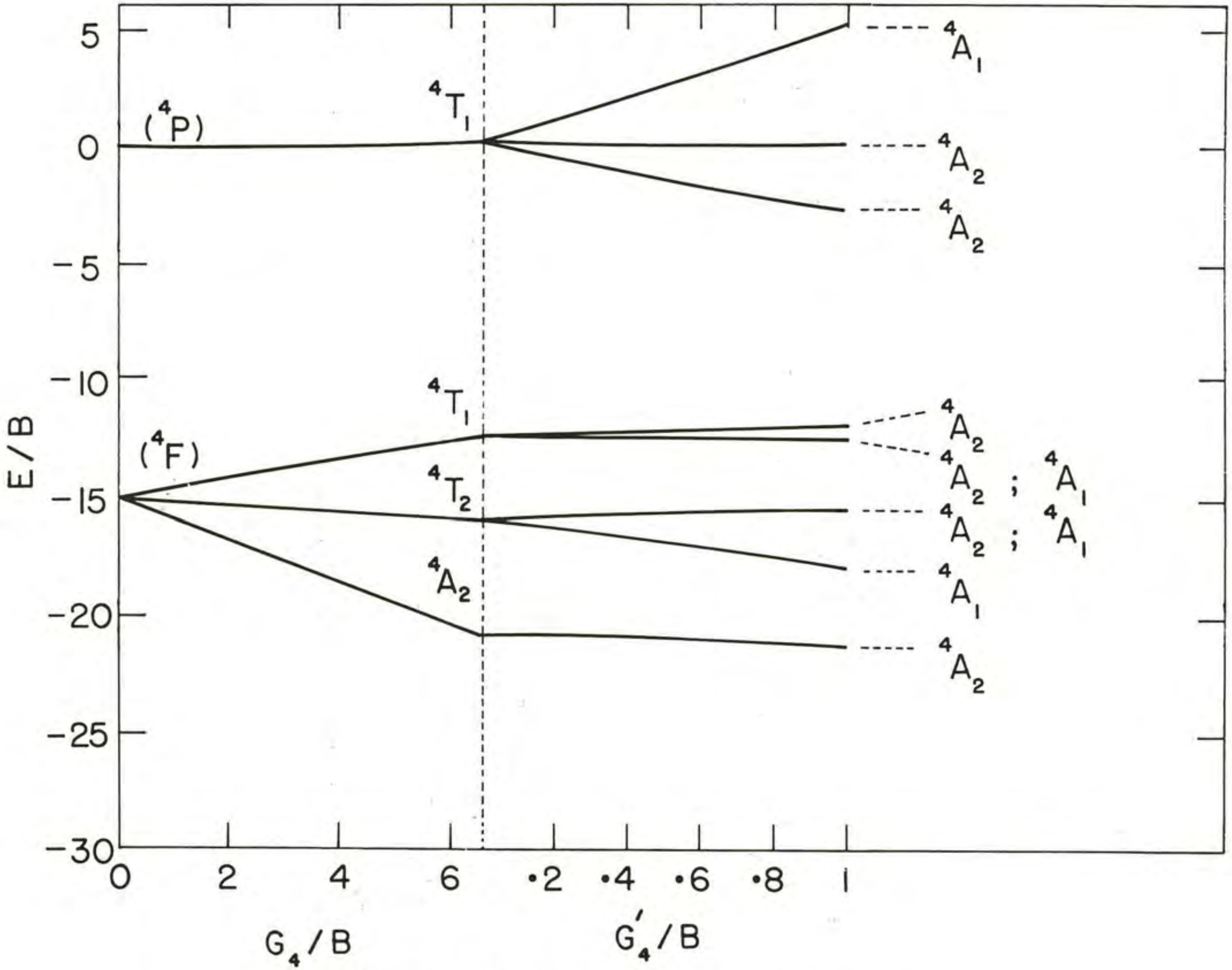


Figure 8. Term Diagram for Co(II)A-Olefin Complexes.

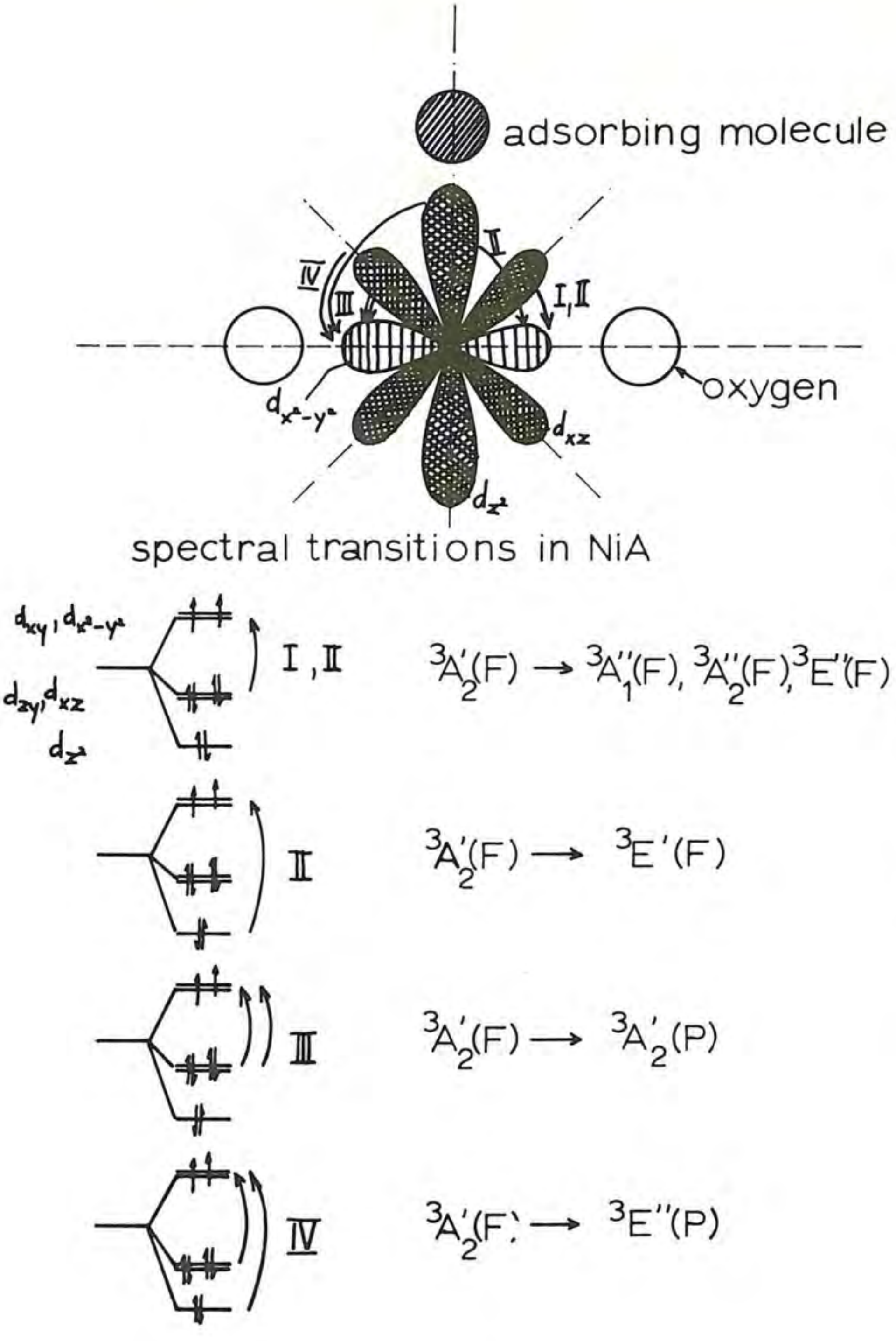


Figure 9. Schematic Representation of the Transitions between the One-Electron Levels in Ni(II)A Sorption Complexes.

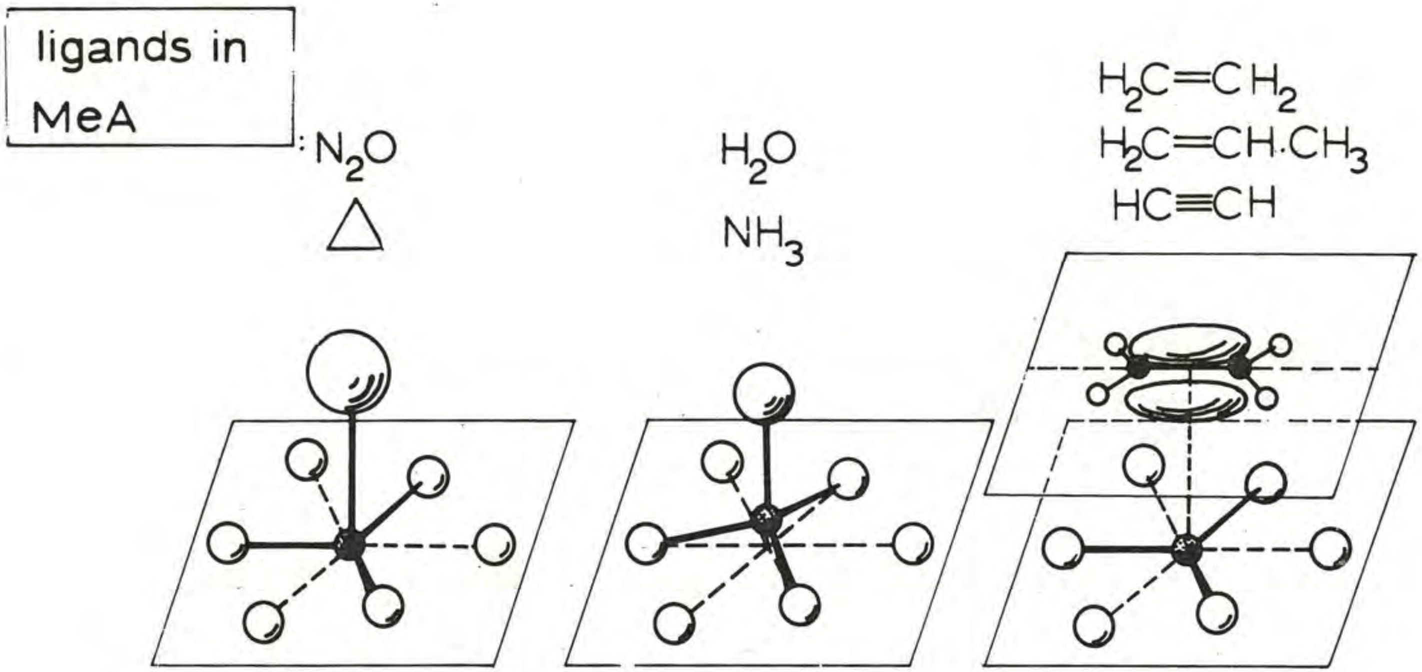


Figure 10. Schematic Representation of the Ligand-Metal-Zeolite Complexes.

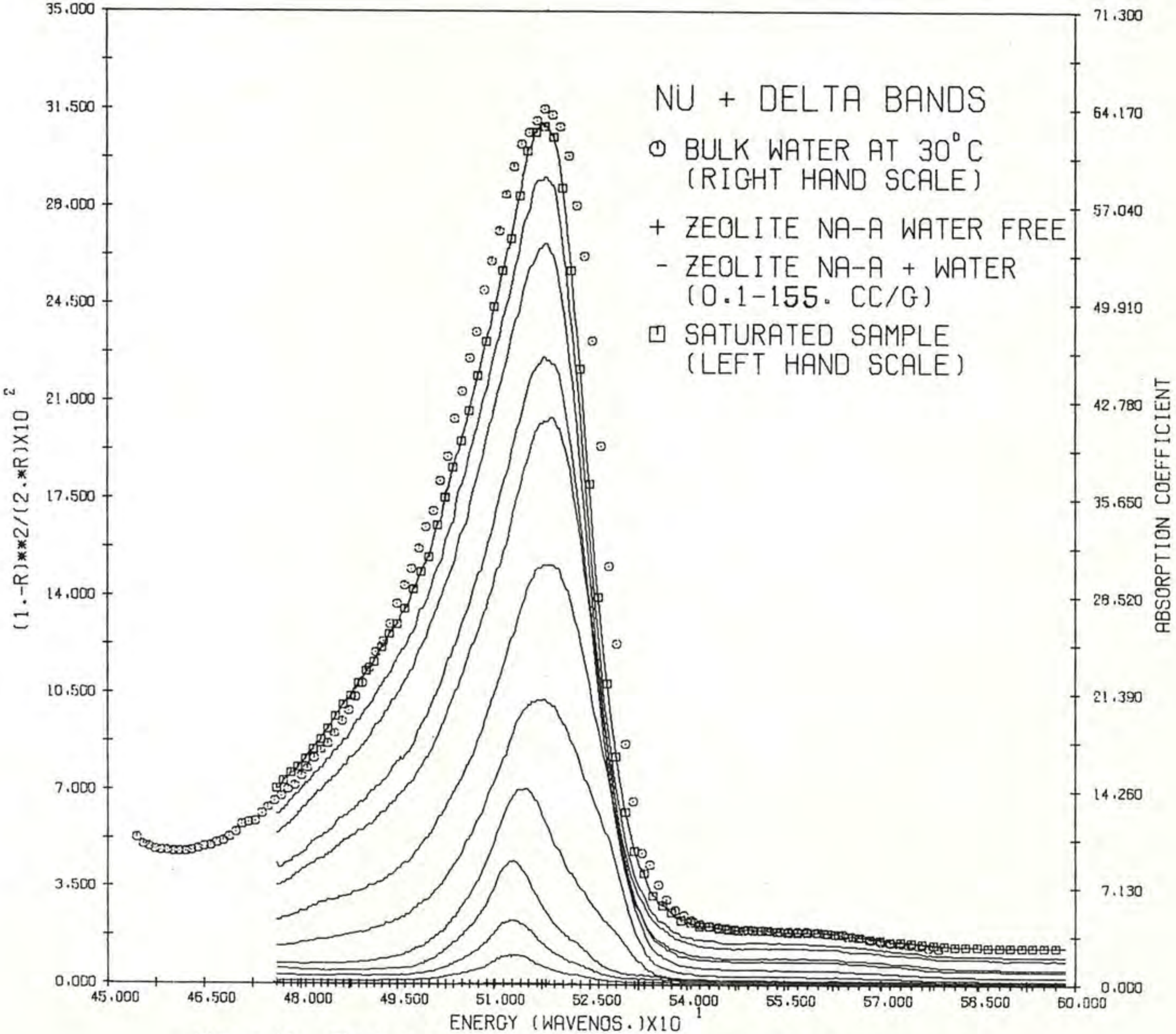


Figure 11. The H_2O ($\nu + \delta$) Bands in the Progress of Water Desorption in NaA_2 Zeolite at 25°C.

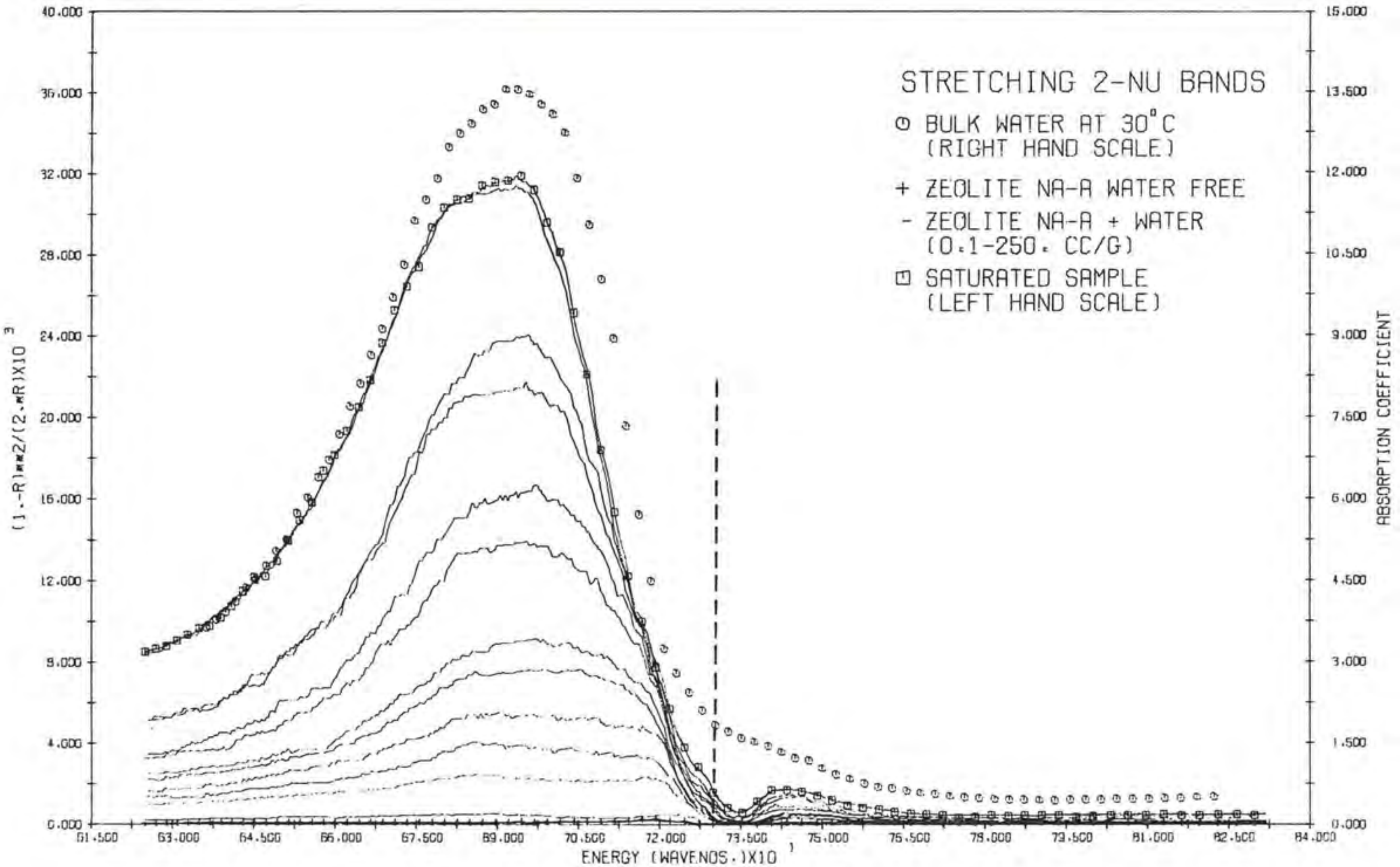


Figure 12. The H_2O (2ν) Bands in the Progress of Water Desorption in NaA Zeolite at 25°C.

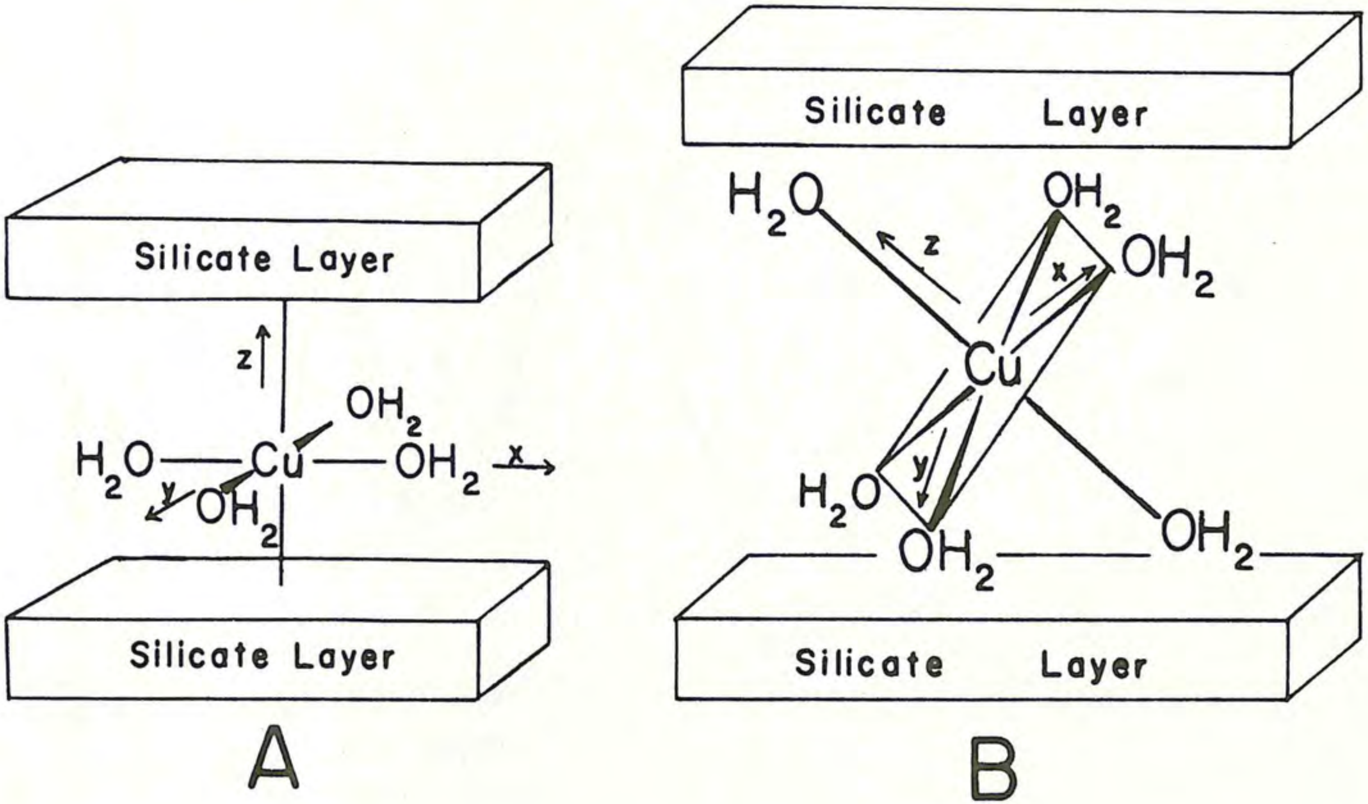


Figure 13. Schematic Representation of the Stereochemistry of Hydrated Cu(II) under Conditions where (A) One Layer and (B) Two Layers of Water Occupy the Interlamellar Regions.

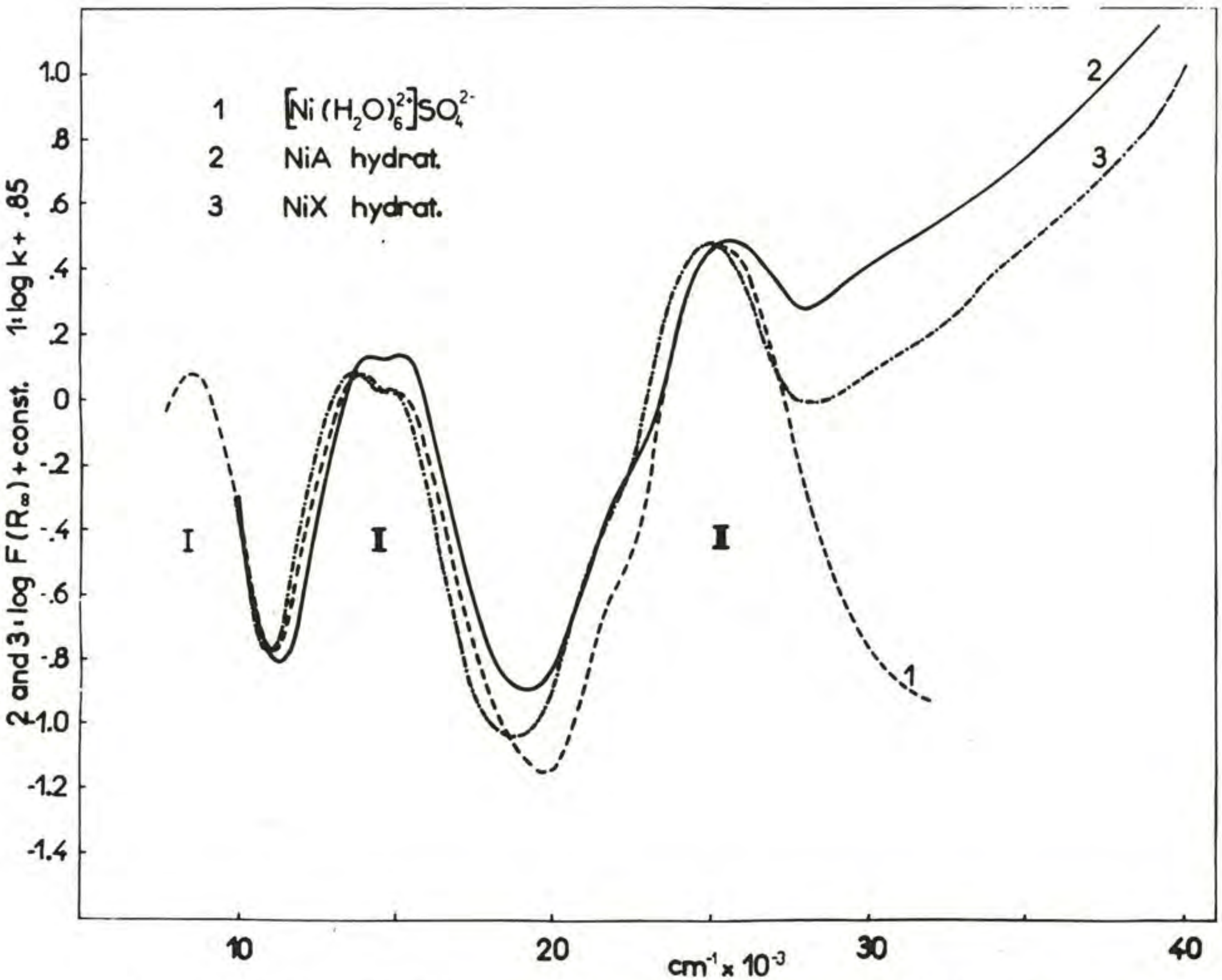


Figure 14. Comparison of Transmission Spectrum of $Ni(H_2O)_6^{2+}$ and Reflectance Spectra of Dehydrated NiA and NiX Synthetic Zeolites.

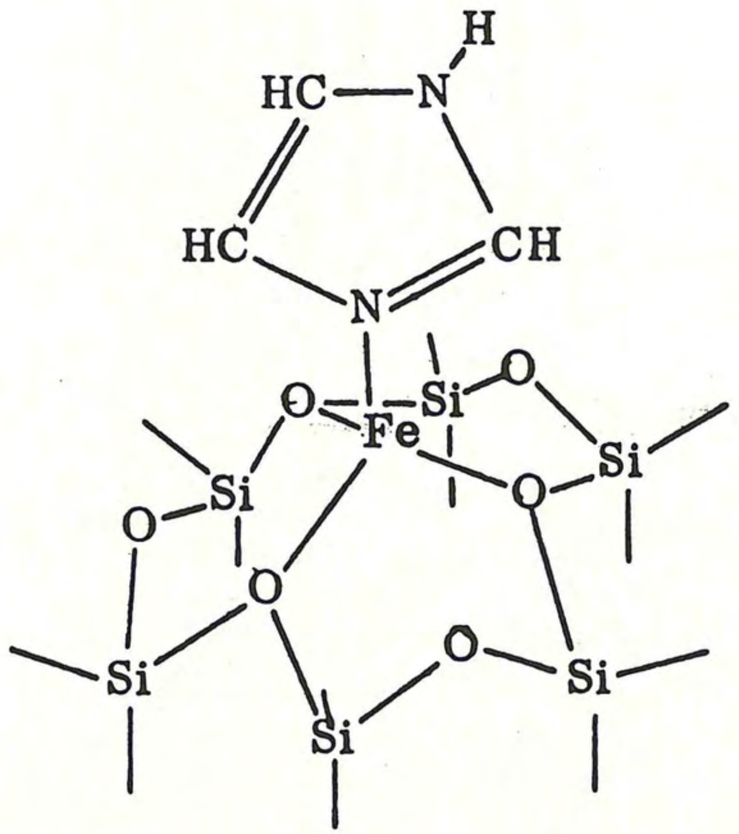
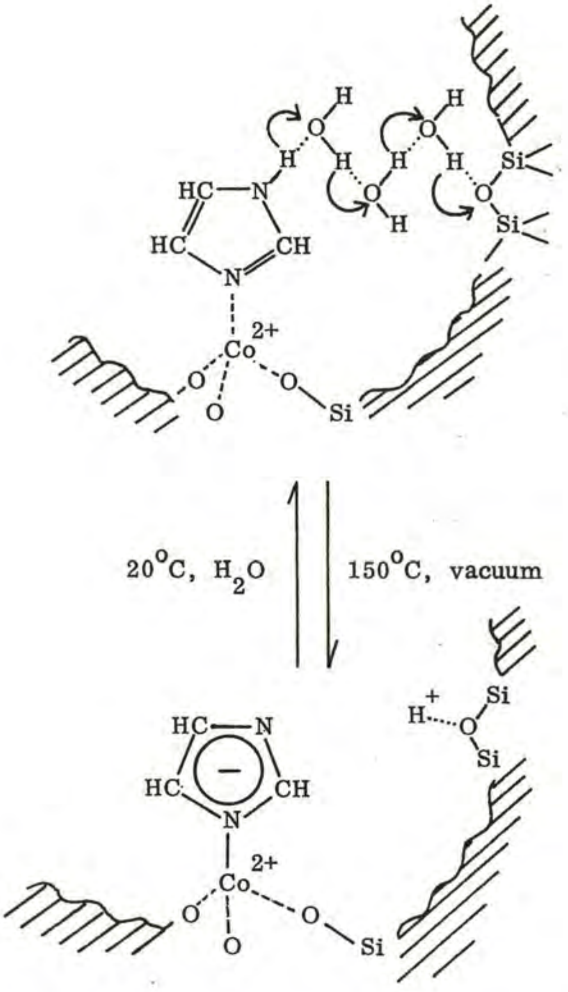


Figure 15. *Iron-Imidazole Complex in Oxygen Six-ring Window of a Clay Mineral.*

REVERSIBLE DEPROTONATION OF THE Co(II) A - ImH COMPLEX



1. Complete loss of water (IR)
2. No loss of imidazole (spring balance)
3. Co^{2+} remains quasitetrahedral (vis.)
4. N-H vibrations are lost (IR)
5. C=N vibrations become more symmetrical (IR)

Figure 16. Reactions of Imidazole Bound to Cobalt (II) in Zeolite Cavity.

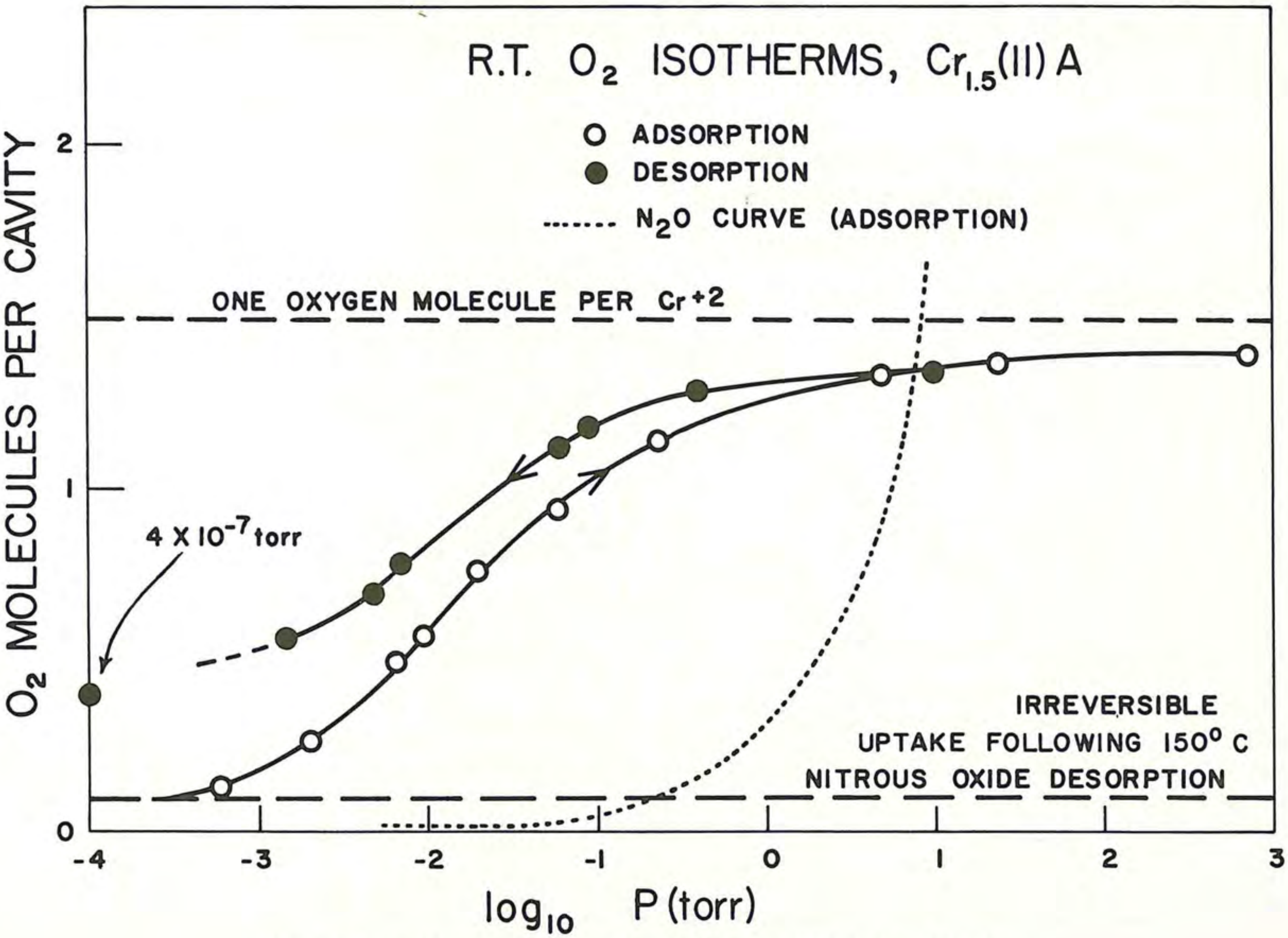


Figure 17. Isotherms of Molecular Oxygen on Cr(II)A Molecular Sieve Zeolite.

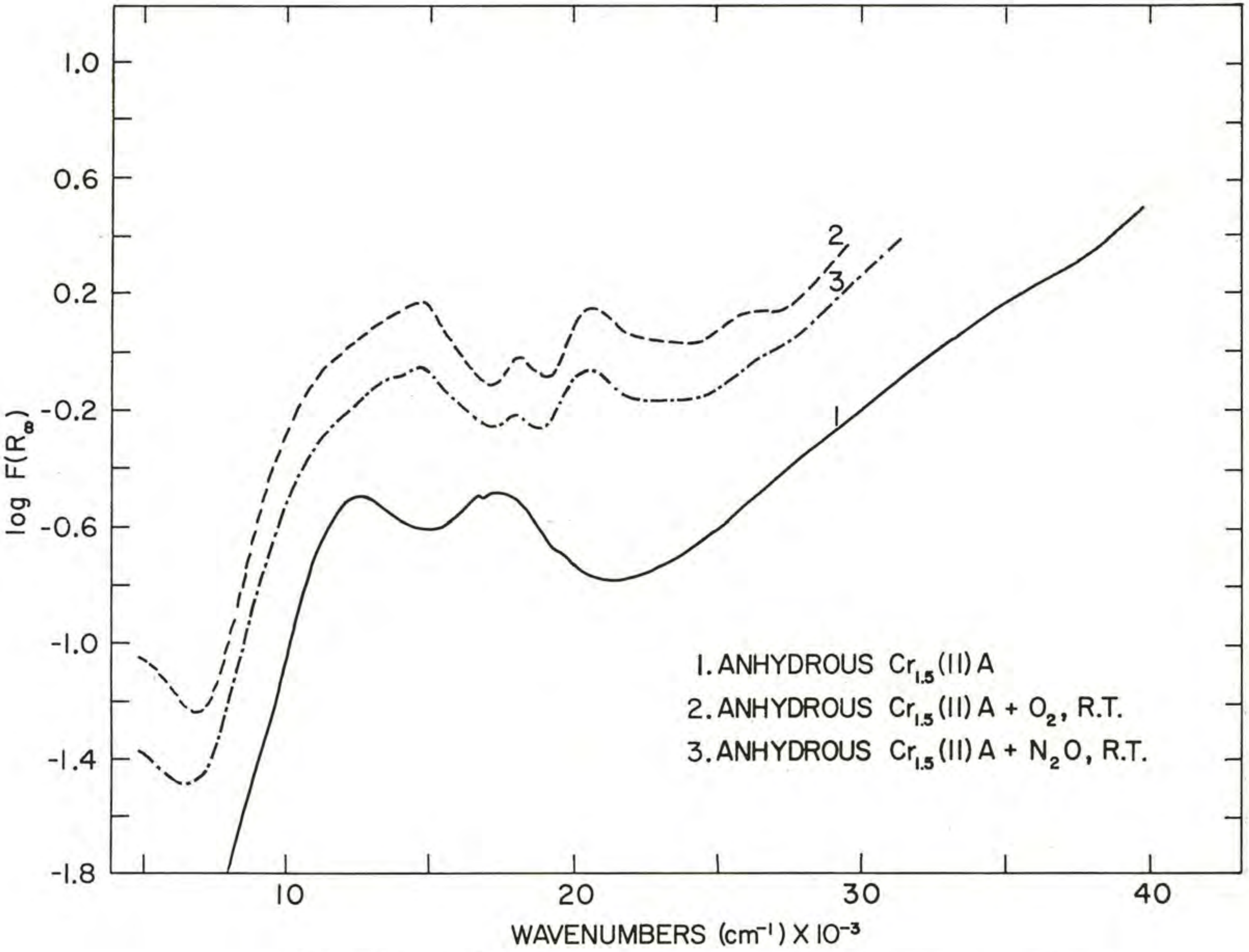


Figure 18. Reflectance Spectra of Anhydrous $Cr_{1.5}$(II)A Pure, and with Adsorbed Oxygen and Nitrous Oxide.

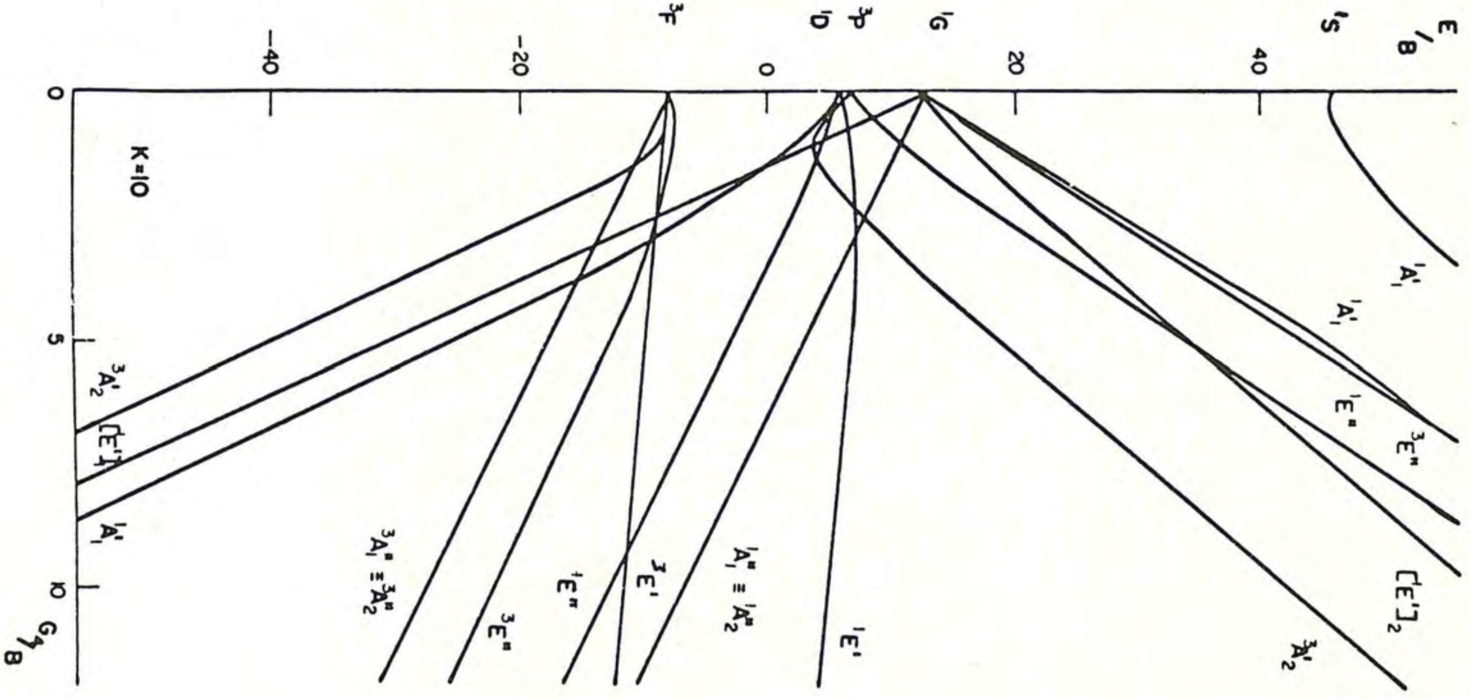


Figure 19. The Term Diagram of the Ni(II) (d^8) Electron System in the Near-D_{3h} Site in Type A Molecular Sieve Zeolite.

Discussion

Mr. Crable: Any questions?

Dr. D. Taylor: I do not know the difference between Z, Y, and A zeolites. Could you explain briefly and show again why the A would probably be preferable in use in solid sorbents.

Dr. Klier: The chemical difference is that A-type zeolite has a large aluminum/silicon ratio. X and Y have a much lower aluminum/ silicon ratio. Since the amount of aluminum determines the ion-exchanging ability, the A type has higher ion exchanging capacity than the X and Y.

The second difference is in the structure. The A type has the cubo-octahedral units connected in an octahedral fashion, whereas the X and Y's, which have identical structure, have the cubo-octahedral units connected in a tetrahedral fashion. These two types of connections give rise to different sizes of cavities and different sizes of connecting windows. So, A-type zeolite has the window which is either 4 angstroms or 5 angstroms, depending on the cations. The A-type zeolite has sodium or divalent ions in it. The zeolite windows would be 5 angstroms, if they have divalent ions in them partially exchanged.

X-and Y-type zeolites have openings which are of the order of 10 Å and X is richer in aluminum than Y. Therefore, X is isostructural with Y, but is a more prominent ion exchanger.

In some applications one wants to hydrophobe the aluminosilicates. In general, this can be done. For that purpose, Y-type is more convenient, and I know of many procedures designed to hydrophobe the surface. For example, you can think of lithium exchange. I am not answering the question -- can I go on?

Dr. D. Taylor: Yes

Dr. Klier: If you have a structure related to the zeolite, such as montmorillonite, lithium is so small that it can pass through the oxygen six-ring window and change places with the OH group below the six ring window. Lithium may also react with it to form an OLi group, and therefore, from an ion exchanger, we have made something that is, all of a sudden, a non-exchanger. This is because the lithium introduced cannot be exchanged back, and the resulting silicate is hydrophobic.

So we can, by multiple exchange, control the properties of silicates from hydrophilic to hydrophobic.

With the X- and Y-zeolites there is one additional difference, that they have structural perturbations which are probably broken bonds. These are strongly reactive sites which do not have uniform or well defined properties, and that is one additional reason why I find the situation in Z- and Y-zeolites much more complicated than in A-type.

For example, the reactions with water in X- and Y-result in the formation of the OH groups on metal ions or on these broken bonds. All these things do not happen in the A-type Zeolite.

Now, why does the ion not assist the formation of the OH group in the A-type? Because the A-type is a stronger anion, and, therefore, the bare cation can be held in a surface, position by the negative charge of the skeleton. But if you have a weak anion, the weak anion needs to pick up some additional ligands, such as OH^- groups, and that results in decomposition of water.

Dr. Zlatkis: What is the physical property of transition ion exchanged zeolites? Could they be used as chromatographic packing material in gas-solid chromatography for separations of oxygen from nitrogen and other things?

Dr. Klier: Well, I am looking for such applications. An example is chromium (II)-containing type A sieve. Normally, chromium(II) is very susceptible to oxidation. However, in molecular sieves, when we have ions in surface positions, the susceptibility to oxidation is much lower. Therefore, chromium(II) forms a reversible molecular complex with molecular oxygen on the surface, and can be used for the separation of oxygen from less reactive gases.

As far as the packing problems are concerned, everything is the same as with a normal zeolite. We just exchange the calcium in the zeolite for chromium, and we can do anything we can do with a type A-zeolite.

Dr. Zlatkis: No questions about thermal stability? You can take it up to 300 degrees?

Dr. Klier: Yes. That is an example. If heating is done in air, however, chromium(II) becomes oxidized to chromium(III). Chromium(III) can be reduced by carbon monoxide at 300 degrees Centigrade, and the original valence state is completely recovered. So I was thinking about the possibility to analyze for ozone.

For example, ozone decomposition can occur on these chromium complexes, which can be utilized for its detection through color changes or subsequent reduction of the surface complex. Interference may occur from molecular oxygen and, therefore, the chromium solid sorbent may not be the most suitable. We would have to look for another system which has less affinity towards molecular oxygen.

Dr. Zlatkis: The thing that brought that to mind is that chromium, itself, in a chromatographic packing, is useful for separating nitrogen from oxygen.

Dr. Klier: Are you talking about chromia gel?

Dr. Zlatkis: Yes. Compared to zeolite solid sorbent, a much less controlled situation occurs in chromia gels. You can have defined individual centers in zeolite. You will never know what these centers are in porous chromia gel. So I think there is a certain advantage in doing this type of work, when the selectivity is in question, with the zeolites.

Mr. Crable: Our next speaker is Dr. Teass, who is Chief of the Organic Methods Development Section within the Physical and Chemical Analysis Branch. He is going to discuss with you our in-house research on solid sorbents.

THE SAMPLING OF ORGANIC VAPORS USING ACTIVATED CHARCOAL

by

Alexander W. Teass, Ph.D., Charles S. McCammon,
C. Paul Roper, and Ann T. Saalwaechter

Introduction

In 1964 Otterson and Guy (1) presented a technique for monitoring workplace air for toxic organic vapors. The air was sampled using a tube filled with activated charcoal, the organic compounds removed from the charcoal with a solvent, and the resulting solution analyzed by gas chromatography. Researchers at NIOSH refined the technique for use in sampling the air in the breathing zone of the worker (2-4). The technique has been used for monitoring personal exposures to over 100 organic vapors, including aromatic and aliphatic hydrocarbons (2,6), halocarbons (2,5,6) esters (2), ketones (2,6), and carbon disulfide (4,7).

This seemingly simple monitoring technique--adsorption, desorption, analysis--has potential problems and limitations. The problem of recovery of the analyte from the charcoal has been explored (2,4), and a desorption efficiency is routinely applied to analytical results obtained by this method. Fraust and Hermann (8), experimenting with the adsorption of acetate esters by charcoal, studied the efficiency of the sampling process and the capacity of the charcoal. For 16/20 and 30/40 mesh charcoal the sampling efficiency was found to be greater than 95% and independent of the mass rate--i.e., the product of air concentration (mmol/ℓ) and sampling flow rate (l/min). The capacity of the charcoal, expressed as breakthrough time, was found to be inversely proportional to the mass rate.*

The effective capacity of the commercially available and routinely used 150-mg two-section charcoal tube is largely unknown. Also, the stability of the vapor-on-charcoal samples is in question. It is the purpose of this paper to present some results of our investigations into these two potential problems.

**Mesh Sizes are U.S. series designations.*

Sampling Procedure

The activated-charcoal sampling device currently used by NIOSH and OSHA, now commercially available, is described in Figure 1. It consists of two beds of 20/40 mesh activated charcoal contained in a 7-cm x 4-mm (i.d.) glass tube. The primary section at the inlet end of the tube contains 100 mg of activated charcoal. It is followed by a backup section of 50 mg of charcoal. The tubes are flame-sealed to protect the charcoal from contamination prior to use, and are provided with polyethylene caps for closing the tubes after sampling. The devices are designed to have a pressure drop of less than 13 in. of water at a flow of 1 ℓ/min so that the available battery-operated personal sampling pumps can be used over an 8-hour period for obtaining samples.

In use, the ends of a tube are broken off to give openings at least 2 mm in diameter (nonlimiting orifices). The tube is then attached via plastic tubing to a sampling pump with the backup section toward the pump. With the tube in a vertical position in a worker's breathing zone, a known volume of air is drawn at or below 1 ℓ/min. The volume of air sampled is usually limited to 5-10 ℓ so that there is no danger of sample loss due to overloading the charcoal. The tubes are capped and shipped to the laboratory where the contents of each section are separately desorbed with carbon disulfide and analyzed by gas chromatography. The amount of analyte present is the sum of the values for the primary and backup sections corrected for the efficiency of desorption of the analyte from the particular batch of charcoal used. Separate analyses of the primary and backup sections allow the analyst to observe if the tube was overloaded.

Sample Stability

To test sample stability a large number of samples of equal volumes of a synthetic atmosphere were obtained and analyzed after different periods of storage at room temperature. The results of a study of 2-butanone on-charcoal samples is shown in Figure 2. The fraction found is the amount of 2-butanone found after a period of storage relative to that found on the front section on Day one. The gradual loss of 2-butanone from both sections could be due either to escape of the vapor from the tube, reaction of the 2-butanone with reactive chemical groups on the surface of the charcoal, or aldol-type condensation of the 2-butanone catalyzed by the acidic groups on the oxygenated surface of the charcoal. The curve for the backup section shows that the 2-butanone also slowly equilibrated throughout the sampling device, with about 30% having migrated to the backup section by Day 50.

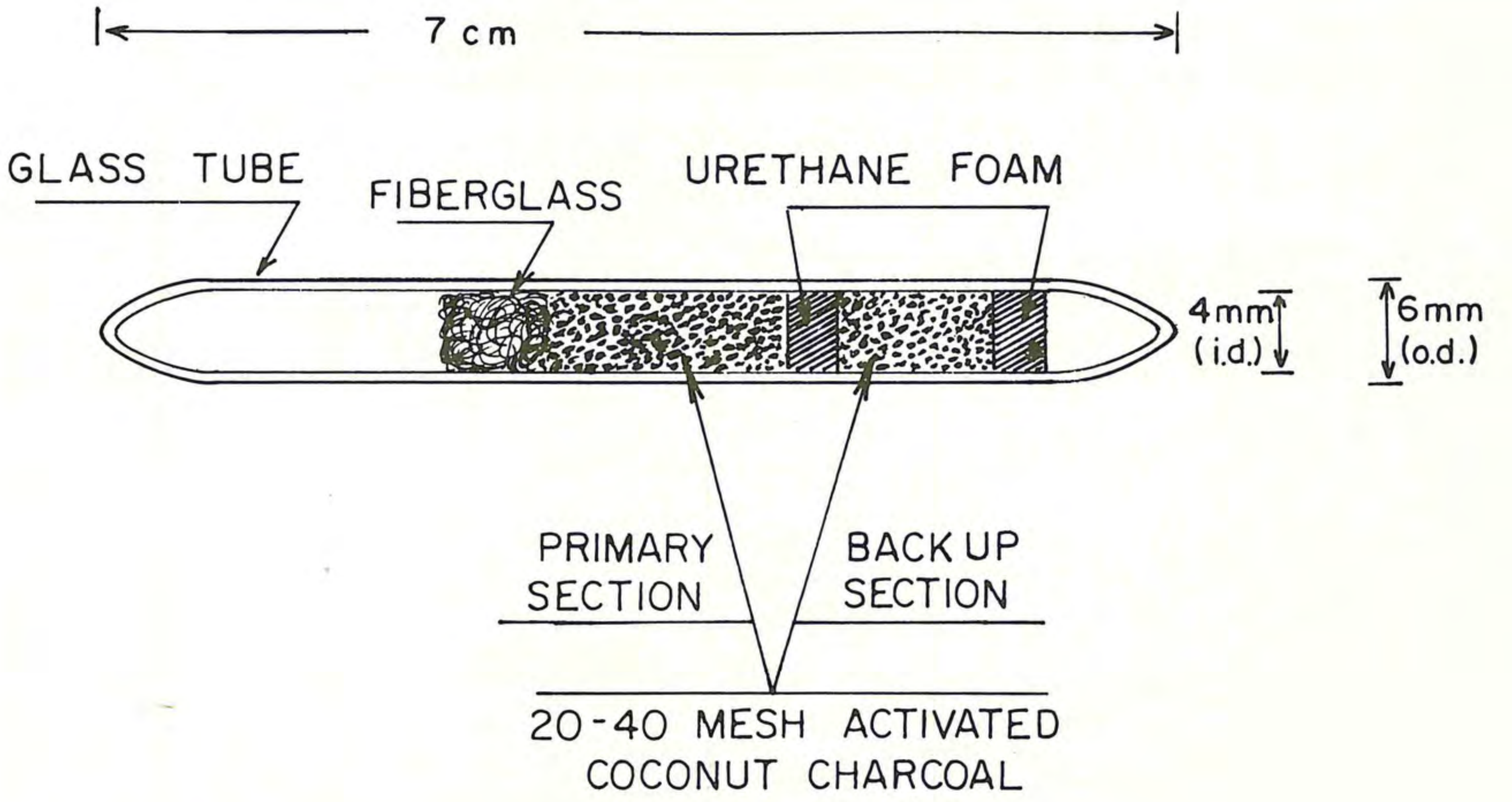


Figure 1. Charcoal Tube Sampling Device.

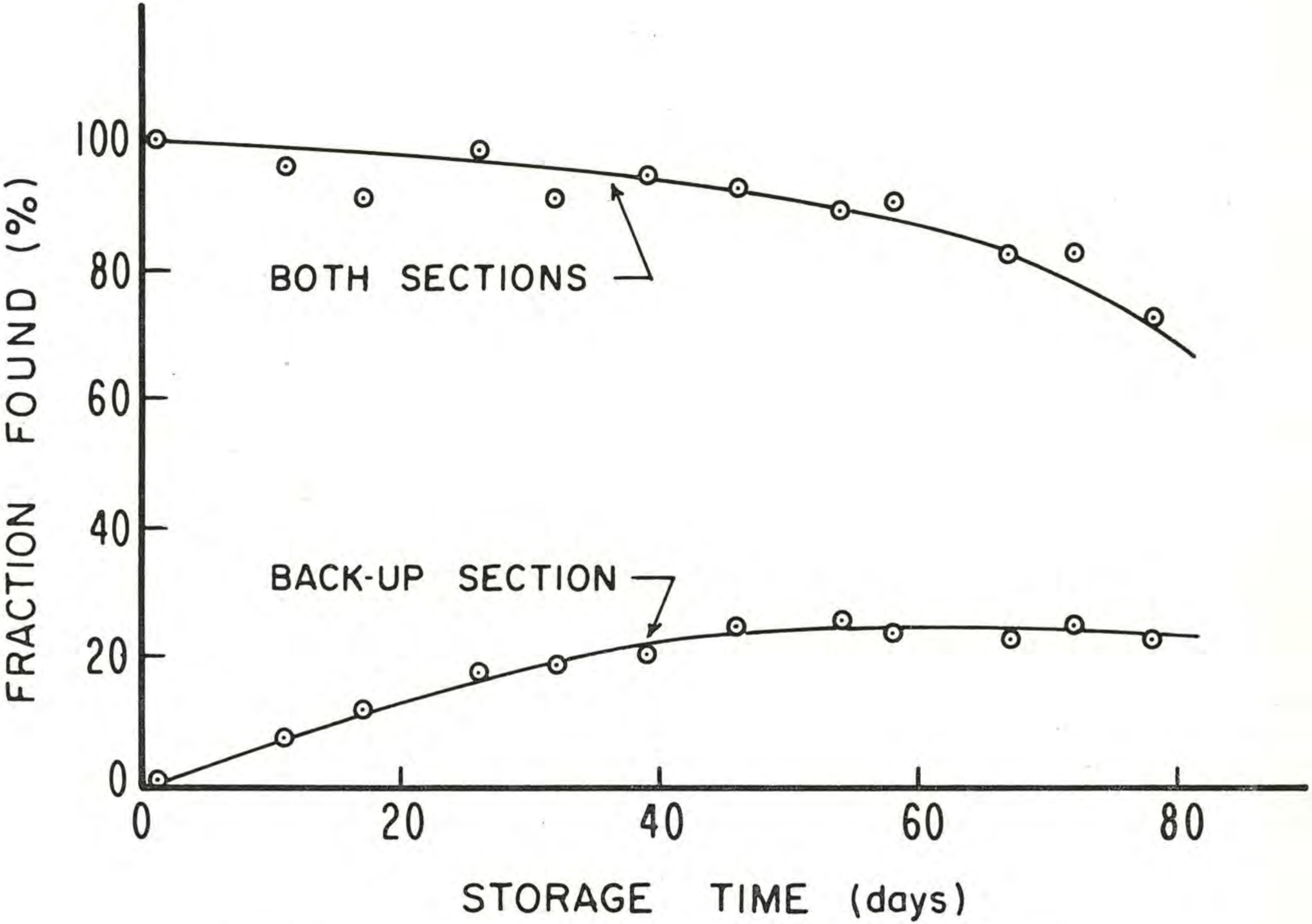


Figure 2. Stability of 2-Butanone-on-Charcoal Samples. Sample Size 7.8 mg. Activated Petroleum Charcoal 580-26.

A study of dichloromethane-on-charcoal samples yielded the results shown in Figure 3. There appears to be a slight loss of total dichloromethane--about 3% in 60 days--probably due to escape around or through the polyethylene caps. Because of its high volatility, the dichloromethane equilibrated fairly rapidly throughout the tube, migration being complete around Day 20 (i.e., the fraction found on the backup section was approximately equal to the weight fraction of charcoal).

Trichloroethylene-on-charcoal samples (Figure 4) were stable over 90 days. Migration of Trichloroethylene to the backup section was not significant (<1% of the total) until after Day 20. Toluene- and styrene-on-charcoal samples (7.8 mg and 9.3 mg, respectively, on activated coconut charcoal MSA-1) showed no loss or migration on storage for 50 days.

From data one may conclude that if the adsorbate is not chemically reactive under storage conditions, the adsorbate-on-charcoal samples are stable for at least 1-2 months. However, in the case of the more volatile adsorbates, the purpose of the backup section, an indicator of tube overloading, is negated by the tendency of the vapor to equilibrate throughout the tube during storage. Storage of these samples in a refrigerator appears to retard the rate of migration some. Use of a redesigned tube where the primary and backup sections can be stored separately would eliminate the problem.

Capacity of Charcoal

The capacity of the charcoal tube for various organic vapors was determined by breakthrough studies. Synthetic atmospheres were generated in dynamic systems similar to that of Roper (9). The experiments were performed at ambient conditions (∿25 C, ∿745 torr), at a relative humidity below 7%, and at a flow of 1 ℓ/min, except where noted. These breakthrough experiments were run by drawing the atmosphere through a 100-mg section of 20/40 mesh charocal 4 mm in diameter. The concentration of adsorbate in the bed effluent was monitored with a flame-ionization detector. In these experiments activated coconut charcoal (Mine Safety Appliances Co., Pittsburgh, Pa.) and activated petroleum charcoal (SKC, Inc., Pittsburgh, Pa.) were used.

The detector signal produced a breakthrough curve like that shown in Figure 5. Breakthrough point G was defined as the point at which the concentration of adsorbate in the bed effluent reached 5% of the initial concentration. The breakthrough volume, the volume of air sampled at breakthrough, was the product of the flow rate and the sampling time. The amount of adsorbate on the charcoal at the point of breakthrough, the breakthrough capacity, was given by the product of the flow rate and the area ABCI (GHI was assumed to be negligible). The total capacity of the charcoal for the adsorbate, theoretically given by the product of the flow rate and the area EFGH, was assumed to be the product of the flow rate and the area ABDJ.

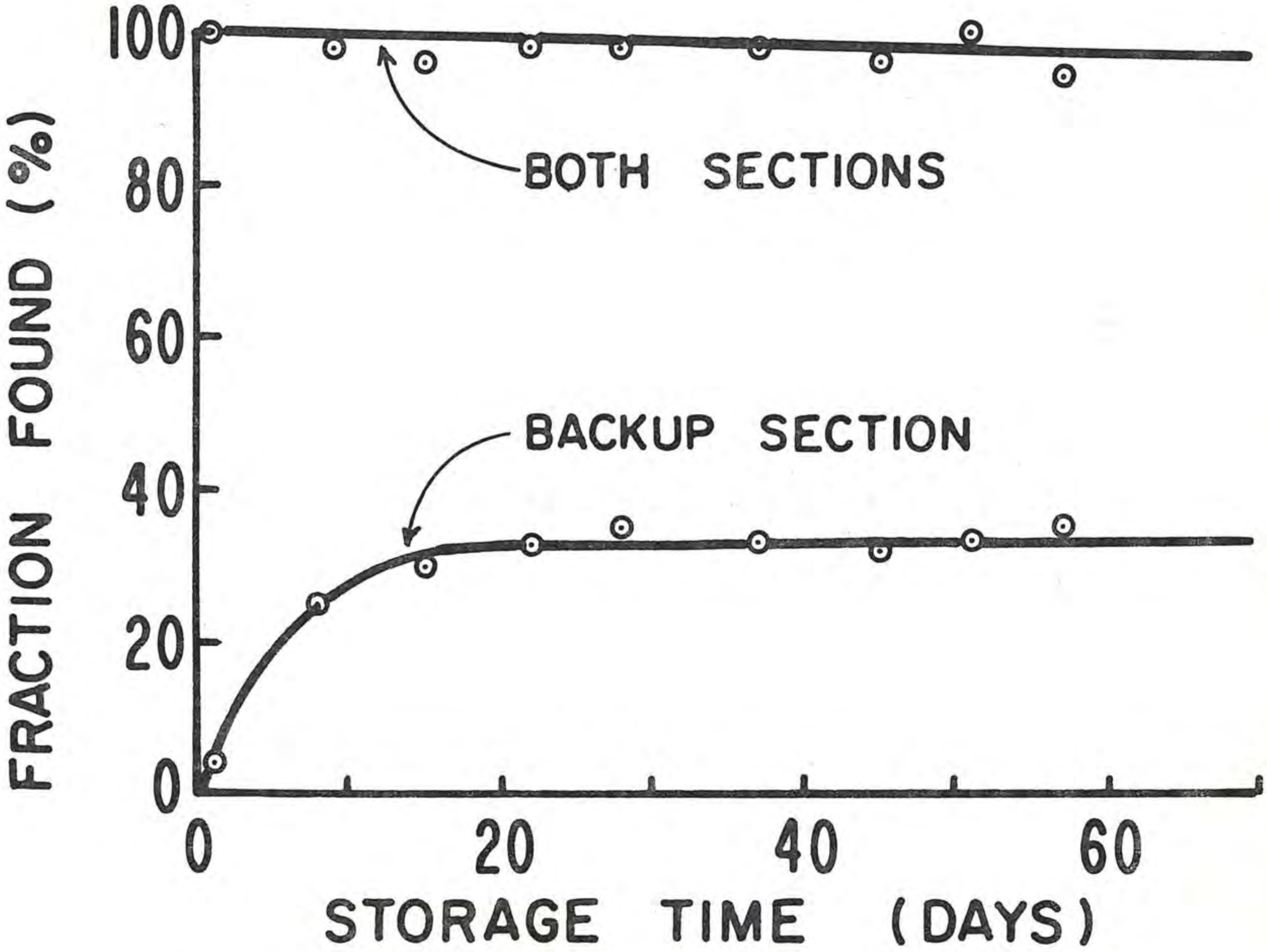


Figure 3. Stability of Dichloromethane-on-Charcoal Samples. Sample Size 5.2 mg. Activated Coconut Charcoal MSA-1.

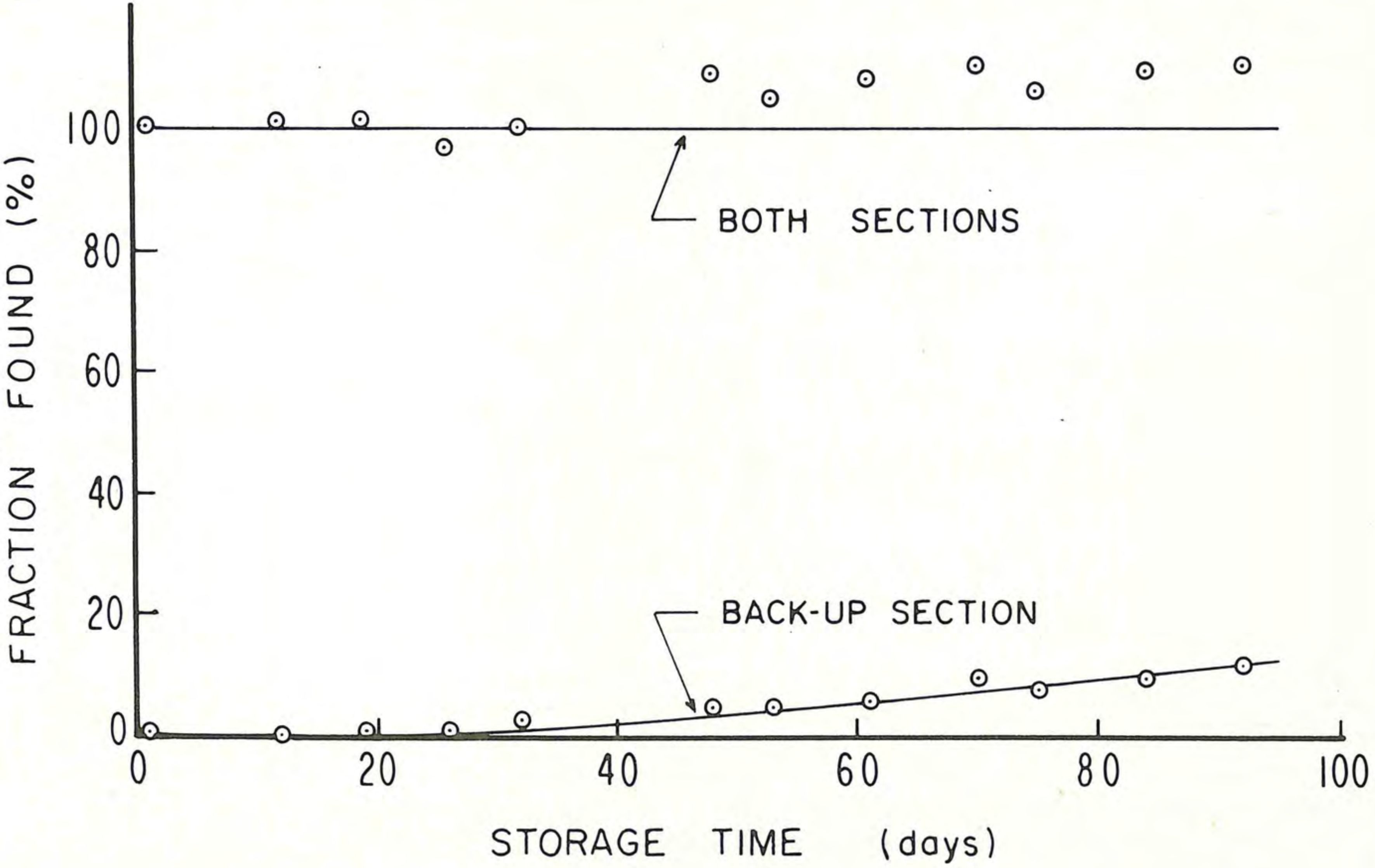


Figure 4. Stability of Trichloroethylene-on-Charcoal Samples. Sample Size 9.3 mg. Activated Petroleum Charcoal 580-26.

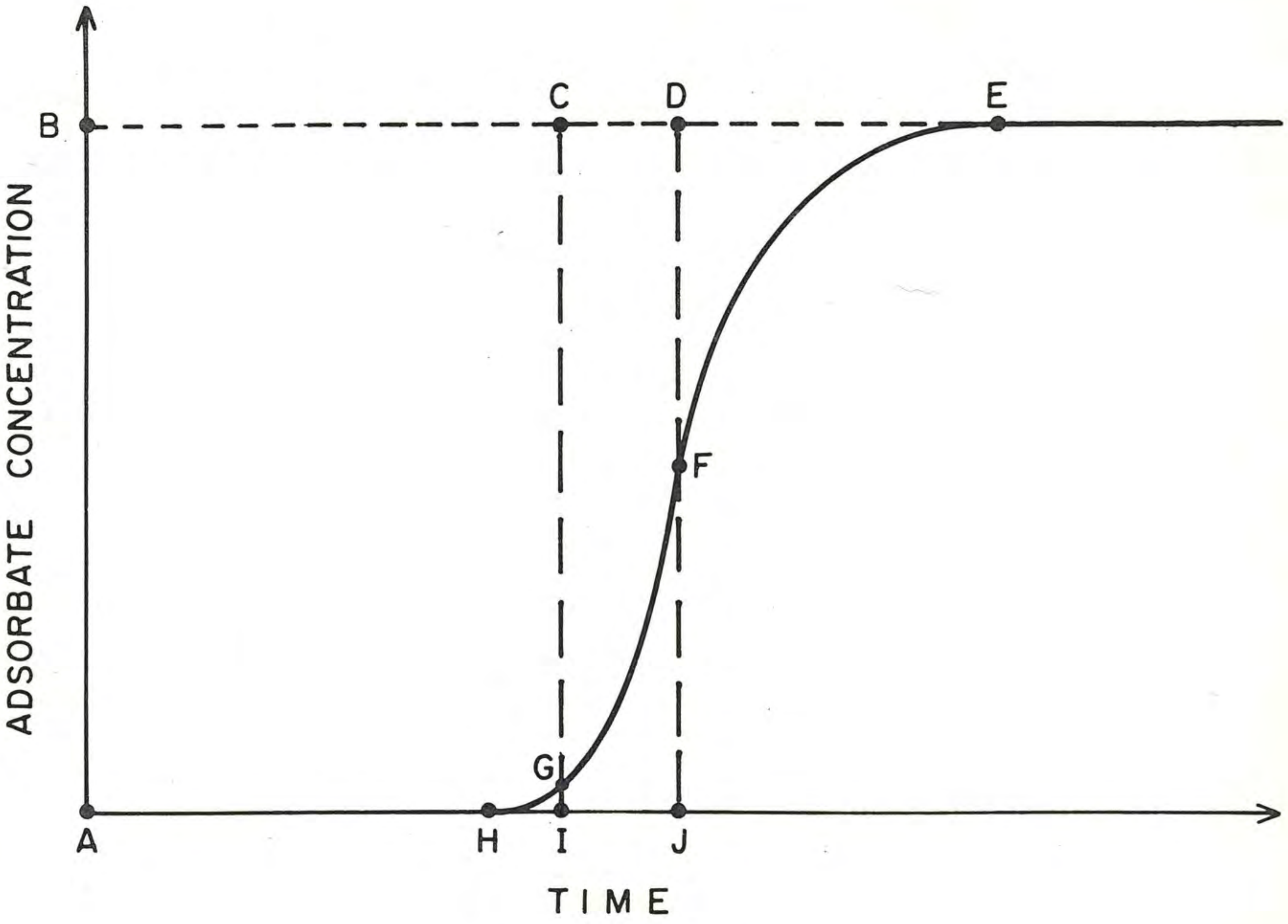


Figure 5. Breakthrough Curve.

The result of a study of the capacity of activated coconut charcoal MSA-6 for toluene, under various conditions are summarized in Table I.

TABLE I

TOLUENE BREAKTHROUGH DATA ON ACTIVATED

COCONUT CHARCOAL MSA-6*

Temperature (°C)	*Relative Humidity (%)*	*Concentration (μg/ℓ)*	*Breakthrough Volume (ℓ)*	*Breakthrough Capacity (mg)*	*Total Capacity 100 mg C*
24	*<7*	*2040*	*15*	*30*	*40*
26	*<7*	*700*	*39*	*28*	*36*
24	*<7*	*45*	*420*	*19*	*26*
49	*<7*	*740*	*38*	*28*	*34*
28	*80*	*690*	*19*	*13*	*34*
49	*73*	*700*	*16*	*11*	*30*

**100 mg sample*

As expected, there was an increase in the breakthrough volume and a decreased in the breakthrough capacity and total capacity. At ~ 25°C and < 7% relative humidity with a decrease in the concentration of the toluene, increasing the temperature at 49°C had only a slight effect on the capacity. However, when the relative humidity was increased to 80%, the breakthrough volume and breakthrough capacity decreased by 50%. The total capacity was not affected so severely, indicating that at equilibrium the toluene displaced much of the water initially trapped. That atmospheric moisture has an adverse effect also on the collection of trichloroethylene (5) and carbon disulfide (7) has been reported.

To compare the activated coconut charcoal MSA-6 with other activated charcoals used in the charcoal tube, two or three breakthrough curves were obtained for 100-mg sections of each. The results, shown in Table II, indicate that the coconut charcoals have a higher capacity for toluene than do the petroleum charcoals.

TABLE II

*TOLUENE BREAKTHROUGH DATA ON ACTIVATED CHARCOALS**

Charcoal	*Breakthrough Volume (ℓ)*	*Breakthrough Capacity (mg)*	*Total Capacity (mg)*
Coconut:			
MSA-6	*39*	*28*	*36*
MSA-5	*41*	*29*	*36*
MSA-4	*34*	*24*	*33*
MSA-1	*33*	*24*	*32*
MSA-0	*32*	*23*	*30*
Petroleum:			
SKC-104	*30*	*20*	*26*
SKC-103	*30*	*21*	*27*

**100 mg sections, 700μg/ℓ toluene in dry air, 745 torr, 27°c*

Breakthrough capacity data should be useful in characterizing charcoals using the Polanyi-Dubinin potential theory (10,11) discussed earlier by Dr. Ballou. In Table III, are tabulated the data from breakthrough experiments performed on petroleum charcoal 580-26 early in this program.

TABLE III

BREAKTHROUGH DATA ON ACTIVATED PETROLEUM CHARCOAL 580-26*

Adsorbate	*Concentration (μg/ℓ)*	*Breakthrough Volume (ℓ)*	*Breakthrough Capacity (mg)*	*Adsorption Potential (deg mol/cm^3)*
2-Butanone	*880*	*8.2*	*7.2*	*8.6*
Styrene	*620*	*29*	*18*	*4.5*
Tetrachloroethylene	*1040*	*33*	*34*	*6.4*
Toluene	*680*	*23*	*16*	*6.5*
1,1,1-Trichloroethane	*1960*	*5.8*	*11*	*9.0*
Trichloroethylene	*1460*	*12*	*17*	*7.8*

**Temperature ~25°C; relative humidity <7%*

In these studies varying amounts of synthetic atmosphere were sampled with the 150-mg two section charcoal tubes containing activated petroleum charcoal 580-26 (Barneby-Cheney, Columbus, Ohio) and the samples analyzed. Breakthrough of the primary section was defined as the appearance of adsorbate on the backup section in an amount 1% of the total collected. The adsorption potential A was calculated from the equation

$$A = \frac{T}{V} \log \frac{P_o}{P}$$

where T is the temperature of the experiment (°K), V the molar volume of the adsorbate (cm^3*/mole),* P_o *the saturation vapor pressure of the adsorbate at T, and P the partial pressure of the adsorbate in the experiment. V was taken as the molecular weight of the adsorbate divided by its density at T. A plot of the log of the breakthrough capacity versus the adsorption potential is shown on Figure 6. In Figure 7 the potential plot for the activated coconut charcoal MSA-6 with toluene as the adsorbate is shown, the data being that in Table I.*

More data are being obtained for the activated coconut charcoal, as it is a type currently used in the charcoal tubes. We anticipate that from a potential plot of this charcoal the breakthrough capacities and, thus, the breakthrough volumes can be predicted for contaminants for which no experimental data are available. A suggested volume of workplace air to sample might be one-half the estimated breakthrough volume for the contaminant of interest at a concentration several times the OSHA standard. In halving the breakthrough volume the adverse effect of other compounds, especially water, on the adsorption of the contaminant of interest is taken into account.

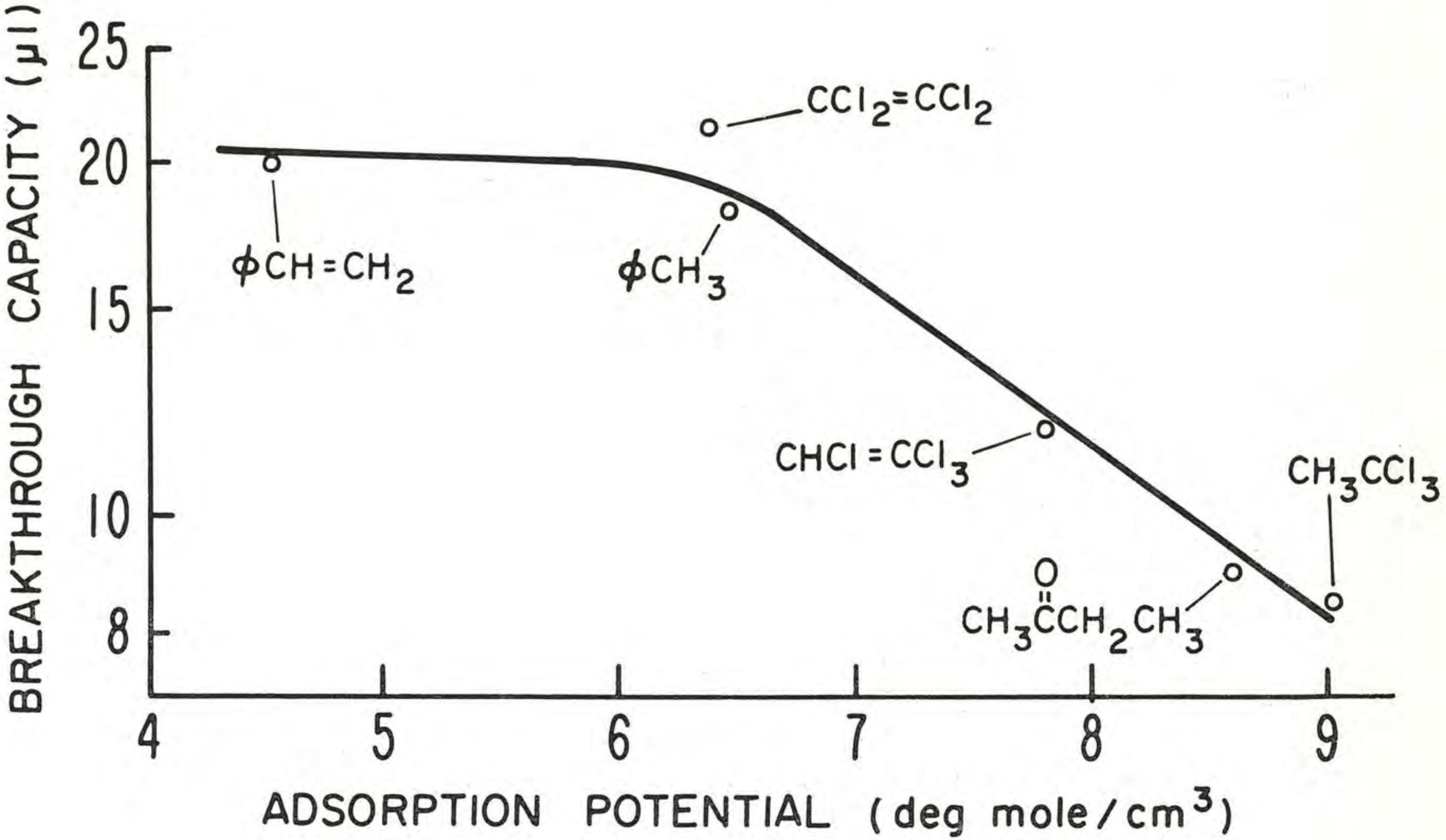


Figure 6. Potential Plot for Activated Petroleum Charcoal 580-26. Data from Table III.

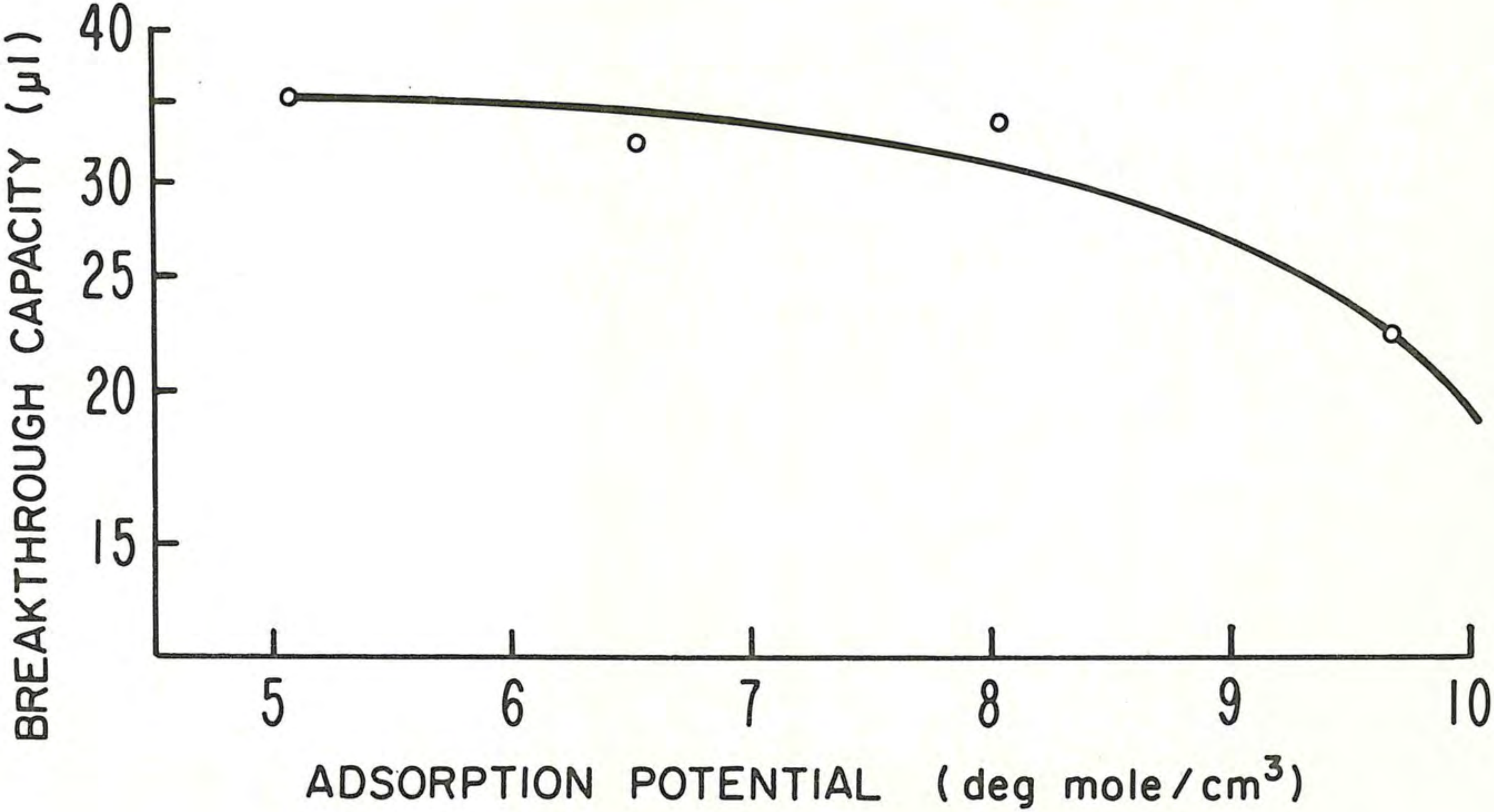


Figure 7. Potential Plot for Toluene on Activated Coconut Charcoal MSA-6. Data from Table I.

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Discussion

Dr. Ballou: How do you relate your time weighted sample to the overall average amounts adsorbed?

Dr. Teass: It's difficult. Soon we are going to get a sampling pump which is capable of sampling at 50 to 200 ml/min. Then we will be able to get the time weighted average from one sample.

Mr. McCammon: You can also approach this problem statistically and figure how many short term samples you need to take - e.g. one 15-minute sample per hour for 7 hours and how high above the OSHA standard you have to be to determine if you are in non-compliance.

Dr. Mieure: Can you use the same pumps? Are you simply measuring with a smaller mesh size and lower flow rate?

Dr. Teass: The pressure drop limitation of the personal sampling pumps is about 13 inches of water. If you don't want breathing zone samples, you can use a stronger sampling pump and a smaller mesh size. This must be done when sampling with porous polymer sorbents.

Mr. McCammon: The first thing you have to take into account is the pump itself and what volume flow it can pull. The commercial pumps now available will pull 1 - 3 liters/min, and will allow up to 13 inches of water pressure drop. The new pump that is coming out is much smaller. The maximum pumping rate is 150-200 cc/min, and it will allow 2.5 inches pressure drop at 200 cc/min. We did do some testing to see if there was any capacity advantage in reducing the mesh size, and the trade-off with pressure drop wasn't worth it.*

Mr. Crable: Who else has a question? Dr. Klier?

Dr. Klier: Is there any relation between these breakthrough capacities and some known properties of the charcoal, such as pore size distribution, surface area, chemical composition of the surface, etc.

Dr. Teass: I don't know. We haven't looked at that.

Dr. Klier: These properties of the sorbents certainly must be characterized in the literature.

Dr. Zlatkis: There is a relationship, but it hasn't been established.

**Sipin Personal Sampler Pump, Anatole J. Sipin Co., 386 Park Avenue South, New York, New York 10016.*

Dr. Klier: There is a university in England which advertises various standard charcoals. You probably have to know all the properties, such as pore volume and surface area, but also you have to establish their relation to the dynamic equilibrium of adsorption and breakthrough.

Dr. Barrett: Do you anticipate the new, small pumps will ultimately replace the larger pumps in the field? Is this an objective?

Mr. McCammon: I doubt if this pump is going to replace the regular coal mine personal sampling pump completely. It will have applications in the area of solid sorbent sampling, specifically with the charcoal tubes. There are a lot of other types of samples-impingers, filters, etc. - that will still need the other pump. This pump is going to open up a new field of sampling, but won't replace the old pumps.

Dr. Zlatkis: One of these areas you might want to look into in the future is the use of carbon molecular sieve sorbents. An advantage might be that they are made by suspension polymerization, and the beads are very uniformly made and very reproducible. The pressure drop could be much smaller than you have in a charcoal column.

Dr. Ballou: I would like to comment on Dr. Klier's question. NIOSH has done a study of the correlation of the physical properties of about 8 or 9 charcoals with the adsorptive capacities. I think the correlation was not too satisfactory.

Dr. Tiernan: What is the history of charcoals you buy? Are they all of a given type and treated the same way , etc?

Dr. Teass: More or less, yes. They are all supposed to be coconut charcoal, activated, and the final treatment is supposed to be heating at 600°C for a certain length of time to remove the volatiles.

Dr. D. Taylor: We do test the batches of charcoal, that are produced by MSA and SKC in our laboratory for desorption efficiency and that type of parameter. The types themselves are also checked for physical characteristics, such as pressure drop and ---

Mr. McCammon: The problem here is that we haven't really known how to specify the properties that the charcoal should have, other than performance specifications. We know what we want it to do when it performs. This is the approach we take on procurement. We have been dealing primarily with one or two suppliers, and they have come up with a process that is fairly reproducible from batch to batch. If anything, it's getting better, so we can't complain.

Mr. Hughes: Has a complete study been started on coated supports, so that you wouldn't have to worry about breakthrough of a large number of organic compounds at room temperature?

Dr. Teass: We are not currently looking at things like porous polymers, although I wish we were.

Mr. Hughes: I would suggest liquid coated supports, like you use for chromatography.

Dr. Zlatkis: Let me point out that the solution to the problem is not as simple as you think.

Mr. Hughes: It is simple from the standpoint that you don't have to worry about breakthrough for a lot of things.

Mrs. Saalwaechter: Yes, you do.

Dr. Zlatkis: First of all, you have to make sure the stationary phase is pure chemical and you cannot use a silicone or a carbowax, of anything that is made commercially in a polymer form of that type, because it won't be reproducible from batch to batch. This is the same difficulty as with charcoal.

Secondly, you will get elution from almost any coating that you use, and from impurities in the stationary phase. With an ultra-pure stationary phase, like pure squalene, which is a C-30 compound, you will have problems of that compound itself coming off in the elution process.

Mr. Hughes: When conditioning chromatographic columns, you presumably purify the liquid support after you make the column. You heat it to 250°C and let the column condition.

Dr. Zlatkis: I know, but the column is different two weeks after you use it, and four weeks after you use it. The elutions are sometimes different, and that is because the stationary phase is changing.

Mr. Hughes: I am talking about an experiment in which you condition the column as reproducibly as you can, pass 70 liters of air through it, and then take it to a laboratory for analysis.

Dr. Zlatkis: I think that would be all right for one compound, but it would be much trouble to get 50 to 100 compounds through the stationary phase.

Dr. Dravnieks: We are talking about sample collection. Column stability is not so important for collection. Sufficient capacity is all that is needed. Considering the actual capacities *for adsorption, activated charcoal is vastly superior to anything else. Highly porous organic polymers are somewhat within 10 or 20% of their capacity. Coated stationary phases are hundreds of times less efficient than porous polymers for collection at room temperature.*

Dr. Zlatkis: The only thing that might be useful in some of the future NIOSH work is controlled porosity supports, or surfaces which have organic ligands on them. These are pretty uniform and fairly stable.

Dr. Klier: Could you tell us again, perhaps, what the principal disadvantages of carbon are? We have records of the advantages, but what are the principal problems with the carbons?

Dr. Teass: Well, one is that you have to use solvent desorption. You cannot use thermal desorption, based on some unpublished work by Gerry Wood, in which he injected benzene into a charcoal bed.

Dr. Wood: I wouldn't conclude that we couldn't use thermal desorption for the charcoal. Under the conditions we were using it didn't work well because a lot of junk came off--tars, etc.--whenever the charcoals were heated.

Dr. Klier: Then one disavantage is a complex chemical composition which on heating, adds to the mixture to be analyzed?

Dr. Teass: As you can see from Table II, they could not make reproducible batches. Also, reaction of the analyte with the active surface may be a problem. The removal of hydrocarbons is high, but with oxygenated compounds you can have reaction at the active surface.

Dr. Klier: Organic surfaces would have an enormous advantage, especially if they can be made hydrophobic. One disadvantage would be that, so far, no larger pore size organic molecular sieves are known. The largest pore size available right now is, perhaps, 13 Å. Chemical dirtiness could be very easily avoided in organic systems.

Dr. Teass: We haven't had any problems with artifacts coming from the charcoal using desorption with carbon disulfide. Generally, when we run blanks, they are, indeed, blank.

Mr. Hughes: When carbon disulfide is used to desorb the trapped species, what is the contaminant species concentration in the carbon disulfide that is injected into the chromatograph?

Mrs. Saalwaechter: In a 10-μl sample --- about one part in a thousand.

Dr. D. Taylor: *Carbon can be used for a large number of species. It has a very high surface area, so it has a fairly large capacity compared to the common inorganic sorbents.*

Dr. Klier: *Molecular sieves have a very high surface area. Type A is just one big surface.*

Mrs. Saalwaechter: *I think our problem is to look at the charcoal batch to batch variability. If there was some way we could characterize charcoal, if we knew what properties we wanted to give us the proper results, we could order it this way or have it made this way especially for our purposes. But we aren't sure about the correlation between the surface area or the pore size and our results; and if your people could help us with that problem, that would be very valuable.*

SULFUR DIOXIDE SAMPLING AND ANALYSIS USING SOLID SORBENTS

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Introduction

The research which is being conducted at the Aerospace Research Laboratories under NIOSH support is primarily directed toward the development and application of mass spectrometric techniques for characterizing solid sorbents. This work has the following objectives: a) to develop mass spectrometric methodology for determining the affinity of various solid sorbents for selected gases, including SO_2, NO, NO_2, N_2O, NH_3 and certain acid mists; b) to apply this methodology to select those sorbents which will most efficiently collect these gases when used with the NIOSH Personal Sampler Pump, and to determine needed data such as capacity of the sorbent, retention characteristics, and the effects of other atmospheric gases, particularly water, on the sorption process; and c) to develop procedures for desorbing and measuring quantitatively the adsorbed gas by mass spectrometry, and to correlate this data with the concentration of the gas of interest in the workplace environment. The studies to be described here are concerned only with SO_2, since most of our attention has been focused on this material this far.

It is appropriate to consider briefly the desirable features of a solid sorbent suitable for gas sampling. The criteria for such sorbents have already been reviewed quite thoroughly at this meeting by Dr. Ballou, but we might reiterate some of these requirements as they apply to SO_2: 1) The sorbent should be capable of adsorbing the material of interest reversibly, that is, so that this material can be recovered quantitatively, or at least, in a known and reproducible percentage. 2) The sorbent must have sufficient capacity to permit detection of the gas of interest at the levels required by OSHA standards. For SO_2 , the 8 hour time-weighted average of the exposure limit is 5 ppm. At the same time, only a minimal quantity of the sorbent should be required in order to be compatible with the NIOSH sampling pump. Typically, this amount is on the order of 0.5 gm. These properties must also apply for sampling at the concentration levels and in the flow regimes which are approximately the same as those encountered under actual workplace sampling conditions. 3) Other atmospheric gases, water, and contaminants should offer no significant interferences to sampling the gas of interest. 4) The sorbent must retain the adsorbed gases for a sufficient time interval to permit storage and shipping from the field to an analytical laboratory (typically up to several weeks). 5) Ideally, the adsorbent should be reasonably inexpensive, capable of regeneration and multiple usage, and not in itself toxic or hazardous. The experimental technique used to identify sorbents having these properties will now be described.

**Systems Research Laboratories, Inc., Dayton, Ohio 45440*

Experimental

Adsorption Test Apparatus and Mass Spectrometer

To accomplish the studies outlined above, a specialized adsorption test apparatus was designed and fabricated at our laboratories. A schematic diagram of this apparatus is shown in Figure 1. All surfaces in the apparatus to which gas is exposed are either stainless steel or Monel metal. The apparatus is heated throughout using heating tapes. Gas is pumped continuously through the apparatus by a forepump which is preceded by a cold trap, to prevent backstreaming into the lines and to minimize contamination of the pump oil. The flow rate and pressure of gas in the apparatus is monitored by sensitive gauges. The flow rate can be accurately controlled by adjusting a throttling valve. A mixture of air is admitted through the intake port (either directly from the lab atmosphere or through a drying tube to remove moisture) and a controlled quantity of SO_2 *is titrated into the stream through a variable leak valve, thereby synthesizing the desired mixture. This procedure was used for most of the general screening experiments to be discussed later. The second method involves direct introduction of a premixed* SO_2 *- air mixture. The latter was obtained from a commercial supplier and contained concentration of about 2000 ppm* SO_2 *in air. This mixture was diluted further by mixing with additional air during injection in some cases.*

By appropriately adjusting valves, the gas mixture can be passed through the adsorption tubes or columns which are packed with the solid sorbent to be tested. Leak valves permit sampling of the gas stream on either the head or back side of the column. The sampled gas passes directly into a CEC 21-103C Mass Spectrometer which is used for analysis. The composition of the gas stream can thus be determined both before and after it has passed through the solid sorbent. By knowing the flow rate accurately, the capacity of the sorbent for the gas of interest is readily determined.

The CEC 21-103C Mass Spectrometer is a modified instrument which is equipped with a 17-stage electron multiplier. This instrument is designed to scan the accelerating voltage while maintaining a constant magnetic field. It also has provision for rapid peak switching, so that several discrete peaks can be rapidly monitored in sequence. The stability of the accelerating voltage and magnet supplies is sufficiently good to permit continuous monitoring of a single m/e peak for a substantial time interval. It is thus possible to obtain an integrated response for a given mass peak by using an electronic integrator; in this case, a Datex Electronic Integrator was utilized for this purpose.

In these experiments, characteristic peaks in the mass spectra of both air and SO_2 *were monitored to determine the composition of the gas stream in the adsorption apparatus. For* SO_2 *, m/e 48, (*SO^+*), was monitored since this is a large intensity fragment ion in the spectrum and there are no*

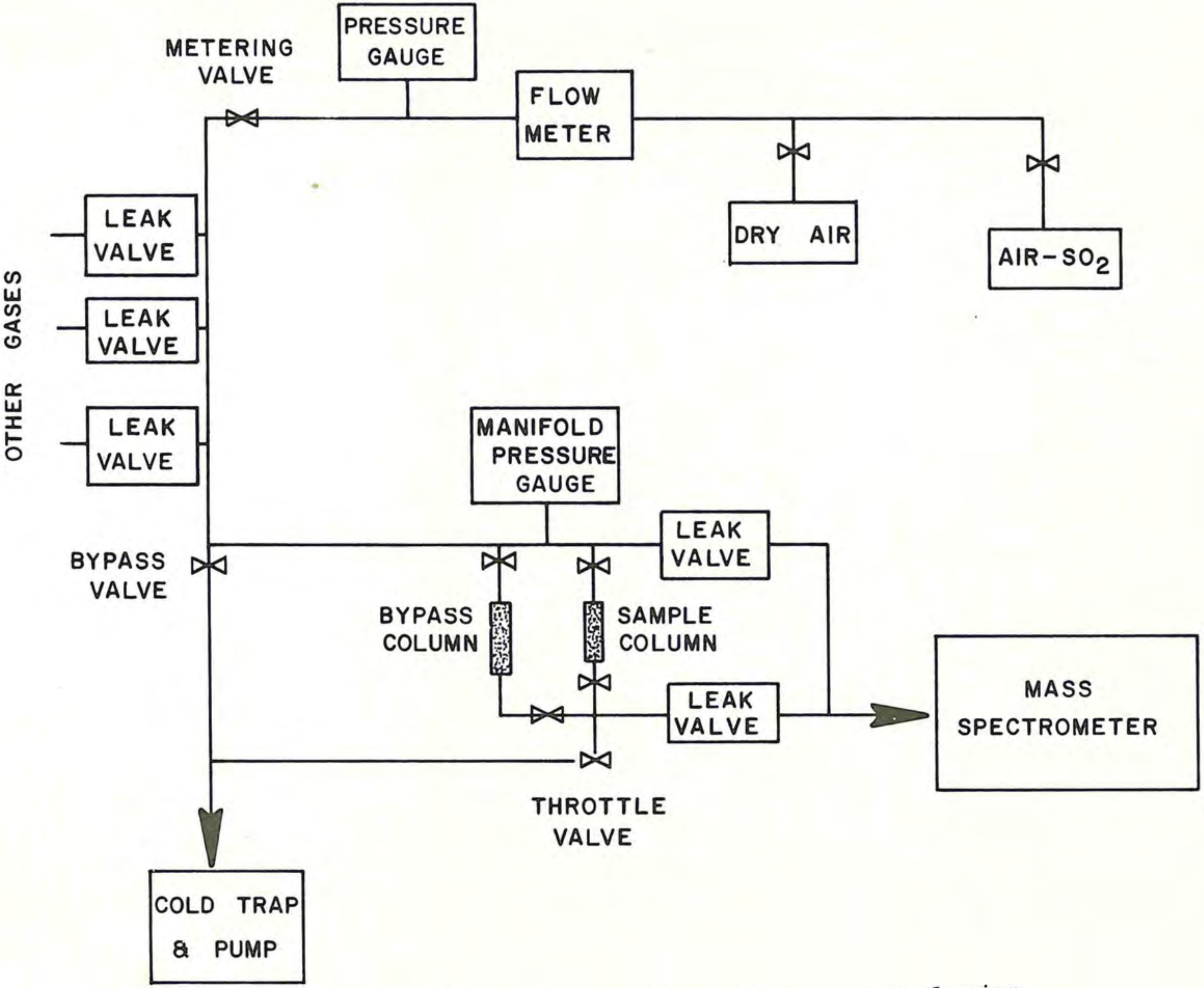

Figure 1. Schematic Diagram of Gas-handling Apparatus for Performing Adsorption-desorption Studies of Pollutants at ppm Concentration Levels.

significant interferences at this mass from other compounds. In the case of air, the major component nitrogen, gives m/e 28 as its principal mass spectral peak. However, since air is by far the largest component in the mixtures of interest, (SO_2 is at the ppm level), it is preferable to monitor the m/e 29 isotope peak (that is, $^{15}N^{14}N^+$), since the intensity of this peak is comparable to that of the SO^+ peak being monitored and changes in the sensitivity of the electron multiplier detector are therefore not necessary when measuring these peaks in sequence. The relative abundance of the isotope peak is well established and thus the m/e 28 intensity can be readily calculated from the measured m/e 29 intensity. This is necessary because it is desirable to calibrate the mass spectrometer response for the m/e 28 peak from air. Obviously, the instrument response is also calibrated for known quantity of SO_2 . The measured peak intensities can therefore be converted to a quantitative basis by using the instrument calibration factors.

Mass Spectrometric and Instrumental Parameters

In order to demonstrate that the gas sample entering the mass spectrometer is truly respresentative of the gas in the adsorption apparatus at the sampling point, it is necessary to show that the mass spectrometer response is a linear function of pressure in the adsorption apparatus. That this is indeed the case is confirmed by the data in Figure 2 which shows the mass spectral response (intensity/pressure) as a function of pressure. In the pressure regime of interest, the normalized intensity/pressure ratio is constant over a substantial pressure range. The constancy of these ratios indicates that the sampling process occurs in the molecular flow regime. The ratio of the normalized intensities,

$$K = (I/P)_{air}/(I/P)_{SO_2} \tag{1}$$

is also plotted as a function of pressure. K is effectively a sensitivity correction factor, and the SO_2 concentration in the air stream can be calculated for a given experiment from the relation,

$$[SO_2] = \frac{I_{48}}{I_{29}} (0.0072)(K) \tag{2}$$

where I_{48} and I_{29} are the appropriate mass spectral peak intensities.

It is also important to know that the sampling efficiency does not vary in an unpredictable manner with flow. Varying the flow of either the SO_2 or air streams should yield concentration changes which follow the relation,

$$Y = \frac{c}{x} \tag{3}$$

where y is the concentration of SO_2, c is a constant and x is the rate of flow of the diluting gas, air. Figures 3 and 4 show the measured SO_2 concentrations in the flowing stream as a function of increasing air flow at two different pressures. Obviously, the SO_2 concentration is inversely proportional to the air flow rate.

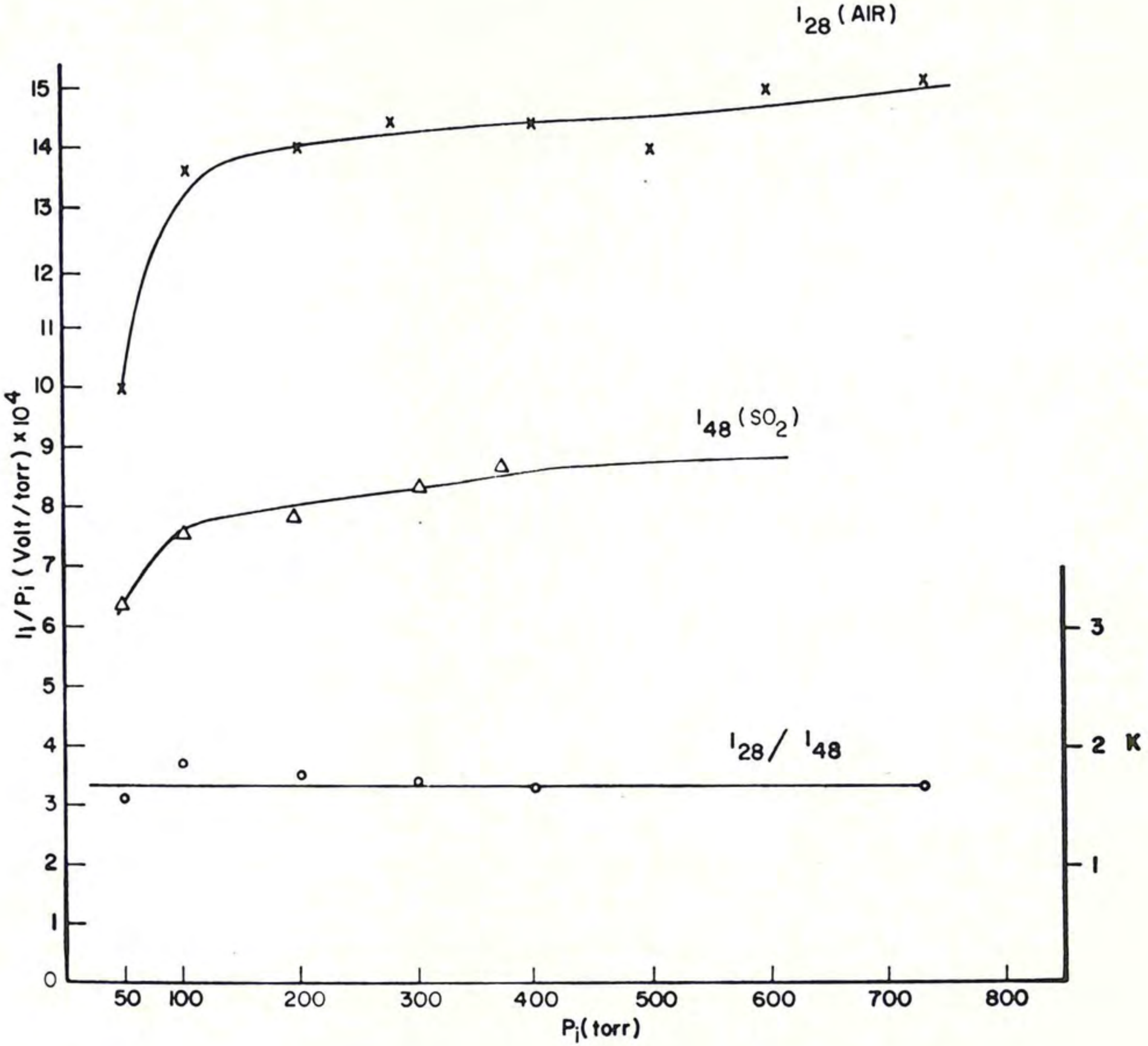

Figure 2. Calibration of Relative Sensitivity of Mass Spectrometer (CEC 21-103C).

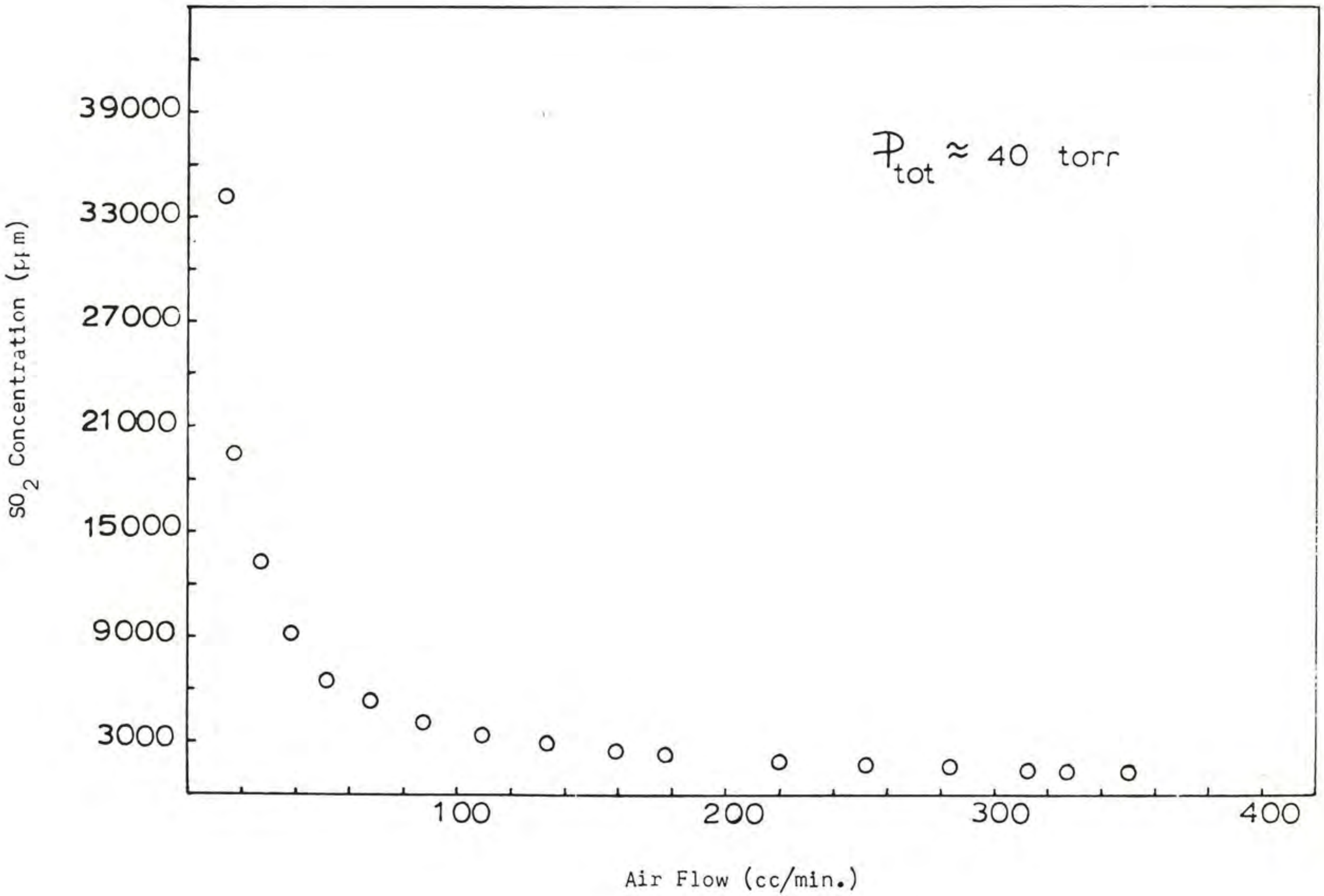

Figure 3. Effect of Increasing the Flow Rate of Diluent Air on the Measured SO_2 Concentration (P_{total} = 40 Torr).

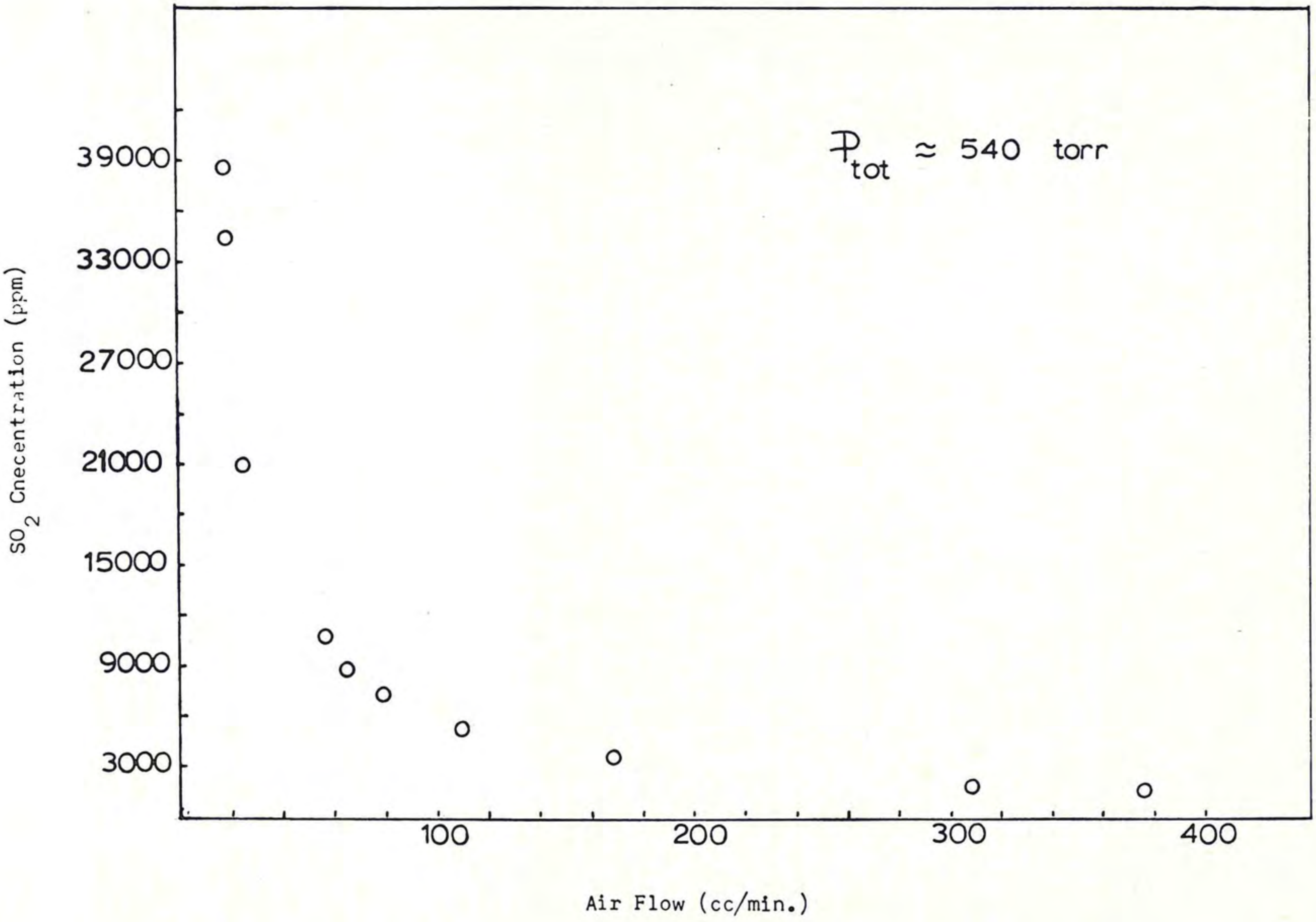

Figure 4. Effect of Increasing the Flow Rate of Deluent Air on the Measured SO_2 Concentration (P_{total} = 540 Torr).

Still another important factor to be considered is the time stability of the ion intensity signals. As shown in Figures 5 and 6, the e SO^+(m/e 48), SO_2^+(m/e 64) and $^{15}N^{14}N^+$(m/e 29) signals are all quite stable as measured for a period extending over some 40 minutes. It should be mentioned that these responses were obtained under optimum operating conditions and after the initial stabilization of the system had taken place. It might be noted at this point that equilibration of the adsorption apparatus can require a substantial period of time under certian operating conditions. SO_2 tends to sorb readily on the surfaces of the apparatus and then it is released gradually over a period of time. These problems are particularly severe when one is dealing with very low concentrations of SO_2 in the air stream and are highly pressure dependent. After considerable experience with these problems, it was concluded that the best procedure to follow was that of accomplishing the adsorption experiments at essentially atmospheric pressure (as appropriate for the actual NIOSH sampling environment), while operating at reduced pressure during desorption (as described below). Background problems are minimized with this procedure. Moisture in the environment to be sampled is also a potential problem, since it is conceivable that this may affect the SO_2 concentration during sampling or adsorption through formation of acids. Acids in turn would likely react strongly with surfaces of the test apparatus. Some preliminary experiments were conducted in which laboratory air having a relative humidity of about 68% was used as the diluent gas. By adding progressively larger quantities of the diluent (that is, increasing the flow rate), it was thus possible to increase the moisture content of the stream and see if the measured SO_2 levels deviated significantly from those expected. As shown in Table I, the measured SO_2 levels exhibited the expected inverse proportionality dependence on air flow rate (c in Table I is the constant indicated in Eq. 3). Over the range investigated here therefore, moisture does not seem to have an adverse effect. However, subsequent work showed a more pronounced effect. Additional experiments to determine the effects of high levels of atmospheric moisture are clearly needed and will be conducted in future studies.

Results

Characterization of Solid Sorbents

Having determined the appropriate operating conditions and experimental parameters for the adsorption test apparatus, we then initiated screening studies on a wide variety of solid sorbents in order to identify those materials which exhibit high affinity for SO_2. Table II lists some of the materials which were investigated. Some of these materials are typical chromatographic packings (including coated packings), while others are standard solid sorbents. Many of the materials listed were suggested by reports in the literature to have some affinity for SO_2.

The preliminary screening experiments were carried out using a dry air stream as the diluent and SO_2 was metered into this stream to produce various desired concentration levels. Usually, rather high concentrations

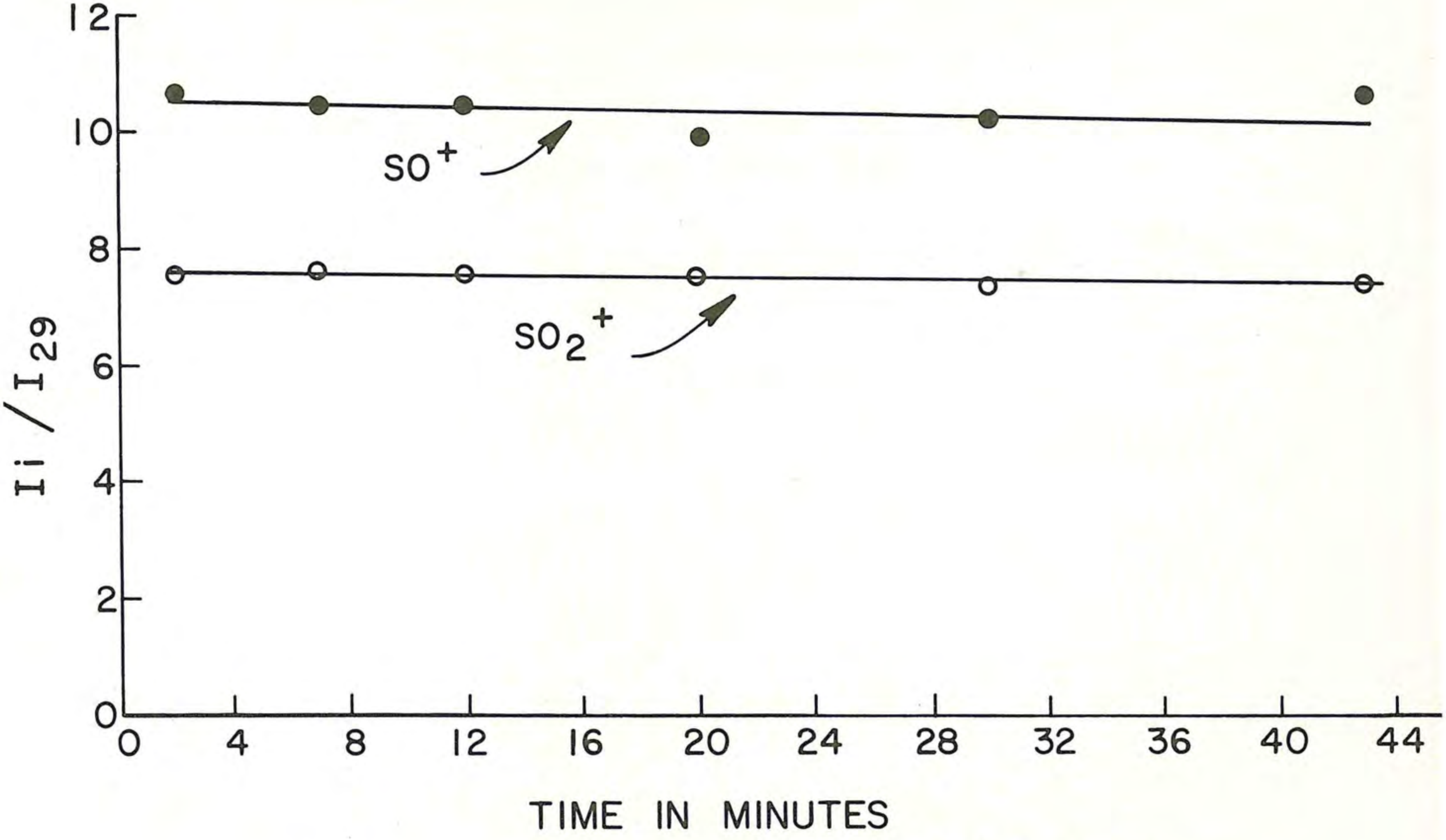

Figure 5. Ratio of Intensities of $^{14}N^{15}N^+/SO_2^+$ and $^{14}N^{15}N^+/SO^+$ Found in the Mass Spectrum of the Standard SO_2-air Mixture as a Function of Time.

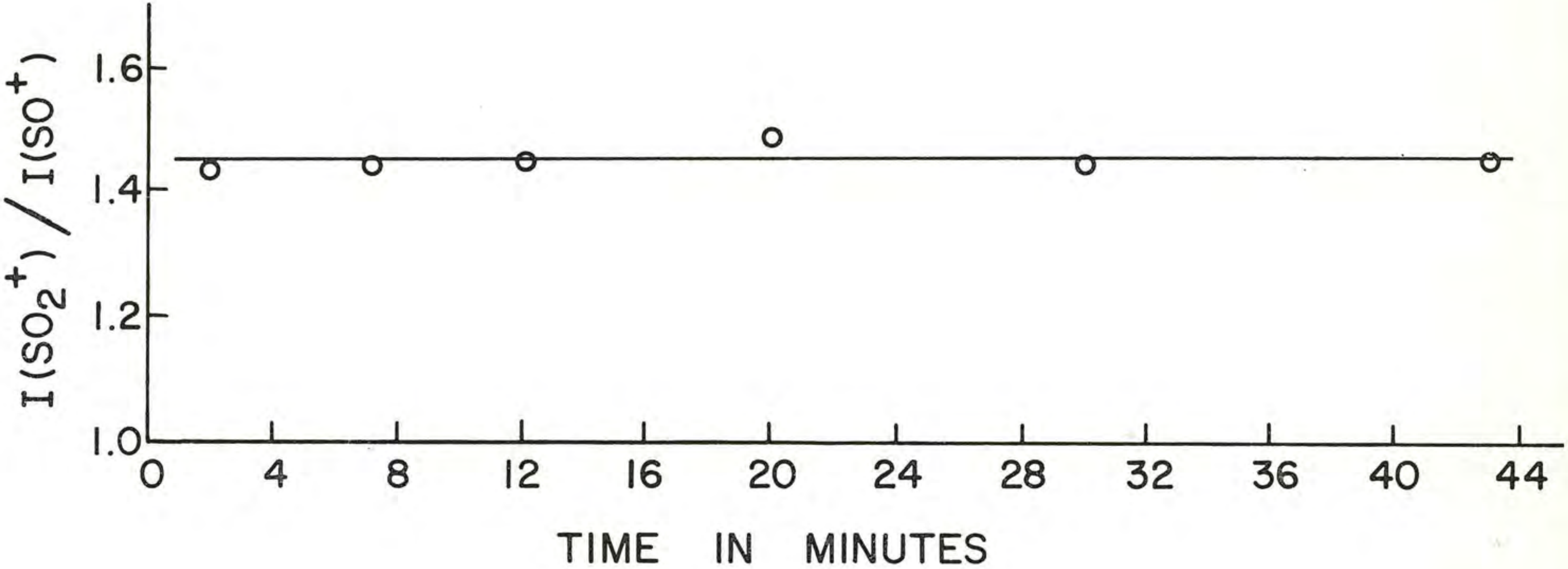

Figure 6. Ratio of Intensities of SO_2^+/SO^+ in the Mass Spectrum of Pure Sulfur Dioxide as a Function of Time.

Table I

Effect of Moist-Air Flow Rate on SO_2 Concentration

Pressure (Torr)	Air Flow Rate (cc/min.)	SO_2 (ppm)	c*
22	0	----	----
31	50	2264	113,200
37	110	1024	112,640
42	150	756	113,400

*equation (3)

Table II

Description of Materials

Adsorbent	Particle Size	Source
Molecular Sieve 5A (Hylar M)	45/60 Mesh	1
Porapak N	80/100	2
Porapak P	50/80	2
Porapak Q	60/80	2
Porapak R	80/100	2
Porapak S	80/100	2
Porasil B	80/100	2
Porous Glass	60/80	1
Spherosil XOA400	40/100µ	1
Alumina, Activated, Alcoa, Type F-1	40-60	3
Chromosorb 101	60/80	1
Calcium Oxide	Fine Powder Approx. 120/140	3
Magnesium Oxide	Fine Powder Approx. 120/140	3
Carbosieve B	45/60	1
Molecular Sieve 13X	45/60	1
Molecular Sieve 4A	80/100	1
Tetraethylammonium Fluoride	Approx. 60/80	4
Porapak T coated with	----	2
Arachlor 1232	----	1
Chromosorb W	60/80	2
Chromosorb T coated with Didecyl Phthalate	40/60	1

1. Supelco, Inc., Bellefonte, Pa.
2. Applied Science Laboratories, Inc., State College, Pa.
3. Matheson, Coleman, and Bell, Norwood, Ohio
4. Eastman Kodak Co., Rochester, New York

of SO_2 were employed since the only objective of these experiments was to obtain an estimate of the capacity of the materials for sorbing SO_2. The procedure followed here was essentially as described earlier. An air-SO_2 mixture was produced by mixing these gases in the test apparatus, and the concentration of SO_2 was determined by direct mass spectrometric measurement. This gas was then admitted to the columns containing the sorbent materials to be tested, while the composition of the gas stream emerging from the column was monitored continously. A typical adsorption plot obtained in this manner at low pressure as a function of time is shown in Figure 7 (plots obtained at higher pressures were essentially identical, although background signals were larger). As seen in Figure 7, the mass spectrometric signal (m/e 29), which is a measure of the air concentration, is essentially constant throughout the experiment, just as it should be. The signal which provides a measure of the SO_2 concentration (m/e 48), is initially constant, but drops to the background level when the stream is admitted to the sorbent column (at time $\Theta_1 = 0$). This indicates that the sorbent is initially removing all of the SO_2 from the stream. At time Θ_2 however, breakthrough begins, and SO_2 is then detected in the stream which has passed through the column. The amount of SO_2 passing through the column then increases sharply and the curve rises to the initial SO_2 level (at $t = \Theta_3$), indicating that the sorbent is saturated and is no longer removing any SO_2 from the stream. Obviously, those materials which exhibit the longest breakthrough times have the largest capacity for SO_2 sorption.

From breakthrough experiments it was concluded that, in general, the chromatographic packing materials (e.g., Chromosorb T coated with di-N-decylphthalate) were not acceptable sorbents since they exhibit little capacity. Several of the solid sorbents (activated charcoal, Porapak Q) showed promise, particularly the Molecular Sieve 5A.

High sorption capacity is one criterion for a suitable sorbent, but it is also necessary that the material desorb or release the material upon suitable treatment, so that the trapped gas can be analyzed. In the present studies, the desorption procedure involved passing dry air through the sorbent (at a rate of 100 cc/min), while heating the material, typically to temperatures as high as 240°C. As already noted, desorption was accomplished at low pressures to avoid problems of sorption on the apparatus surfaces. Molecular Sieve 5A was the only material tested with acceptable desorption characteristics. Other materials, such as Porapak Q, activated charcoal, Carbo-sieve B, and Chromosorb T, either desorb SO_2 at room temperature (indicating poor retention ability, and possible loss during storage), exhibit poor desorption peak shape, or retain the SO_2 indefinitely. A satisfactory desorption response curve, (such as plotted in Figure 8), is essentially Gaussian in shape, which permits an accurate integration of the area for quantitative determination.

A series of more detailed screening experiments were accomplished using ordinary laboratory air (relative humidity ~ 70%) as the diluent to prepare the SO_2 mixtures. These experiments were conducted under lower

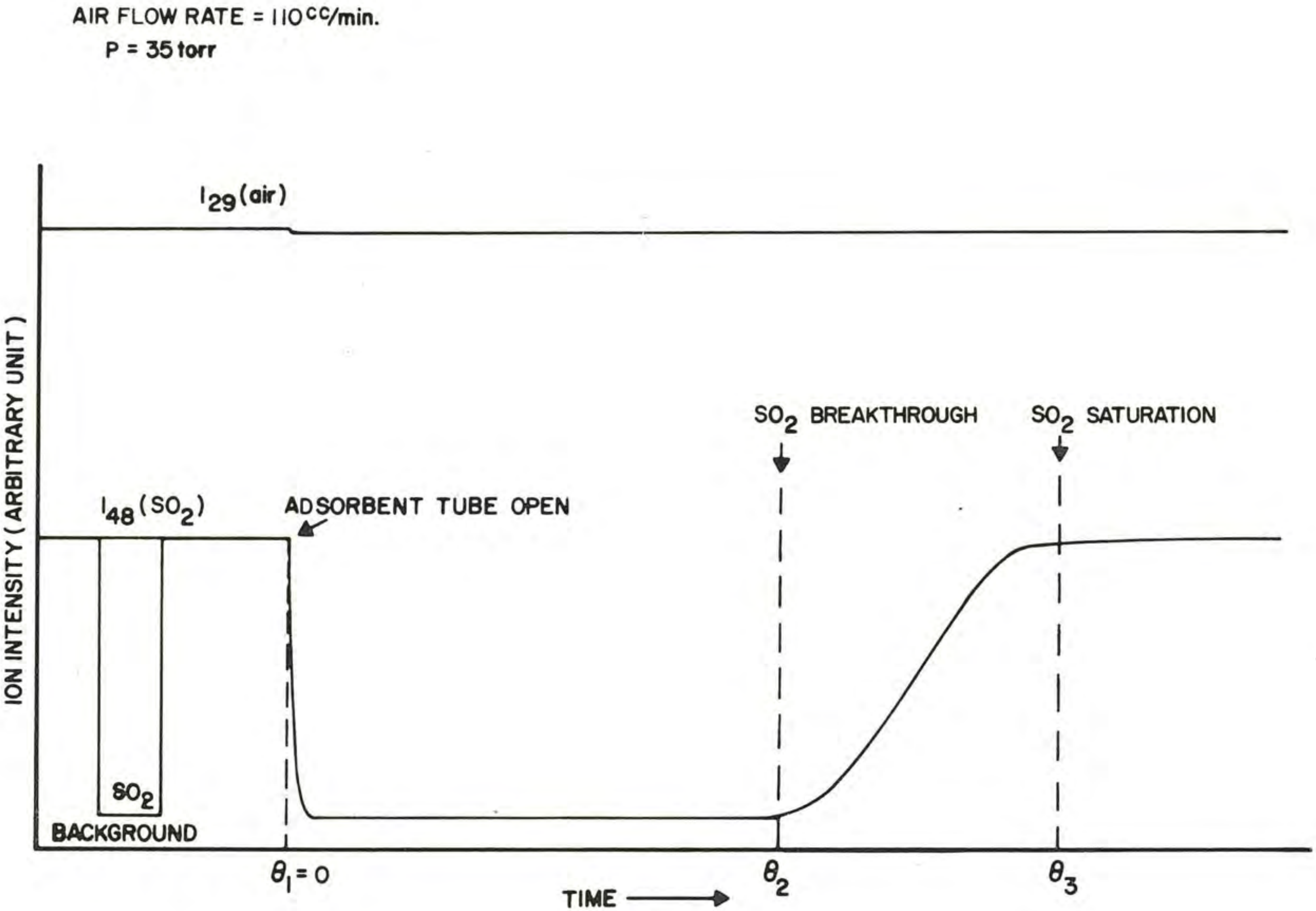

Figure 7. Typical Adsorption Curve at Low Pressures.

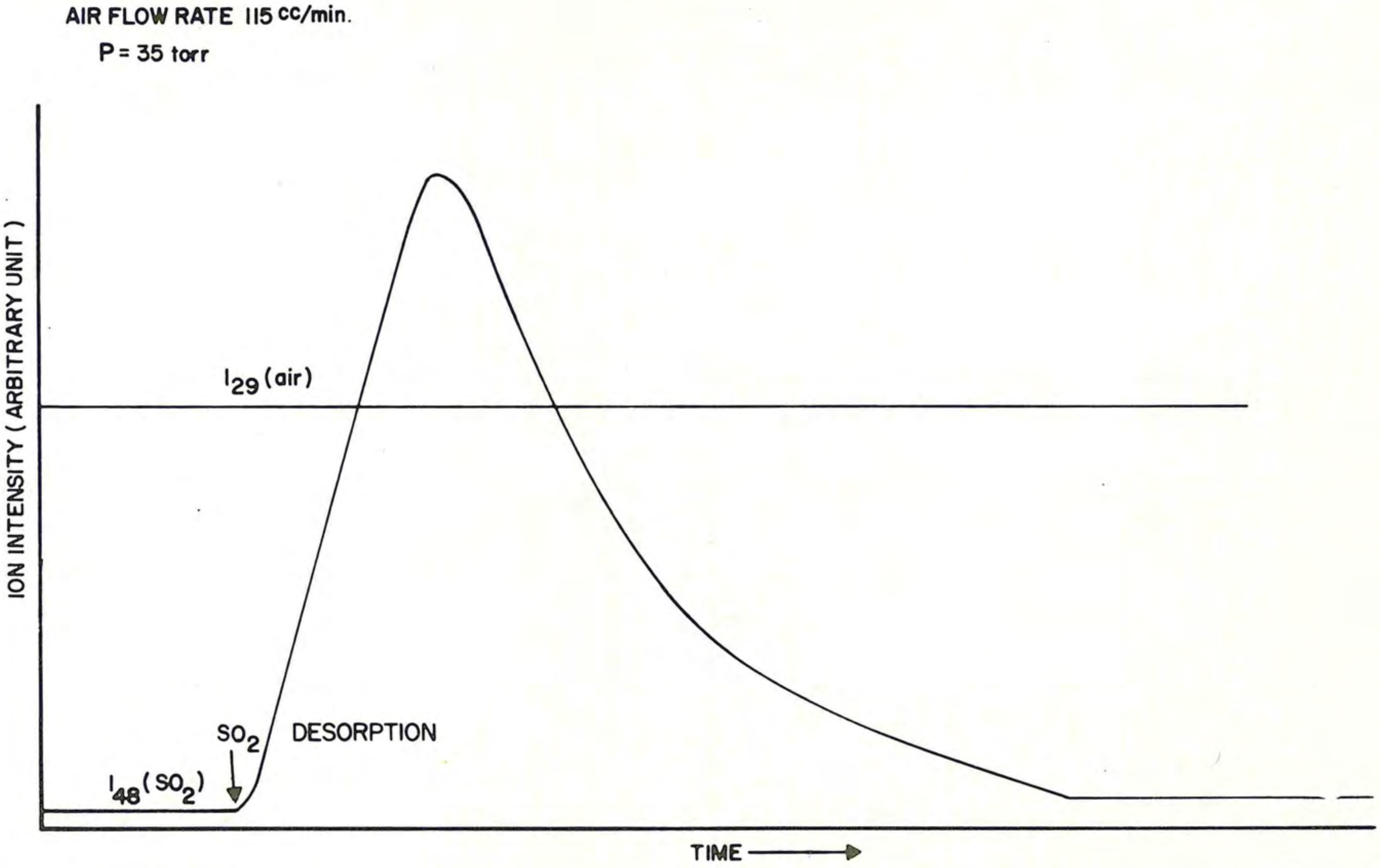

Figure 8. Low Pressure Desorption of SO_2 from the Sorbent.

pressure conditions to minimize background problems. Breakthrough and saturation times are shown in Table III for some of the sorbents investigated. Noteworthy in this data is the large capacity of Molecular Sieve 5A for SO_2. Some of the Porapak materials (particularly Porapak S), alumina, and Spherosil also appear to be highly effective sorbents. However, desorption tests for these same materials indicated that the latter materials either retained SO_2 even under vigorous desorption conditions, or desorbed SO_2 too readily (that is, at room temperature). Only the Molecular Sieve 5A exhibited satisfactory characteristics for both adsorption and desorption of SO_2.

Quantitative measurements of the amount of SO_2 recovered upon desorption were also made, and preliminary data are shown in Table IV. These data suggest that the percentage recovery on MS-5A is dependent upon both the concentration of SO_2 in the air stream and the frequency of usage of the sieve. The very low recoveries shown for experiments (3) and (4) are apparently due to the very small quantities of SO_2 sorbed in these experiments. As later results showed, a small amount of SO_2 appears to be irreversibly sorbed on the molecular sieve and this is a significant fraction of the total sorbed SO_2 for low level experiments. It is not clear whether this phenomenon indicates that there are a certain fraction of active sites on the sieve which do not release the sorbed species. The fact that the molecular sieve exhibits better recovery upon repeated use after the initial sorption-desorption cycle with SO_2 indicates a conditioning effect. This might be due either to the need for saturating certain active sites on the sieve, or to the presence of water or other materials on the sieve, which are removed after the first sorption cycle.

The preferential retention of SO_2 by Molecular Sieve 5A is shown more clearly in Figure 9. Here the desorption peaks are shown for four successive sorption-desorption cycles with the same sieve sample. In all four of these experiments, the same quantity of SO_2 was passed over the sieve, (340,000 mv. s.), and it is evident that the recovery is essentially identical for cycles 2, 3 and 4, but markedly lower for the first cycle. The data plotted in Figure 10 indicate that this retention effect on the first adsorption cycle is observed over a wide range of sorbed SO_2 levels. After this intial cycle, however, the relative amount of SO_2 desorbed is directly proportional to the adsorbed SO_2.

Quantitative Studies

In order to accomplish more accurate quantitative measurements of SO_2 sorption, some modifications to the adsorption test apparatus were made to minimize "memory" effects resulting from SO_2 sorption on walls of the apparatus. These changes resulted mainly in reducing the path length between the sorbent column and the mass spectrometer. In addition, to eliminate possible uncertainties which might arise from incomplete mixing of SO_2 and air in the case where mixtures were prepared "in situ," a premixed SO_2-air mixture was used in these studies (2080 ppm SO_2 in air),

Table III

Low-Pressure Adsorption Experiments for Various Adsorbents

	Experimental Conditions				
Adsorbent with Weight (G)	*Air-Flow Rate (cc/min.)*	*Relative Humidity*	*SO_2 (ppm)*	*Time Required For SO_2 Break-Through (Θ_2, min.)*	*Time Required For SO_2 Satuaration (Θ_3, min.)*
(1) MS-5A (0.478)	*115*	*56*	*5358*	*45*	*60*
(2) Porapak N (1.810)	*80*	*56*	*4916*	*15*	*27*
(3) Porapak P (2.62)	*80*	*56*	*4544*	*3.5*	*19.5*
(4) Porapak Q (1.646)	*80*	*56*	*4551*	*4*	*17*
(5) Porapak R (1.50)	*80*	*56*	*4610*	*11*	*25*
(6) Porapak S (1.79)	*70*	*56*	*4522*	*25*	*31*
(7) Porasil B (1.940)	*78*	*48*	*4605*	*8.3*	*25*
(8) Porous Glass (4.16)	*100*	*42*	*5661*	*5*	*15*
(9) Spherosil XOA400 (1.907)	*38*	*42*	*5355*	*14.7*	*15.7*
(10) Alumina (4.772)	*100*	*42*	*4709*	*194.5 No breakthrough*	
(11) Chromosorb 101 (1.661)	*100*	*61*	*3325*	*3.5*	*12.5*
(12) CaO (0.315)	*58*	*67*	*2121*	*10*	*15*
(13) MgO (0.348)	*58*	*67*	*2698*	*9*	*20*

Table IV

SO_2 Recovery Study for Various Adsorbents under Low-Pressure Adsorption and Desorption Processes

	Adsorption Conditions				
Adsorbent with Weight (G)	Air-Flow Rate (cc/min.)	Time for Adsorption (Min)	SO_2 (ppm)	SO_2 in the Adsorbent Before Desorption (Days)	% Recovery of SO_2 (+ 10%)
(1) MS-5A^1 (0.478)	115	45	5358	1	62
(2) MS-5A^2 (0.478)	100	53	2570	1	94
(3) MS-5A^2 (1.145)	108	15	254	7	33
(4) MS-5A^5 (0.478)	108	12	323	5	23
(5) MgO^1 (0.348)	58	9	2698	1	23
(6) CaO^1 (0.315)	58	10	2121	1	0

1: First time used
2: Second time used
5: Fifth time used

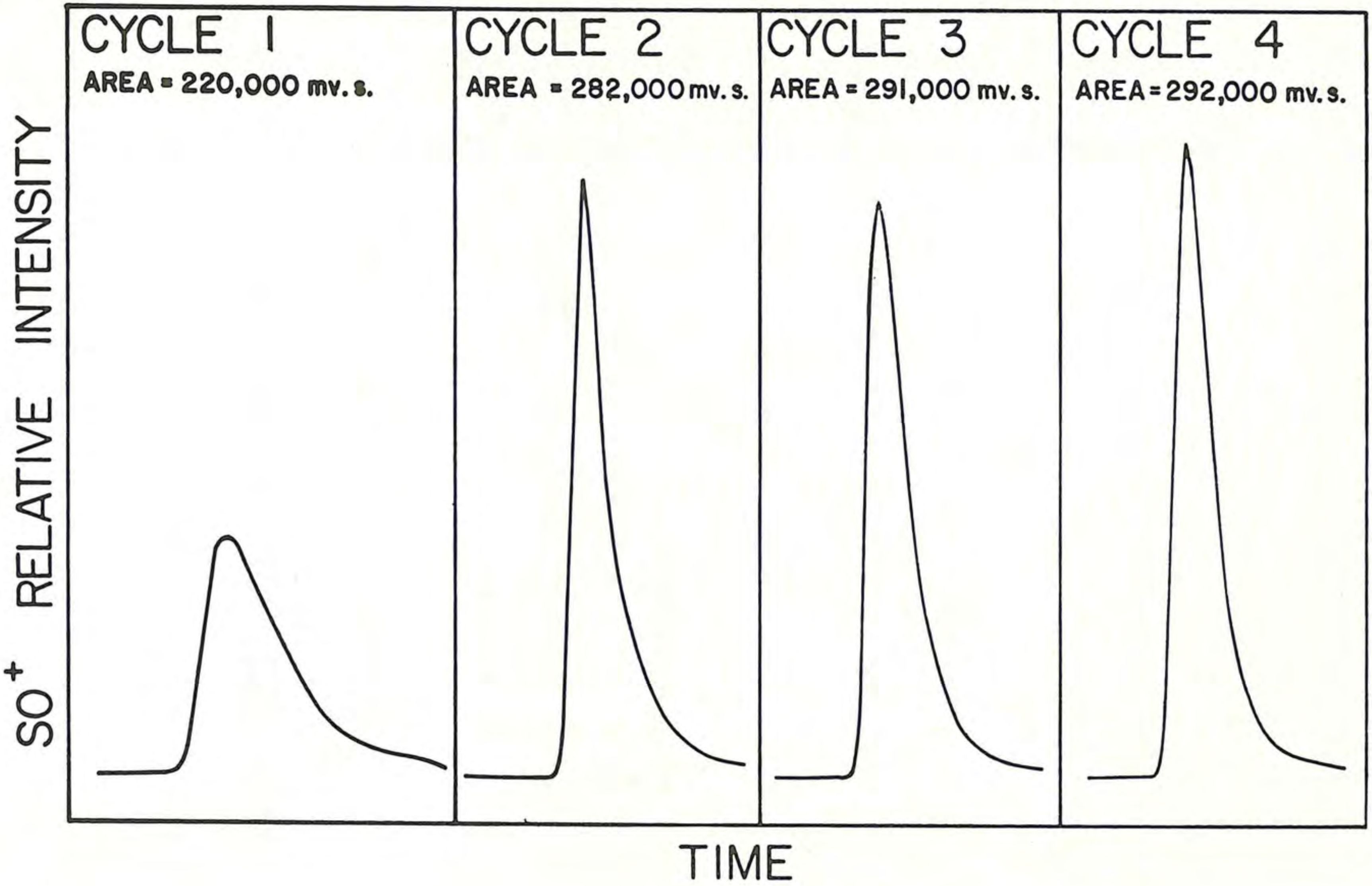

Figure 9. Recovery from Untreated and Pretreated Molecular Sieve 5A.

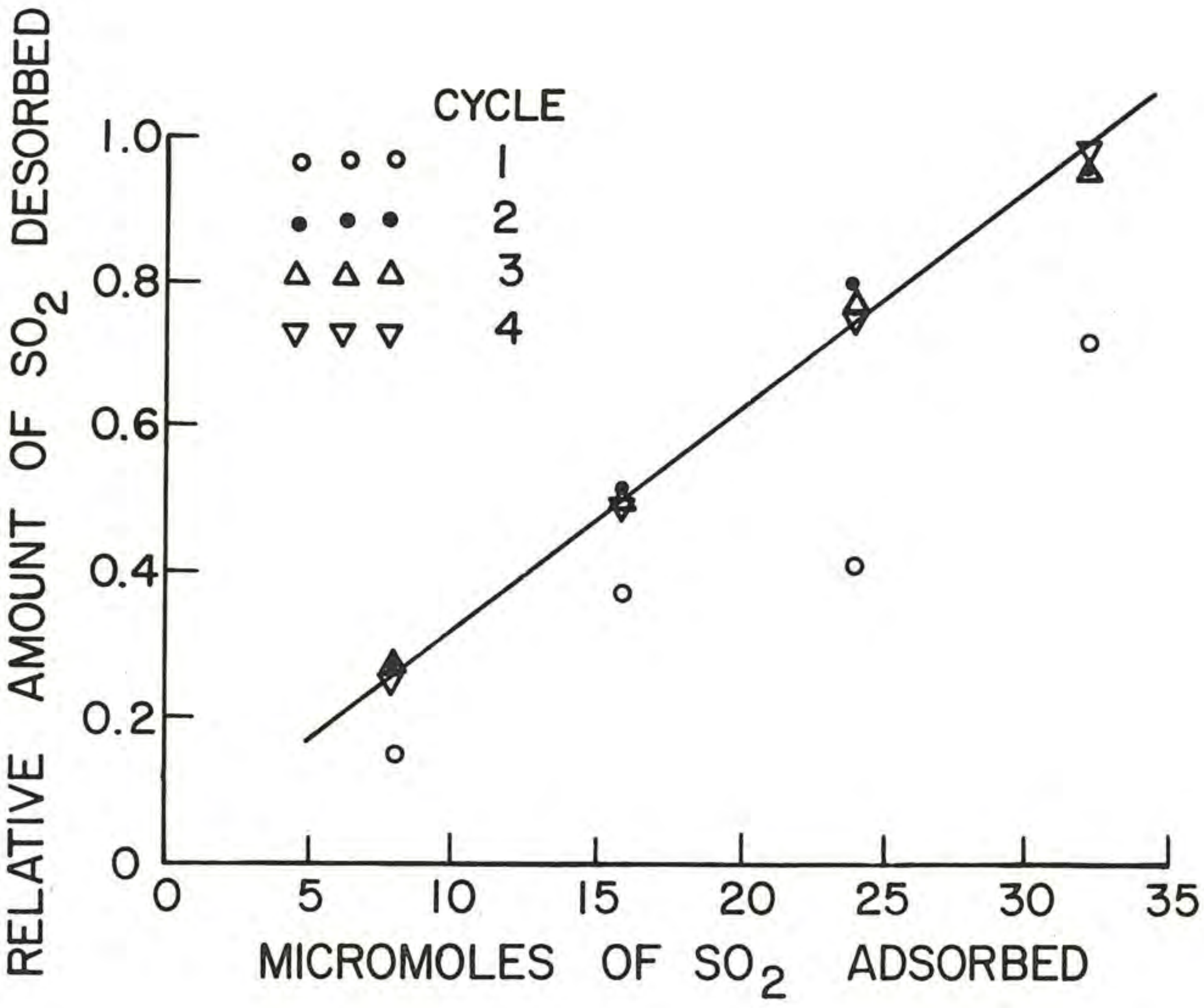

Figure 10. Recovery of SO_2 from Pretreated and Untreated Molecular Sieve 5A Columns as a Function of Quantity of SO_2 Adsorbed. "Cycle" Indicates Number of Adsorption-desorption Cycles to which the Four Different Columns were Subjected.

as already noted. Accurately known quantities of SO_2 could thus be introduced into the sorbent columns since both the composition of the standard mixture and the flow rate were measured. It was further established that pretreatment of the Molecular Sieve 5A, by heating it to 200°C while flushing with dry air, eliminated the retention effect on the first adsorption cycle which was discussed above. Under these optimum conditions, the relationship between the quantity of SO_2 desorbed and that adsorbed is linear over a wide range of total sorbed SO_2 levels (2 - 220 micromoles), as illustrated in Figures 11 and 12. Some sieve samples were successfully used as many as 12 times in these experiments with no degradation in capacity of performance.

Data showing the quantities of SO_2 adsorbed and desorbed on Molecular Sieve 5A are given in Table V. It is seen that an essentially constant percentage of the sorbed SO_2 is not recovered in these experiments. A determination of the limits of reproducibility can be made from the data for experiment numbers 23 - 26. In these experiments, an equal quantity of SO_2 was adsorbed and desorbed in four successive experiments and the average recovery was found to be 85%. The overall reproducibility was within 10%. At this point in our investigations, it is not clear why a constant fraction of the sorbed SO_2 is retained on the sorbent.

Storage Experiments

As discussed earlier, it is desirable that the sorbent be capable of retaining the sorbed SO_2 for periods up to 2 weeks without loss or conversion of the gas. Experiments to estimate the retention capacity of Molecular Sieve 5A for SO_2 have thus far been conducted for storage periods up to six days. The results, shown in Table VI, indicate that there is no loss of sorbed SO_2 even when the sieve (with sorbed SO_2) has been stored as long as 145 hours prior to desorption and analysis. Experiments extending over longer time intervals are in progress.

Detection Limits

It is possible to estimate from the data obtained in the present studies the lower limits of detectability for SO_2 using the Molecular Sieve 5A sorbent. The smallest quantity of SO_2 successfully adsorbed and desorbed in the experiments was 3.2 micromoles. If the NIOSH sampling pump were operated in a typical monitoring situation at a rate of 1.2 liters/minute for a period of 8 hours, a total volume of 560 liters or 26 moles of air would be sampled. This volume would correspond to an effective SO_2 concentration in the atmosphere of 3.2×10^{-6} per 26 moles of air or 0.1 ppm, which is well below the TLV values of 5 ppm specified by NIOSH for SO_2.

The upper limit of adsorption capacity is limited only by the quantity of sorbent used. For 0.5 gm. of the Molecular Sieve 5A, and SO_2 concentration of 200 ppm could be effectively sampled under the same conditions described above.

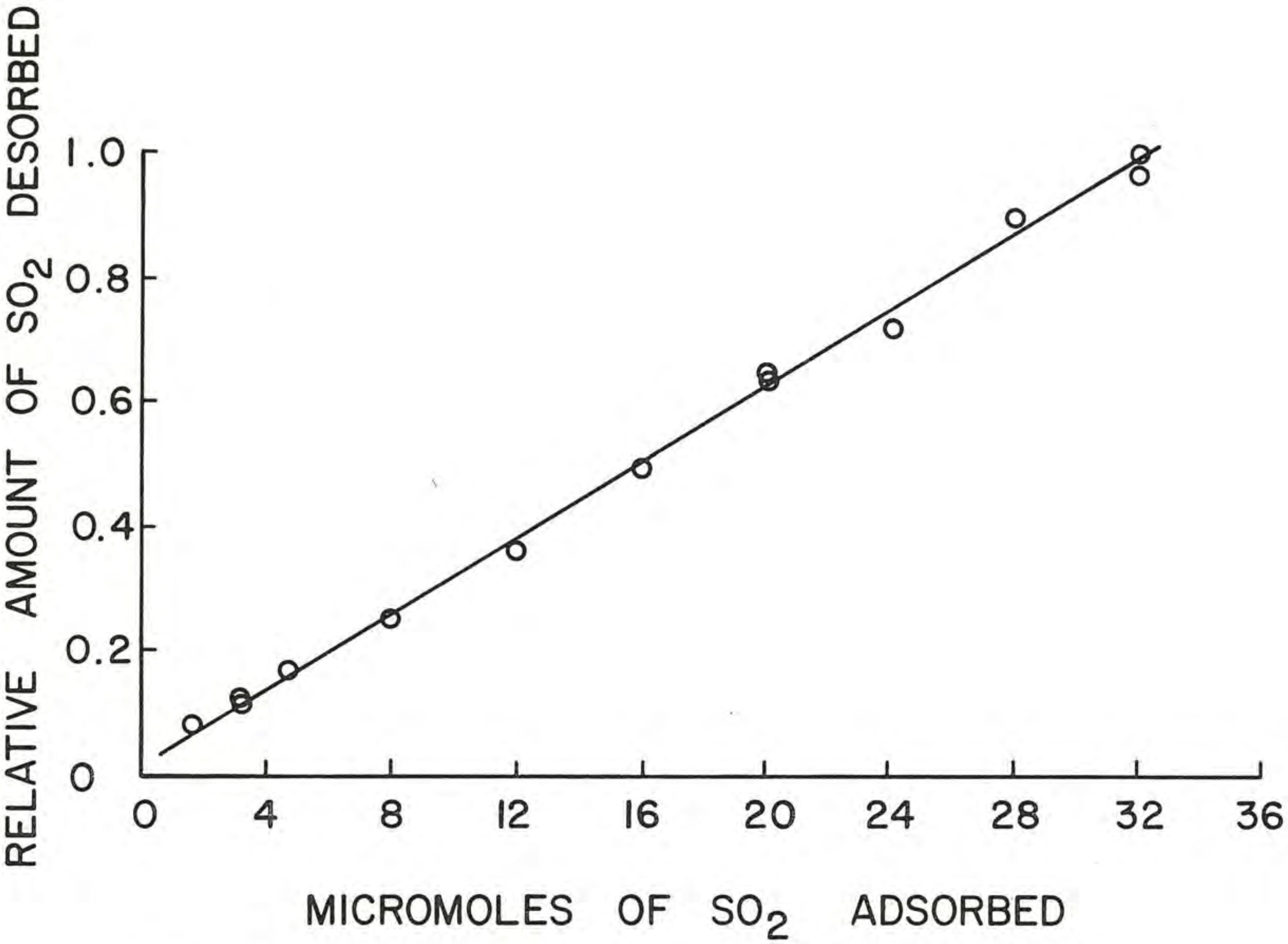

Figure 11. Relationship Between Quantity of SO_2 Adsorbed on Molecular Sieve 5A and that Desorbed. Flow Rate, 55 cc/min.

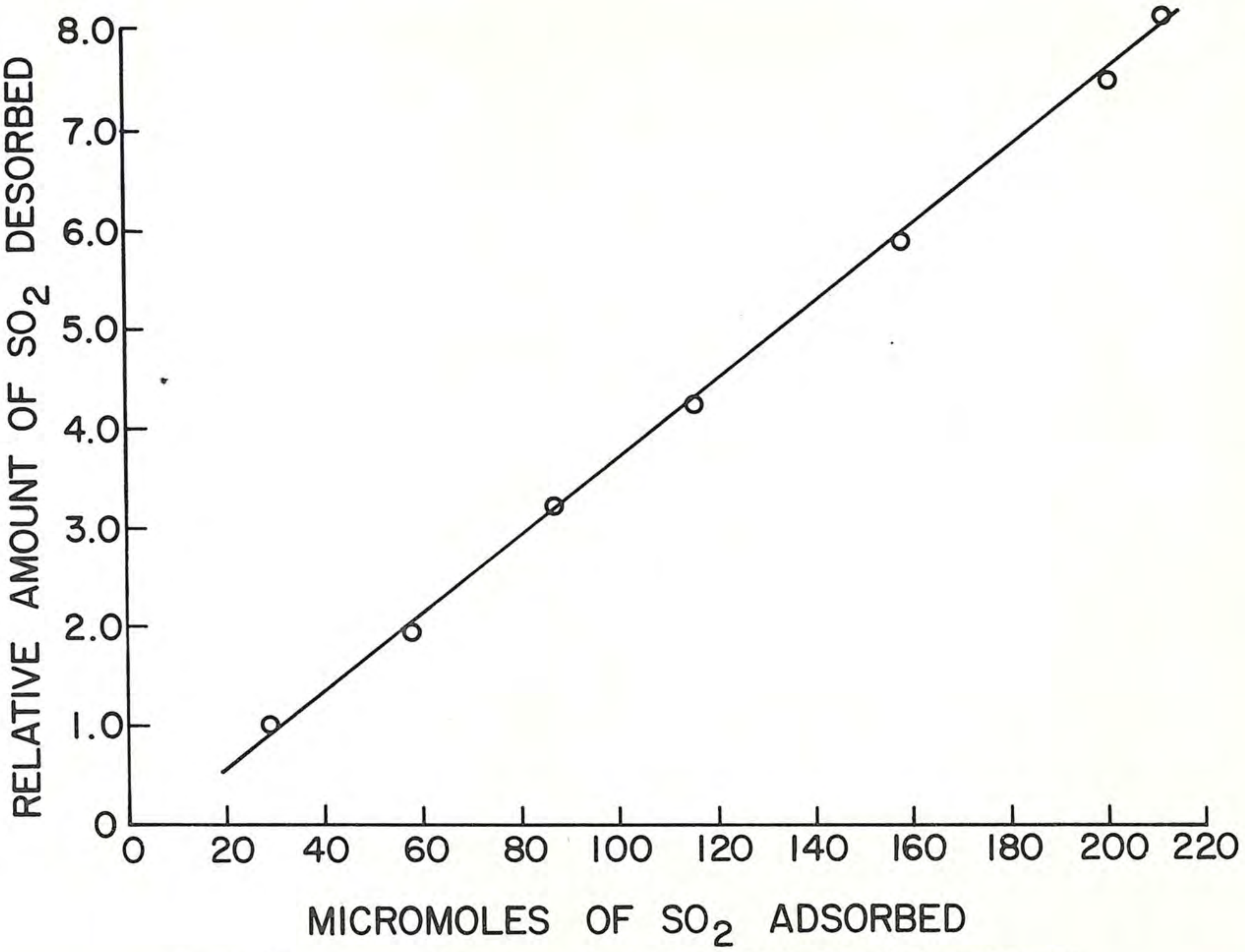

Figure 12. Relationship between the Quantity of SO_2 Adsorbed on Molecular Sieve 5A and that Desorbed. Flow Rate, 200 cc/min.

Table V

Recovery of SO_2 from Molecular Sieve 5A

Experiment No.	*Amount of SO_2 Adsorbed (Micromoles)*	*Amount of SO_2 Desorbed (Micromoles)*	*Percent Recovered*
8	31.8	26.6	84
9	31.8	25.4	80
10	27.8	23.6	85
11	23.8	18.9	79
12	19.9	16.6	84
13	19.9	17.0	85
14	15.9	12.9	81
15	11.9	9.6	81
16	8.0	6.6	83
23	28.9	24.9	86
24	28.9	23.4	81
25	28.9	23.5	81
26	28.9	23.8	82

Experiments 8-16, flow rate = 55 cc/min.
Experiments 23-26, flow rate = 100 cc/min.

Table VI

*Storage Experiments with Molecular Sieve 5A Columns**

Column	*Storage Time (Hours)*	*Amount Desorbed (Micromoles)*	*Percent Recovered*
1	*17*	*22.7*	*79*
2	*26*	*24.9*	*86*
3	*50*	*23.4*	*81*
4	*92*	*23.5*	*81*
5	*145*	*23.8*	*82*

**Each column had adsorbed* 28.9×10^{-6} *moles of* SO_2

References

1. *Tiernan, T.O., Hughes, B.M., Haartz, J.C., Taylor, M.L., and Wu, R.L.C., Progress Report, "Mass Spectrometric Studies of Interactions of Selected Adsorbents with Gaseous Pollutants, " Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio 45433, Submitted to NIOSH, 15 September 1973.*

Discussion

Dr. J. Taylor: What is the time scale for the desorption shown in Figure 8?

Dr. Tiernan: This depends upon the temperature of the sorbent. For Molecular Sieve 5A, desorption begins almost immediately when the temperature of the sorbent is raised to 170°C. Below this temperature, no significant quantity of SO_2 *is released. When the sieve has reached the critical temperature, complete desorption typically requires about 10 minutes. Thus the desorption peak shown in Figure 8 covers a time span of about 10 minutes. The temperature can, of course, be raised very rapidly.*

Dr. Ballou: When you speak of the pressure, are you always talking about the total pressure?

Dr. Tiernan: Yes, I mean the pressure in the manifold at the point of measurement. The adsorption apparatus is designed so that there should be no significant local pressure fluctuations. There may be some pressure drop across the sorbent column itself, of course, and the magnitude will depend upon the volume of sorbent, particle size, porosity and so forth.

Dr. Dravnieks: Are you desorbing the same direction as you are adsorbing or backwards?

Dr. Tiernan: We are desorbing in the same direction.

Dr. Ballou: I have trouble correlating some of these results with the sampling needs in relation to the TLV, because it is 5 ppm for sulfur dioxide.

Dr. Tiernan: Yes, the TLV for SO_2 *is 5 ppm.*

Dr. Ballou: Many of your experiments were done at levels of 1000 ppm or greater, and in many cases one could not tell what levels were used.

Dr. Tiernan: We have done some experiments at relatively low levels but you are correct that most of the studies I discussed were concerned with high SO_2 *levels. The reason for this is* *that we were mainly interested thus far in screening various sorbents to determine their gross capacity for SO_2 and this is much more easily accomplished by high level experiments. For an efficient sorbent, the capacity of the material in terms of the quantity of SO_2 it traps should be the same regardless of whether the sorption procedure involves sampling at high SO_2 levels for a short period or sampling at low SO_2 levels for a long period (as would be the case in NIOSH applications). Preliminary results we have obtained indicate that this is indeed the case, that the capacity does not vary with concentration or sampling rate (at least over a limited range). The adsorption efficiency of Molecular Sieve 5A seems to be very high as demonstrated by the breakthrough experiments cited earlier.*

Dr. Ballou: Why don't you do your experiments near the TLV level?

Dr. Tiernan: Quite frankly, because it is very difficult. The background and "memory" problems to which I alluded make it very difficult to monitor changes in small concentrations. Thus the sorbent characterization experiments are very difficult to accomplish at low SO_2 levels. This does not however, preclude the detection and analysis of very low concentrations of SO_2 following desorption from the sieve because this is accomplished at low pressures, where "memory" effects and apparatus sorption problems are less significant. You will recall that the screening studies were done largely at near-atmospheric pressures where these "memory" effects become very severe when you are dealing with low SO_2 concentrations. I should mention however that we are planning to do some low level adsorption tests near the TLV in the near future, just as soon as we have installed some more sensitive linear mass flowmeters. In these experiments we will use the premixed 2080 ppm SO_2-air gas and dilute it with additional air. The composition of the stream which is passed through the sorbent will then be determined from the flow parameters rather than by the mass spectrometer. This will avoid the "memory" problems. We also plan to replace certain sections of the test apparatus which are now stainless steel with glass lines, which should further reduce sorption problems in the apparatus itself.

Mr. O'Keeffe: If you have stainless lines I wonder if you don't lose a lot of SO_2. I recommend you don't use glass at all either, but teflon.

Mr. Crable: Teflon is way down as compared to glass.

Dr. Tiernan: That is true, but stainless does condition over a period of time, and even the adsorption problems referred to are not severe if one can work at low pressures. Stainless was used because of the ease of fabrication and general application to *a variety of materials. Glass is more fragile and a test apparatus made entirely of glass would be difficult to fabricate. An apparatus made entirely of teflon is simply not feasible, although we could experiment with teflon lines.*

Dr. Klier: *I was wondering why you did not go to higher temperatures than you did to see if you could completely desorb the sulfur dioxide. The sieve will safely survive 500 degrees Centigrade.*

Dr. Tiernan: *The reason was simply one of practicality. The apparatus is heated by heating tape wrapped around all the lines (heating is mandatory to prevent severe sorption problems on lines) and the same is true of the sorbent columns. One really can't heat them to higher temperature using this arrangement. In any case, it is not clear whether the sieve is really retaining some of the* SO_2 *or whether this is an instrumental effect. We are contemplating doing a weight-change experiment to shed more light on this, in which we would adsorb a sufficient quantity of* SO_2 *on the sieve to accurately weigh and then desorb and weigh the sieve again.*

Dr. Klier: *I cannot understand what is the main cause of the "memory".*

Dr. Tiernan: *It is mainly due to adsorption on the apparatus walls. We know that because we have shortened sections of the apparatus and replaced other stainless sections by glass, which is a bit better for* SO_2*, and this definitely improves the situation. The sieve itself has no significant "memory". There is some tailing of the desorption peak, but it is relatively short and desorption is quite efficient.*

Another point here is the possibility of interferences from other materials that the sieve might adsorb, and we have briefly looked for the mass spectral peaks from possible interferences such as CO_2 *(after passing large volumes of laboratory air through the sieve and subsequently desorbing), but found nothing significant. Another question?*

Dr. Ballou: *I believe that you conjecture, then, that the desorption becomes more efficient after you poison certain centers on the sieve.*

Dr. Tiernan: *At this point I am reluctant to say what is really the cause. All I can say is that if you precondition the sieve by flowing air over it while heating it for a few hours, then from the first adsorption cycle and extending through many cycles, you get a consistent quantity of* SO_2 *recovered. If the sieve is not preconditioned, then the amount of* SO_2 *recovered on the first adsorption-desorption cycle is invariably much smaller than for subsequent cycles.*

Dr. Ballou: Is this consistent with your data showing the relative amount desorbed, which levels off at about 85 percent. If you poison certain centers these should just be lost and on subsequent cycles you should desorb a hundred percent.

Dr. Tiernan: We have thought about that and the results are still potentially explainable, because we desorb under different conditions from those which exist during adsorption. Desorption is at low pressure while heating, while adsorption is at high pressure and ambient temperature. Let's assume that the sieve has a certain number of irreversible sites. In a particular adsorption experiment, a certain number of these sites are saturated, but probably not all of them (we don't usually adsorb to the full capacity of the sieve). Upon desorption, the pressure is lower and the temperature is much higher, so that the SO_2 which comes off the area where it was sorbed and migrates through the rest of the column probably would not be picked up by the remaining irreversible sites. This is pretty hypothetical and I agree that the constant percentage recovery is disturbing. I am really more inclined to believe that this is an instrumental factor. But again, that really doesn't matter if one is measuring an unknown quantity of sorbed SO_2 by calibrations against a known sample, as discussed earlier.

Dr. Lonnes: You mentioned that you are using a very retentive sorbent. And on your first cycle with this strong adsorbent there is a possibility that not all of the sorbent was used, that you did not exceed the capacity of the sorbent. So you have a situation where the last half of your column has not seen any sulfur dioxide. Now you do a desorption, but instead of reversing the column, you are taking that sulfur dioxide off and you are passing it through the section of sorbent which has not seen any sulfur dioxide.

Dr. Tiernan: That is exactly what I was saying. However, during desorption the column is at high temperature and low pressure, which is quite different from the adsorption case, where the column is at atomspheric pressure and room temperature.

Dr. Lonnes: Have you determined the temperature coefficient?

Dr. Tiernan: No, but we have determined that at temperatures of 160°C or higher, SO_2 comes off the sieve rapidly.

Dr. Lonnes: I am wondering how important the temperature coefficient is at low temperature.

Dr. Tiernan: We have little evidence on that although adsorption is certainly efficient at room temperature. As you can see, our approach thus far has been strictly empirical. We haven't tried to correlate the effects with physical parameters, or determine whether we are dealing with chemisorption or physical adsorption or other such considerations. That would perhaps be worth doing, but it is a question of time and cost.

Dr. Lonnes: If it is still a relatively efficient sorbent at the temperature at which you are doing adsorption, I think you would have considerable gain by reversing the direction and desorbing in the opposite direction.

Dr. Tiernan: That is a possibility and could easily be done. These columns are mounted using Swagelok fittings and can readily be reversed.

Dr. Dravnieks: There are just a couple of small points. It's very easy to replace stainless steel with a teflon coating, you can just put teflon inside, which wouldn't require much change. Another thing, does this relative 83 or 86 percent recovery apply to the molecular sieve in the heated condition?

Dr. Tiernan: That's right. That was the amount recovered when it was heated and flushed with dry air.

Dr. Dravnieks: This seems to me rather complicated, a lot of Swageloks. When you heat them you get air leaks.

Dr. Tiernan: No, we don't have problems with air leaks. We can continuously monitor the air peak in the mass spectrum (as shown in some of the earlier graphs) and it does not change as the apparatus is heated. If leaks occurred, the signal would increase.

Dr. Dravnieks: You don't look at the decrease, you look at the actual value.

Dr. Tiernan: Yes. We were especially careful to monitor the air peak when operating the apparatus under low pressure conditions, since this is the condition under which leaks are expected to be most severe, and no leaks were observed.

Dr. Dravnieks: Is there some oxidation of SO_2 to SO_3 in the apparatus?

Dr. Tiernan: It is quite possible.

Dr. Dravnieks: And that wouldn't come off so fast.

Dr. Tiernan: It's quite possible. At this point I would not rule this out.

Dr. Klier: I am concerned with the variable leaks, are they copper?

Dr. Tiernan: They are Monel, which is resistant to dry SO_2 *but may be attacked by* SO_2 *under wet conditions.*

Dr. Klier: I think one could have an all glass apparatus, which would be much safer with glass or copper leaks.

Dr. Tiernan: Glass leaks are pretty difficult to use in a variable sense.

Dr. Klier: You have to have one or two and use them in turns.

Dr. Tiernan: It is very likely we could improve the apparatus in terms of components, but again we assembled the apparatus in a relatively short time by using fairly standard vacuum components. Granville-Phillips leaks were used since these are of high quality and are readily available. If you went to an all glass system you would certainly have to worry about broken joints and leakage of joints when the device was heated. So you would likely have to blow a solid glass apparatus.

Dr. Klier: That is why I mention this, because we actually have a working system in which the glass leak goes into the ionization chamber of a quadrupole mass spectrometer. This also greatly increases the sensitivity.

Dr. Tiernan: I'd be interested in hearing more about your system. Do you buy these glass leaks or make them?

Dr. Klier: We buy capillaries from which we make these leaks.

Appendix

In subsequent work following the NIOSH Solid Sorbents Roundtable, SO_2 *sampling experiments were successfully accomplished at levels ranging from 0.1 to several hundred ppm. The effects of moisture on the adsorption process were shown to be severe when small amounts of* SO_2 *were sampled. These problems were obviated by using a dual-section column consisting of a foresection containing phosphorus pentoxide as a dessicant for water removal and a second section containing the Molecular Sieve 5A sorbent for* SO_2 *collection. The technique was shown to be applicable to quantitative sampling, desorption (100% of adsorbed gas), and analysis of* SO_2 *at very low levels near the TLV. Prototype sorbent tubes were prepared for field testing and a tentative method document was prepared. This additional work has been described in detail in a later report, "Development and Evaluation of Solid Sorbents for Monitoring Workplace Air Pollutants", Annual Summary Report, 31 December 1973, Aerospace Research Laboratories, Wright-Patterson AFB, Ohio 45433.*

A NEW ADSORBENT FOR THE CONCENTRATION AND ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN THE ENVIRONMENT

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Background

Several years ago this laboratory was involved in experimental work in the analysis of flavors, and it appeared to us at that time that biological fluids were similar in nature to flavors from an analytical point of view. In particular, the low molecular weight volatile compounds had never really been investigated. If one examines previous analyses done in this area, i.e., steroids, amino acids, fatty acids and carbohydrates, these materials are not volatile from a gas chromatographic point of view. They require derivatization before gas phase methods can be employed for their analysis. Some work had been done for acetone, alcohol, respiratory and anesthetic gases.

Using conventional procedures for analyzing flavors, i.e. extractive distillation, a 100 ml urine sample was concentrated and analyzed by high resolution gas chromatography. More than 300 compounds of low molecular weight (under 200) were resolved. Once the procedure was established, about 60 of these compounds were identified by mass spectrometry. Since each analysis took two days, the procedure did not lend itself to the screening of a large number of samples. In spite of this shortcoming, about sixty normal samples were examined and the results showed that most urines gave characteristic volatile profiles which were readily recognizable.

Use of Solid Sorbents to Concentrate Sample

In order to develop a simpler method, a new concentration technique was deemed necessary and the headspace of biological fluids was used as the sample. Conventional adsorbents such as carbon, carbon molecular sieves and porous polymers exhibited problems in the desorption step, although the capacity of these adsorbents was adequate for the compounds of interest.

Tenax GC (1) (Applied Science Laboratories, Inc., State College, Pennsylvania), a porous polymer, 2,6-diphenyl-p-phenylene oxide, appeared to fulfill both requirements of efficient adsorptivity and desorptivity, as it can sustain relatively high temperatures (375°C limit). Samples were desorbed at 200-300°C with good reproducibility, and regeneration was effected at 375°C. It is quite possible that some compounds are retained *at high temperatures, but comparisons of quantitative desorption by heat and solvent extraction were not made. In any event, it is now routinely possible to evaluate samples containing a wide range of volatile organic compounds by first adsorption, followed by desorption at high temperatures, and subsequent transfer into a capillary gas chromatographic column. After establishing methods of headspace analysis for compounds of biological interest (2-4), we adapted the procedure to air analysis.*

Air Analysis

To date, no facile, generally applicable system for sampling of air pollution samples from various environments, has been introduced. Such a system should not only be available for pollution laboratories but also should be usable in such varying locations as industrial working places, households and space capsules. The technique herein described is designed for these tasks. It should be noted, that very volatile substances up to approximately C_8 *will not be considered here, and different principles have to be applied for the analysis of these.*

To evaluate the merits of the newly proposed adsorbent for air analysis, it may be in order to look more closely into the potentialities of the different techniques which are presently applied. Some desirable features for a good sampling system are: a) concentration of volatiles from a large air sample with minimum interference of moisture, b) complete collection in the volatility range considered, c) quantitative and unaltered regeneration at time of analysis, d) ability to collect and analyze at several locations, and e) storage of sample without loss or change in composition for analysis at a later time. In order to be useful for practical applications in an average laboratory, the procedure should also allow: f) samples to be taken with a minimum of interference during handling and transference, g) speed of sampling be sufficient to follow rapid compositional changes, h) regeneration to be done without intermediate steps such as extraction, and i) the collection apparatus to be handled by unskilled personnel. As expected, all sampling procedures have shortcomings, and the information expected determines the most suitable method for particular analytical needs.

Comparison of Sampling Techniques

Basic principles underlying sampling technology fall into four categories. Each technique has its specific advantages and disadvantages, as outlined below:

1. *Cryogenic techniques (container at low temperature)*

    Advantages: *a) total sample can be taken and substances of high volatility are effectively collected*

    b) fractional distillation possible

    c) secondary reactions minimized

    d) simplicity of construction

Disadvantages:

a) difficulties in regenerating the sample, especially high molecular weight compounds

b) strong interference by excess water

c) depending on concentration, losses due to fog formation

d) expense of operation

Potential: Superior technique and often the only possible method to collect very volatile material (substances which are gases at room temperature). Problems are often encountered if drying agents are employed for removal of water.

2. Adsorption at subambient temperatures (solid adsorbents or conventional GLC packing)

Advantages: a) trapping efficiency essentially 100%

b) low molecular weight compounds effectively retained

c) speed of sampling less critical than with most other methods

d) no adverse effects due to displacement

Disadvantages:

a) interference from water

b) sample size limited

c) depending on adsorbent, incomplete recovery (same problem with adsorbents at room temperature)

d) viscosity problems with GLC packings

e) artifacts quite common

Potential: Very useful for analysis where water does not seriously interfere. Useful especially in the analysis of low boiling substances. Can be automated.

3. Adsorbtion at room temperature (solid adsorbents and conventional GLC packings) with heat desorption

Advantages: a) easy to handle

b) simplicity and economy

c) "combination packings" are possible

d) selectivity by proper choice of phase or adsorbent

Disadvantages:

a) loss of low molecular weight compounds to various degrees, depending on nature of adsorbent

b) surface reactions more likely than with many other techniques

c) choice of adsorbent critical

d) excessive heat necessary for very active adsorbents

e) flow rate restricted, especially with GLC packings

f) decreasing efficiencies of recovery with high molecular weight compounds

Potential: Can be more easily automated than other techniques; especially useful for compounds of medium volatility with proper adsorbents.

4. Adsorbtion at room temperature (solid or adsorbents with chemically bonded stationary phases) with liquid extraction

Advantages: a) active adsorbents can be chosen due to effective recovery process

b) selectivity by proper choice of adsorbents

Disadvantages:

a) time consuming

b) sample is diluted with extractant, which is difficult to remove without loss

c) surface reactions possible

d) requires skill

e) automation difficult

Potential: Very useful in skilled hands. Can span a wide range of volatilities and especially useful for high molecular weight substances.

Obviously there are many disadvantages to the use of adsorbents at room temperature. The methods have not been very successfully applied, except for a few isolated cases with charcoal as the adsorbent. The advent of synthetic porous polymers has now opened new avenues for this area of research.

It should be pointed out that any procedure, using an adsorbent at room temperature which utilizes heat as the method of recovery, is limited in range of applicability by two inherent contradictory factors. If the recovery is to be favorable for low molecular weight compounds, an adsorbent with high activity and large surface area must be used. This makes recovery of high molecular weight substances very difficult.

Tenax GC Adsorbent

Tenax GC has some unique properties, besides its temperature stability, which makes it useful for the concentration of compounds of medium volatility from large volumes. Our work has demonstrated that samples trapped on Tenax can be conveniently stored or shipped to another laboratory for later analysis. Its application in headspace analysis seems to have become accepted. Tenax GC shows a different capacity for substances of widely different polarity and molecular weight. The limits of this material with respect to trapping efficiency and recovery need to be explored for the common volatiles present in air as pollutants. Tenax shows selectivity for certain classes of compounds. High molecular weight substances are more easily retained than low molecular weight substances. A striking example of selectivity can be demonstrated by the adsorption of a gas sample on Tenax. Sulfur components, regardless of volatility, are retained on the beginning of the adsorbent. A 500 ml sample of household gas required 10 ml of Tenax to trap all substances beyond C_4. Arrangement of several Tenax traps in series shows that all sulfur components are concentrated in the first sampling tube. This tube also enriches high molecular weight substances.

Experimental

The equilibrium on the adsorbent is determined by the affinity of a particular substance at a given temperature for the adsorbent. Displacement occurs by compounds with higher affinities. If equilibrium is reached, the quantity adsorbed is characteristic for each substance and can in principle be used for qualitative analysis once these data have been established for standard compounds. Several instruments were used for gas chromatography with high resolution open tubular columns. These included a Perkin-Elmer 900, a Shimadzu GC 5A and a Bendix 2600.

In order to achieve reproducible results and, at the same time, provide convenient methods of sampling, transfer, and analysis, a prototype glass trapping chamber was designed. This trap ultimately becomes an insert for a modified injector port as described below. The trap is a glass tube (11 cm x 10 mm; 8 mm ID) containing 2 ml of Tenax GC (35/60 mesh). One end is tapered in order to provide an efficient seal inside the injector port. Figure 1 shows a drawing of this injector port with Tenax tube.

A 10 ft. x 0.04 in. ID open tubular column is attached to the outlet of the injector port. This column is coated with the same phase as is the separating column. In order to deposit the sample at the beginning of the pre-column as would be the case in an injection system, the pre-column is cooled with dry ice. The sample is transferred (purged) from the Trap-Insert at 300°C for 20 minutes at 20 ml/min. Chromatography is begun when the sample is transferred to the separating column. A 300 ft. x 0.02 in. ID nickel column was selected and is specially prepared by etching with an acid solution of (1:1) 70% nitric and 50% acetic acid (5). The polar liquid phase is Emulphor-ON 879 (Applied Science Labs., State College, Pa.), and was chosen because of its polarity and temperature stability (200°C). Columns of lengths up to 900 feet were used.

Programmed temperature GC commenced at a temperature of 30°C or 50°C for 15 minutes and then taken up to 150° or 170°C at 2°C/min. Hydrogen and air flows were adjusted to 14 and 50 psig respectively. The injector and detector temperatures were 300° and 280°C, respectively.

An LKB 9000 mass spectrometer, modified by replacing its GC unit with a Perkin-Elmer 900 gas chromatograph, served for identification purposes. The ionization voltage was 70 eV and scan time for a mass range of 20 to 200 mass units was 4.5 seconds. Temperatures of separator and ion source were 220° and 250°C, respectively. Analytical methods were the same as for the GC instrument.

Interpretation of mass spectra was done by comparison with known spectra, which were collected in our laboratory in the form of a library. Spectra which were not available were identified with the Index of Mass Spectral Data. Confirmation of the spectra was done by comparison with data published by the American Petroleum Institute.

A simple system was designed to collect air samples from different locations including enclosed atmospheres. It basically consisted of only 3 parts.

1) *Vacuum source*
2) *Flow regulator*
3) *Sampling tube*

For sampling inside a laboratory building, vacuum was readily available; for field analysis, the vacuum source consisted of a pump and a portable generator as power supply. The flow measuring and regulating device, a large bubble flow meter was made in our laboratory. Figure 2 shows a block diagram of the sampling apparatus. Several samples can be collected in parallel by the use of a divider. We have been involved in this project of air analysis over a period of about 15 months and have taken more than 150 samples during that period.

Results of Air Sampling

Samples considered to be representative of urban, industrial, and agricultural environments were taken at various locations around Houston, Texas. Figure 3 shows a representative gas chromatographic profile. Aproximately 100 substances, almost exclusively hydrocarbons, were identified and are summarized in Table I (6). Alkanes represent the major part, especially at the low molecular weight end of the spectrum, whereas substituted aromatics are more abundant for the high molecular weight end. As discussed, collection is incomplete for low molecular weight substances. All compounds eluting after benzene (peak no. 18) however, are well retained.

The breakthrough capacity for a number of isolated substances was determined using a small sample collected in a closed chemical laboratory, with contributions from solvents and other chemicals. The relative amount of material escaping from the first tube is a function of the flow rate at which the sample is collected.

Flow rate of sampling and temperature were found to be most important parameters with air pollution samples. The amount of packing and the particle size of the adsorbent were found to be less important. Regardless of sampling rate, losses for more volatile materials are always observed. As expected, losses increase with increasing flow rate. A sampling rate of approximately 200 ml was found to be acceptable from both sample loss and time requirement for a suitable sample size. Compounds eluting before benzene in our system were only partially adsorbed. High molecular weight substances were essentially completely retained with two notable exceptions, benzaldehyde and acetophenone.

As expected, automobiles are the major source of volatiles in air. The air pollution profiles have been consistent over the entire period observed, and only minor compositional changes were found, primarily depending on weather conditions. The total amount of volatiles per unit of volume, however, varied at least 20-fold. Table II gives the concentration range of a few selected substances determined by comparison with an external standard.

Alkanes and substituted aromatics account for the majority of the volatiles. From comparison of peak areas it can be estimated that the ratio of substituted aromatics (eluting after benzene) to saturated *hydrocarbons is approximately 1:0.9. Among the saturated compounds, normal alkanes are the dominant peaks in the chromatogram, but the total branched alkane isomers are present in excess.*

Striking similarities were found in the profiles of gasoline and air. Figure 4a shows a chromatogram of a gasoline sample and Figure 4b shows the profile of an urban air sample. Although intensities are different and the gasoline sample is more complex, the peaks are very similar. Figure 4c shows the profile of air taken close to a plastic manufacturing plant in a highly industrialized area. Many of the major components can be recognized. The main differences are essentially limited to changes in the concentrations of the major components.

Samples taken from highly industrialized areas, although often malodorous do show the same basic patterns in their profiles. The ratios of some of the characteristic peaks are markedly changed and usually not very reproducible. It may be assumed that trace compounds with low threshold values do not show up in the chromatograms under the conditions applied.

This work is being continued and the principles of selective detection and selective adsorption will be applied to substances of physiological interest (7).

Acknowledgement: This work was supported by the National Aeronautics and Space Administration, Life Sciences Directorate, Johnson Space Center, Houston, Texas (Contract NAS 9-13457).

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Table I
Substances Identified in Chromatogram (Fig. 3) of Environmental Air Sample

Peak Number	*Compound*	*Peak Number*	*Compound*
1	*isobutene (tent)*	*25*	C_{10} *branched alkane*
2	*n-pentane*	*26*	*toluene*
3	*2,3-dimethylbutane*	*27*	*tetrachloroethylene*
4	*ethylene oxide (tent)*	*28-34*	C_{10} *branched alkanes*
5	*n-hexane*	*35*	*n-decane*
6	*methylcyclopentane*	*36*	C_{11} *branched alkane*
7	*2-methylhexane (tent)*	*37*	*ethylbenzene*
8	*3-methylhexane*	*38*	C_{11} *branched alkane*
9	*2,4-dimethylpentane (tent)*	*39*	*p-xylene*
10	*n-heptane*	*40*	*m-xylene*
11,12	*heptene isomers*	*41-45*	C_{10} *branched alkanes*
13	C_8 *branched alkane*	*46*	*o-xylene*
14	*2,3,3-trimethylpentane*	*47*	*1-methyl-4-ethylbenzene (tent)*
15	*3-methylpentane*	*48*	C_{11} *branched alkane*
16	*n-octane*	*49*	*n-undecane*
17	C_9 *branched alkane*	*50, 51*	*propylbenzene +* C_{12} *branched alkane*
18	*benzene*		
19,20	C_9 *branched alkanes*	*52*	*1-methyl-3-ethylbenzene*
21	*2-methyloctane*	*53*	C_{12} *branched alkane*
22	C_9 *branched alkane*	*54*	*limonene*
23	*chloroform*	*55*	*1,3,5-trimethylbenzene*
24	*n-nonane*	*56*	*isobutylbenzene*
57	*1-methyl-2-ethylbenzene*	*78-80*	C_5 *benzene*
58	C_4 *benzene*	*81*	*methylindane*
59	C_{12} *branched alkane*	*82*	C_{14} *branched alkane*
60	*dimethylethylbenzene*	*83*	*tetramethylbenzene*
61	*1,2,4-trimethylbenzene*	*84*	*methylindane*
62	*1,2-diethylbenzene*	*85*	*ethylisopropylbenzene (tent)*
63	*n-dodecane*	*86*	*n-tetradecane*
64	*methylpropylbenzene*	*87*	*p-tolualdehyde*
65	*n-butylbenzene*	*88*	*m-tolualdehyde*
66	*1,2,3-trimethylbenzene*	*89*	*acetophenone*
67	*dimethylethylbenzene*	*90*	*o-tolualdehyde*
68	*methylpropylbenzene*	*91*	C_{15} *branched alkane*
69	*methylvinylbenzene*	*92*	*n-pentadecane*
70-72	*dimethylethylbenzenes*	*93*	*methylacetophenone*
73	*dichlorobenzene*	*94*	*naphthalene*
74	*dimethylethylbenzene*	*95*	*methylacetophenone isomer*
75	*methyldiethylbenzene (tent)*	*96*	*n-hexadecane*
76	*n-tridecane*	*97*	*methylnaphthalene*
77	*benzaldehyde*	*98*	*MW 140 compound*

Table II
The Concentration Range of Selected Substances Determined by Comparison with an External Standard

Compound	Concentration (ppb)
benzene	1.3 - 15*
n-nonane	1.6 - 4.4
toluene	0.3 - 9.7
n-decane	1 - 2.7
ethylbenzene	3.1 - 4.5
p-xylene	2.1 - 3.4
m-xylene	5.4 - 7.8
o-xylene	3.0 - 4.8
methylethylbenzene	1.5 - 4.0
limonene	0 - 5.6

*Corrected for loss due to incomplete adsorption

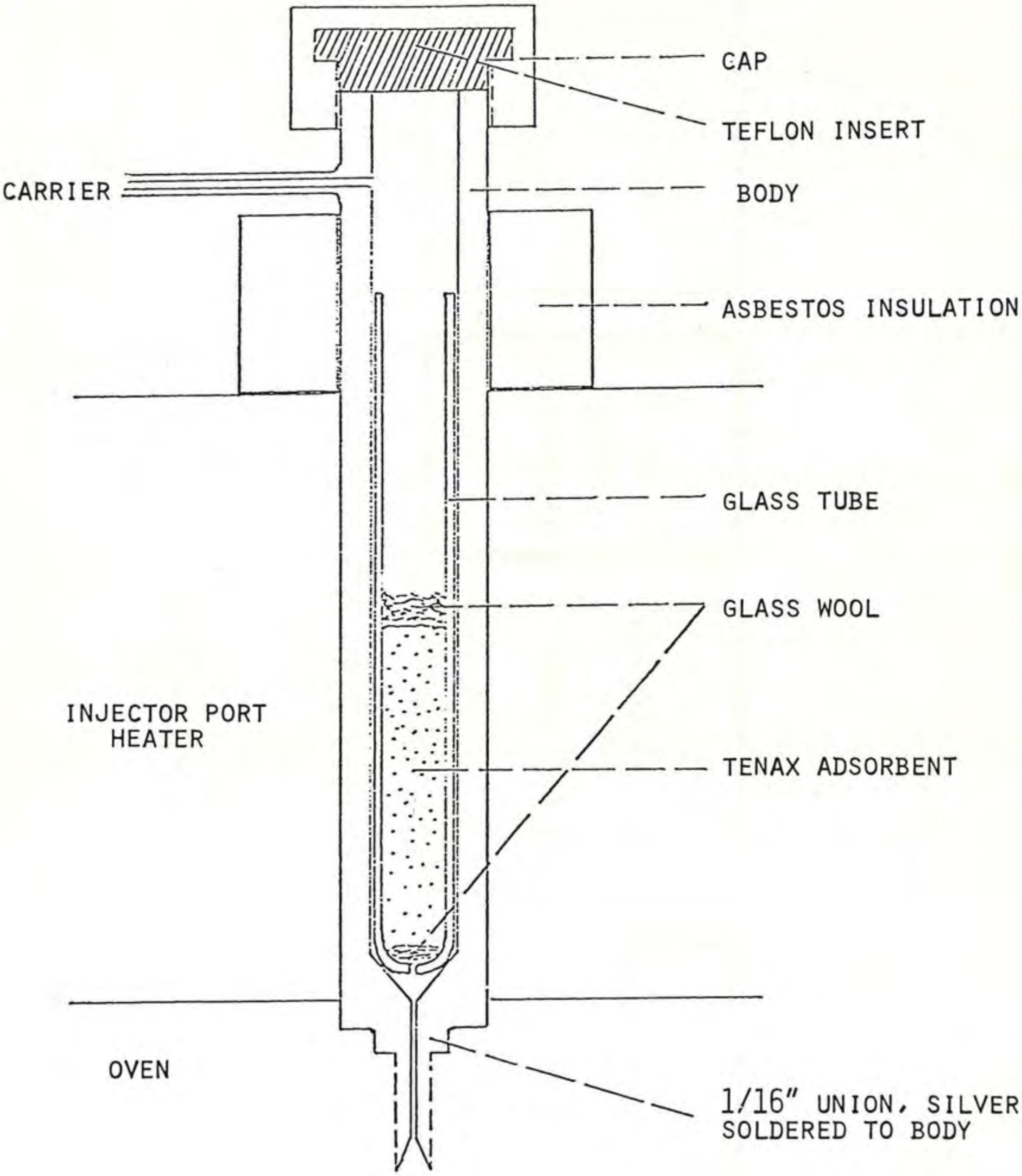

Figure 1. Tenax Injection Port.

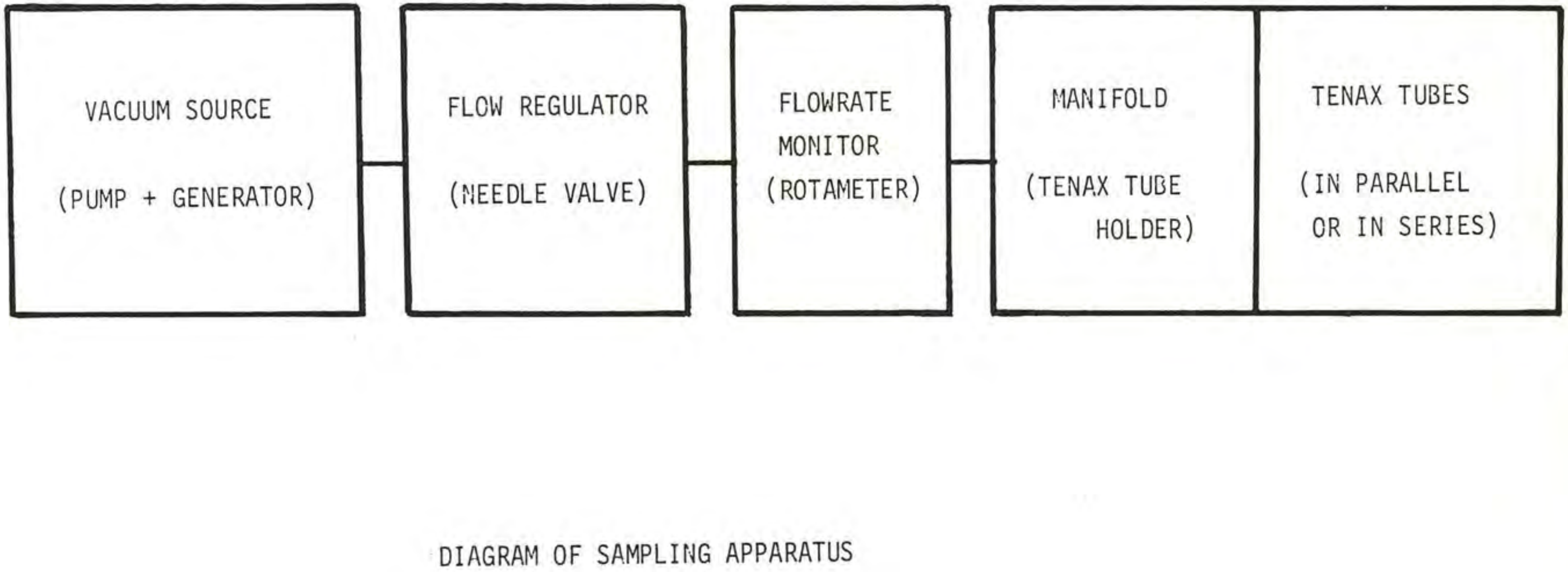

Figure 2. Diagram of Sampling Apparatus.

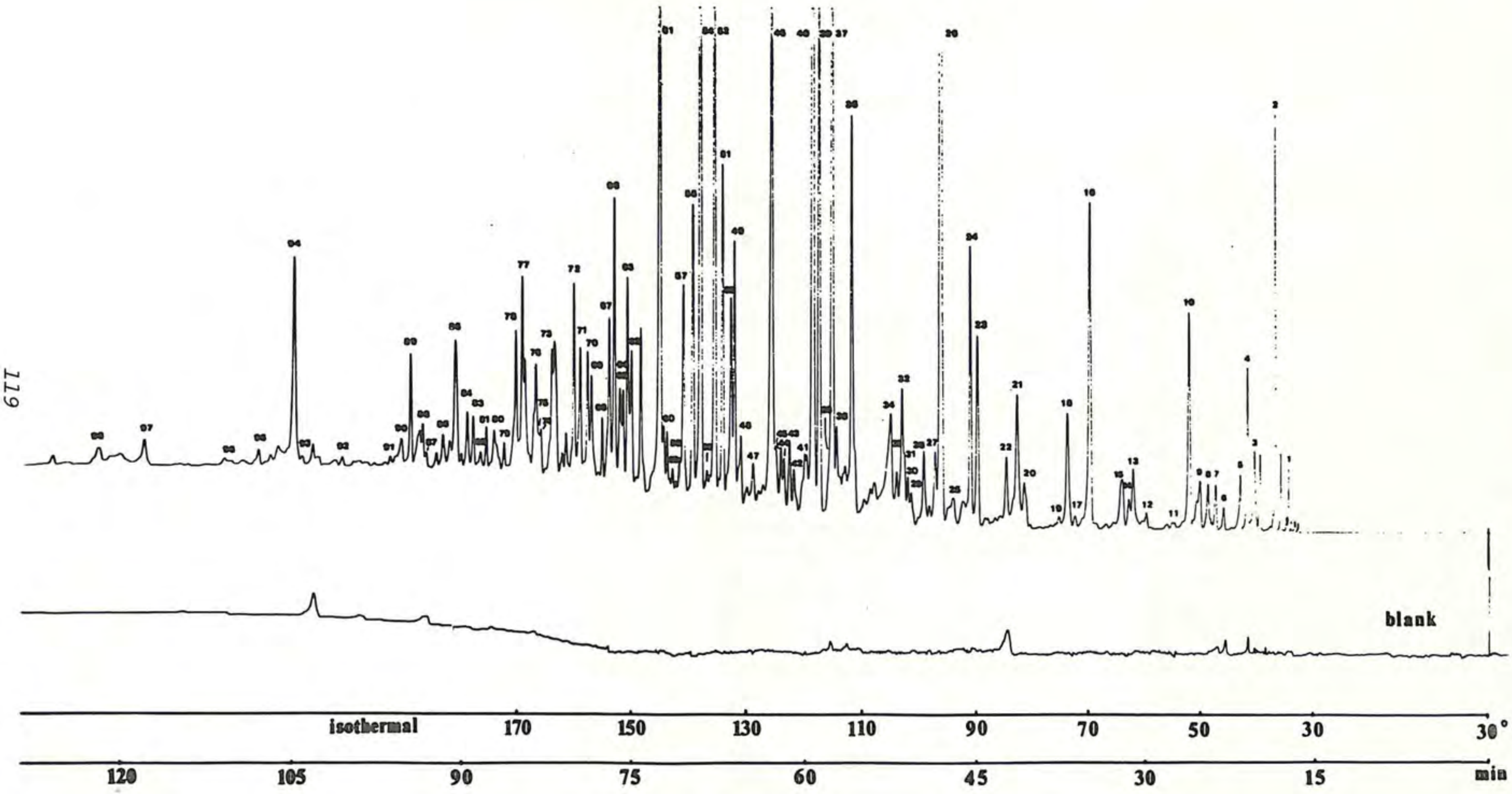

Figure 3. *Chromatogram of 200 l. of Air - Collection Site: Campus, University of Houston.*

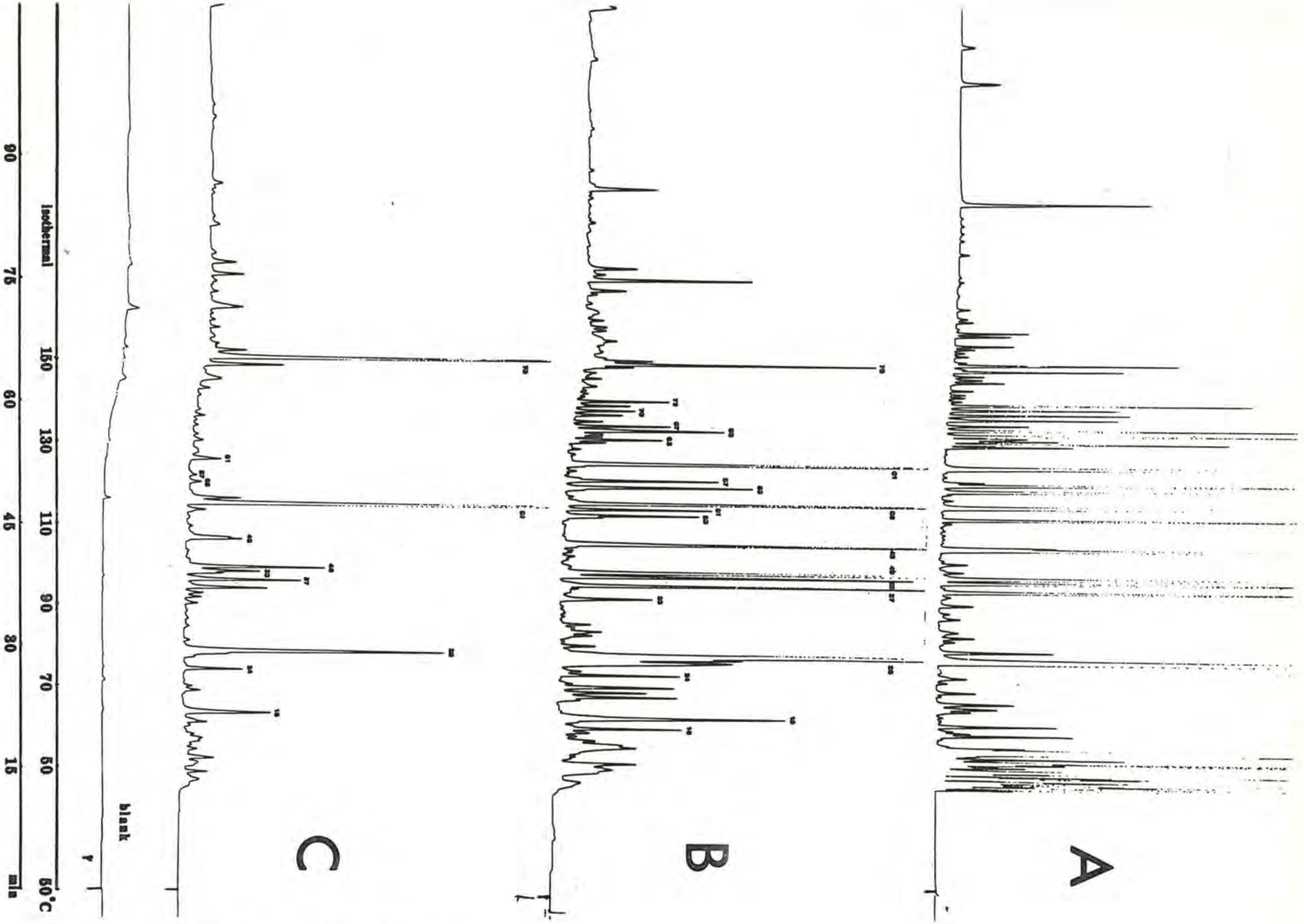

Figure 4. Chromatograms

A. Gasoline Sample (regular grade) - 0.3 l by Direct Injection
B. 120 l. of Air, Taken Close to a Freeway
C. 120 l. of Air from an Industrialized Area (plastics plant) with Little Contribution from Traffic

POROUS POLYMER SORBENTS FOR ANALYSIS OF ORGANIC AIR POLLUTANTS

by James P. Mieure

Monsanto Research Center, St. Louis, Missouri

The procedure I am about to describe is similar to that just presented by Dr. Zlatkis. Because of this, I am going to omit some of my planned introductory remarks and use this time to present additional details on applications of our method.

Scope

The method I will be describing has been used by Monsanto to identify and measure more than a hundred different compounds in air at concentrations ranging down to about one part per billion. Our desire was to have a method which would allow us, with one experiment, to measure as many different organic compounds in air as possible. This is in contrast to some of the procedures that have been described which might be specific for just one compound class.

The scope of my talk is summarized in this light. We are interested in measuring compounds in air at trace levels.

The procedure is based on using porous polymer beads to trap the organic compounds, followed by analysis by gas chromatography. I will be discussing odor analysis and applications to determine organics in an automobile interior and in ambient air at manufacturing sites.

Analytical Approach

The analytical approach we use is as follows:

- *Organics are concentrated and isolated from the matrix.*
- *The components of interest are identified.*
- *The identified compounds are measured.*

I am going to treat these in the order just given, that is, concentration, identification and then measurement.

Porous Polymer Packings

As Dr. Zlatkis has mentioned, porous polymer bead packings, because of their ability to greatly retard the progress of organic compounds through a column, are very useful for concentrating organics from air. The air to be sampled is drawn by a vacuum through the sampling columns. Under these conditions the organics are quantitatively retarded by the packing.

Some of the advantages of porous polymer packings in general are given below.

- *The retention of organic components is quite good.*
- *Water is not retained.*
- *Air does not seem to chemically alter either the packing or the organic components that are adsorbed onto the packing.*

Characterization of Collection Columns

These collection columns can be considered to be gas chromatographic columns operated at ambient temperature. In this context, air is the carrier gas, as well as the means of continuous sample introduction. Individual components elute through these columns at a rate proportional to the interaction with the packing.

A column quantitatively traps components until the retention volume of the first molecules of that component is reached. After this time, a steady state is reached with as many molecules of that particular component leaving the packing as entering the column per unit time, assuming, of course, a constant source concentration. The retention volume of the earliest eluting component of interest defines the maximum volume of air which can be sampled quantitatively.

A conventional analytical column has been used as the collection column by some researchers. The same long column is used for collection and for analysis. These columns are rather bulky, and in addition, they have a large pressure drop, so either high sampling pressures or very long times are required to sample a large volume of air. Others have used short columns and correspondingly higher sampling rates to collect organics from air. This was followed by heating the column with a carrier gas flow to elute the components into a cold trap. Aliquots of this condensate were analyzed by gas chromatography or various other procedures.

In the work I will describe as used at Monsanto, we sample air with short columns four to six inches long containing porous polymer bead packings. After collection has been completed, these columns are directly coupled into the gas chromatograph as the head of the analytical column.

The advantage of using short collection columns is that high flow rates are attainable, varying from half a liter per minute up to two liters per minute, depending on the column diameter. This permits short sampling times for a given sampling volume. By connecting the collection column directly into the gas chromatograph the entire sample, rather than an aliquot, is analyzed. This provides maximum sensitivity for a given sampling volume. We have noticed no loss of analytical column resolution *when using this GC configuration. Sample handling consists merely of uncoupling the collection column from the vacuum and connecting it into the gas chromatograph. Total sampling and analysis time is typically on the order of 30 minutes for components that we normally encounter in ambient air.*

Samples which are collected in this manner can often be stored for a few days or even weeks prior to analysis. Duplicate samples analyzed immediately and after a period of two weeks were essentially identical.

Sensitivity of Procedure

The high sensitivity of the procedure can be calculated, assuming a flow rate of 2 liters/minute and a 10-minute sampling interval for a total volume of 20 liters. Using a flame ionization detector capable of detecting 10 nanograms, components present at half a microgram per cubic meter can readily be detected. This corresponds to a concentration of one part per billion for compounds with molecular weights around 100. Sampling larger volumes of air will give proportionally lower detection limits. We have sampled volumes of air ranging from half a liter up to 60 liters.

Apparatus

The appartus that I will be describing has been kept simple to facilitate transfer of the method to other laboratories without requiring any instrument modification.

The sample collection columns are short GC columns made of glass or stainless steel filled with porous polymer packing. These columns are packed and conditioned using conventional GC techniques with glass wool plugs. Columns can be constructed to connect into the gas chromatograph in either of two configurations. The simplest approach is to attach the column into the GC oven with the analytical column. This configuration is shown in Figure 1.

In this configuration the analytical column normally contains the same packing as the collection column. For example, if you are using Tenax GC in the analytical column, you would normally use Tenax GC in the collection column. If a less retentive analytical column packing is used, significant peak broadening occurs. Since both columns are in the same oven, they are subjected to the same temperature. In this mode of operation the collection column is connected into a gas chromatograph while the chromatograph is at ambient temperature. Then the carrier flow is started and the temperature is programmed upward. Components elute from the collection column and are separated on the analytical column as in conventional chromatography. This situation is virtually analogous to the technique of on-column injection, except here, instead of injecting the sample, one is connecting a column already containing the sample at the head of the analytical column.

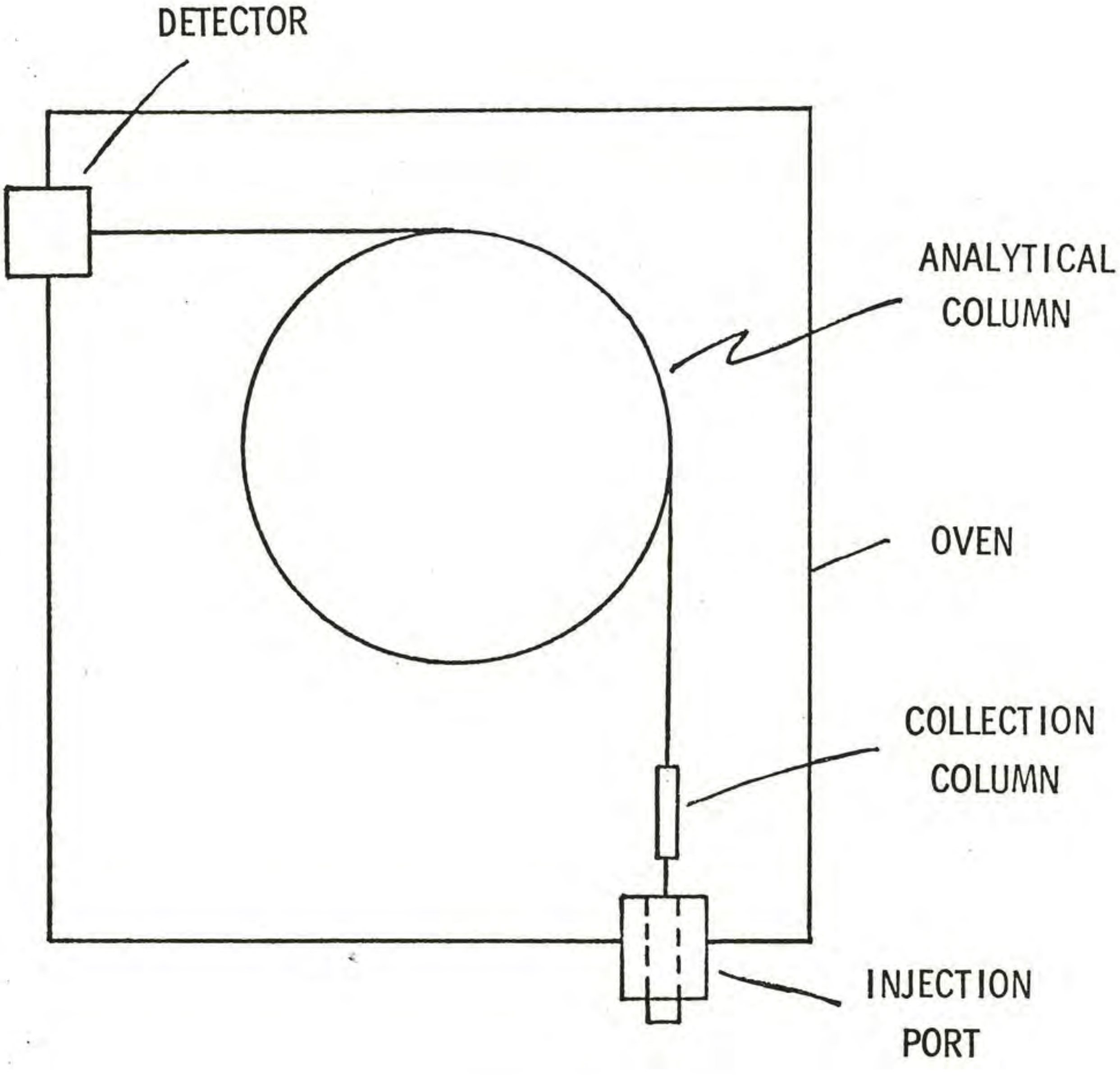

Figure 1. Collection Column Connected into a Gas Chromatograph Oven.

This mode of operation is suitable for compounds with boiling points up to about 300°C because porous polymer packings are highly retentive for organic compounds. Even at the maximum temperature which can be tolerated by these columns, organic compounds with boiling points above 300°C will be retained for very long periods of time. This slightly limits the usefulness of this configuration. It has the advantage, though, of being very simple to use and can be used by people without a great deal of gas chromatographic training. Fortunately, most of the organic compounds found at significant levels in ambient air do have boiling points below 300°C.

If it is desirable to use an analytical column different from the collection column, the collection column must be heated separately. This can be conveniently accomplished by constructing the collection column as an insert to fit into the chromatograph heated injection port. The insert dimensions should be chosen to fit the injection port of the chromatograph to be used. Figure 2 shows the collection insert in the injection port.

Experimental

For analysis, the analytical column is first coupled to the insert. Then the insert is connected into the pre-heated injection port and carrier gas flow is started. The temperature of the analytical column is maintained at ambient or subambient levels, as required.

Under these conditions components elute from the hot collection insert in a very few minutes and are condensed on the head of the cool analytical column. Then the temperature of the analytical column is programmed upward and the components separated, again as in conventional chromatography. Some chromatographs do not have a heated injection port and hence are not capable of accepting inserts. For these, other heating means, either internal or external to the GC oven, would have to be supplied.

Collection columns are typically 1/4 in. or 3/8 in. OD X 4 - 6 in. in length. They can be made of glass or stainless steel. We haven't found a universal column packing which is capable of quantitatively retaining and later releasing all volatile organic pollutants. In practice, columns prepared from more than one type of packing are used to characterize an unknown air sample. This insures that all components which can be determined by gas chromatography are adsorbed and are later regenerated. A set of three packings has proven satisfactory for most of the situations which we have encountered.

Column Packings

I will mention Tenax GC first because it was the subject of the previous talk. It is very useful for high-boiling components, because it can be heated up to a temperature of 350°C. It is also efficient for neutral

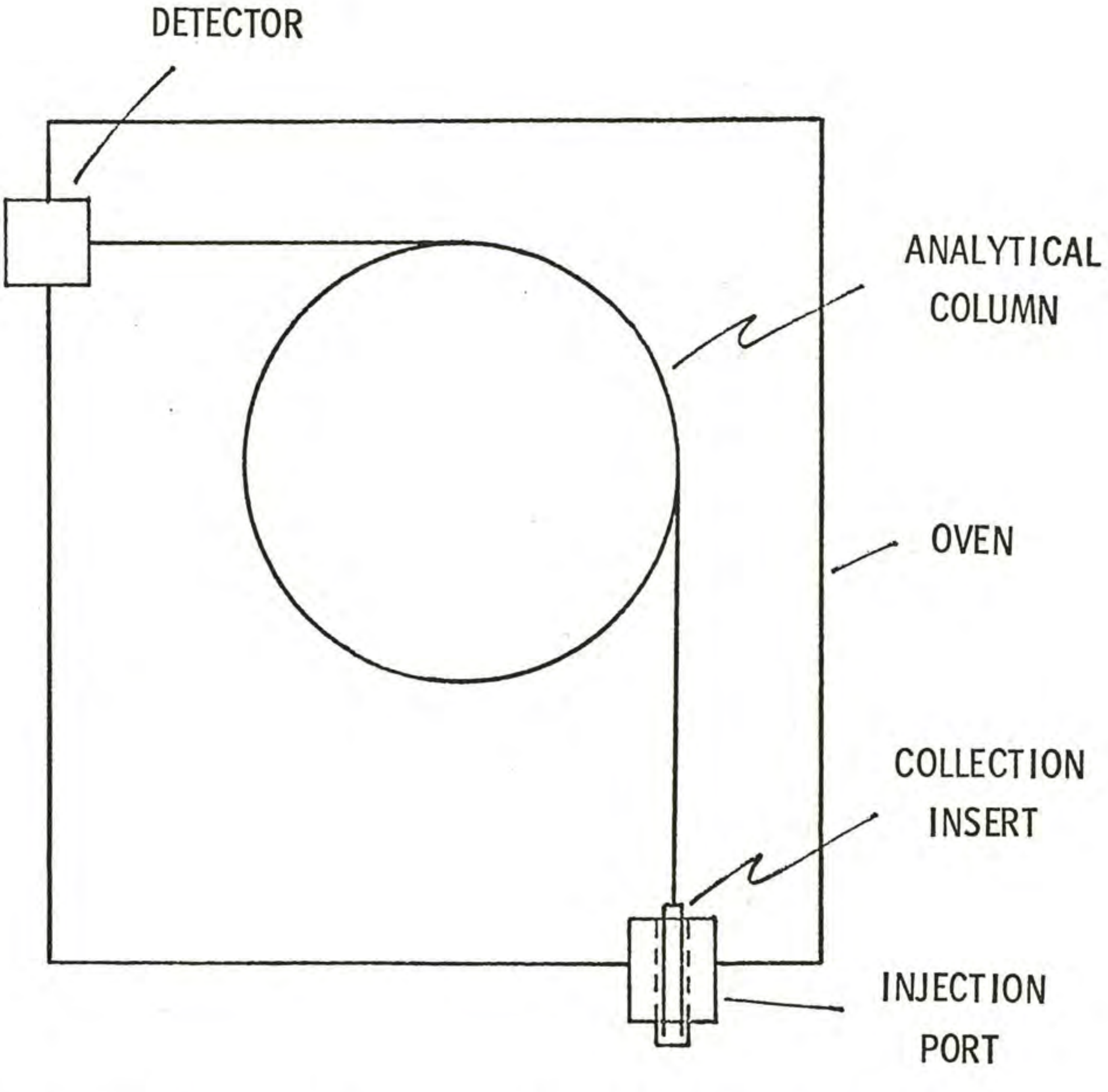

Figure 2. Collection Column Connected into a Gas Chromatograph as an Injection Port Insert.

and basic compounds. Chromosorb 101 is useful for neutral and acidic components, which sometimes tail significantly on Tenax GC. Chromosorb 105, which has much higher surface area than Tenax GC, is useful for low-boiling components. Other similar packings are available.

The sample columns can either be calibrated for air flow per unit time prior to use, or they can be used in conjunction with an air flow meter. We prefer the former approach, since once the column is calibrated, if other variables are not changed, only the sampling time needs to be recorded in the field. From this time value, one can determine what volume of air has been sampled.

Chromatograph Detector

The requirements for the gas chromatograph to be used for this analysis are that it must be equipped with a suitable detector and analytical column and should be capable of programmed temperature operation. We have used Hewlett-Packard 5750 and 7620 instruments in our laboratory.

Identification of Components

Components which have been separated by the gas chromatograph can be identified by several procedures. One, of course, is by GC retention time, but this is useful only if the number of possible components in the sample is small or if a great deal is known about the particular source that is being sampled. A more general procedure for GC component identification is the use of spectroscopic techniques, such as mass spectrometry or infrared spectroscopy. Commercial instruments are available which can be coupled to the GC exit. A unique spectrum useful for identification can be obtained for each component as it emerges from the gas chromatograph.

We have validated the quantitative collection and recovery of organics using these columns by several types of experiments: First, constant sources were sampled for varying lengths of time at the same flow rate. The weight of components collected was found to be proportional to the sampling time, according to prediction. Secondly, two columns in series were used to sample a source. None of the components were found in the second column until the retention volume for that component was exceeded on the first column. Thirdly, we have injected samples onto some of these columns with just enough carrier gas flow to insure that the compounds which were injected were swept into the column. Then we disconnected these columns from our sampling device, stored them for a few days and analyzed them. We were able to recover quantitatively the material that was injected onto the column. And, finally, we have simultaneously sampled a source using a column and a conventional solvent scrubbing train. For both biphenyl and dibutyl phthalate, results from solvent scrubbers and collection columns are virtually identical.

Results

Phthalate Esters and New Car Interior

Let me mention some examples that we have encountered in the field. Phthalate esters are commonly used as plasticizers. Their use in automobile vinyl upholstery has led to the suggestion that plasticizers are responsible for the fogging on the interior of new automobiles. In response to this claim and to verify the absence of a health hazard from phthalate esters in automobile interiors, we sampled the air inside a new car.

We found a complex mixture of more than 60 organic components, including a variety of aromatic and aliphatic hydrocarbons, some phenolic materials and very low levels of phthalate esters. Phthalate esters were detectable only when sampling a few inches from the dash while it was exposed to direct sunlight at surface temperature exceeding 100°C.

A portion of the mass spectrometer total ion monitor chromatogram as reconstructed by our computer system is shown in Figure 3 to give an idea of the complexity of the chromatograms. In this particular plot the phthalate esters are not visible because of their very low level. We don't know if any of these components are actually responsible for the "new car smell", but our data suggest that the new car smell is not due to phthalate esters.

Volatile Organics near Manufacturing Sites

The measurement of volatile organics in air in the vicinity of manufacturing sites has a great deal of interest to most of the people assembled here. The concentrations are needed to confirm safe work site concentrations, to comply with air pollution regulations and to minimize process losses. The procedure described earlier has been applied to the identification and measurement of trace organic components at several sites, both within and external to Monsanto. Determinations were made on both ambient air and stack gases. The versatility of this technique for measuring a wide range of compound types at differing concentrations can be seen from Table I.

A chromatogram of a typical air sample is shown in Figure 4. This chromatogram was obtained with a 1/8 in. x 2 meters long packed column. This provides adequate resolution for the measurement of the major compounds, but many minor components are not observable. Figure 5 shows the same source analyzed using a high resolution support coated open tubular column as the analytical column. More than twice as many components are observable than in the previous example. This emphasizes the need to use high resolution columns if one is interested in measuring minor components in a complex mixture.

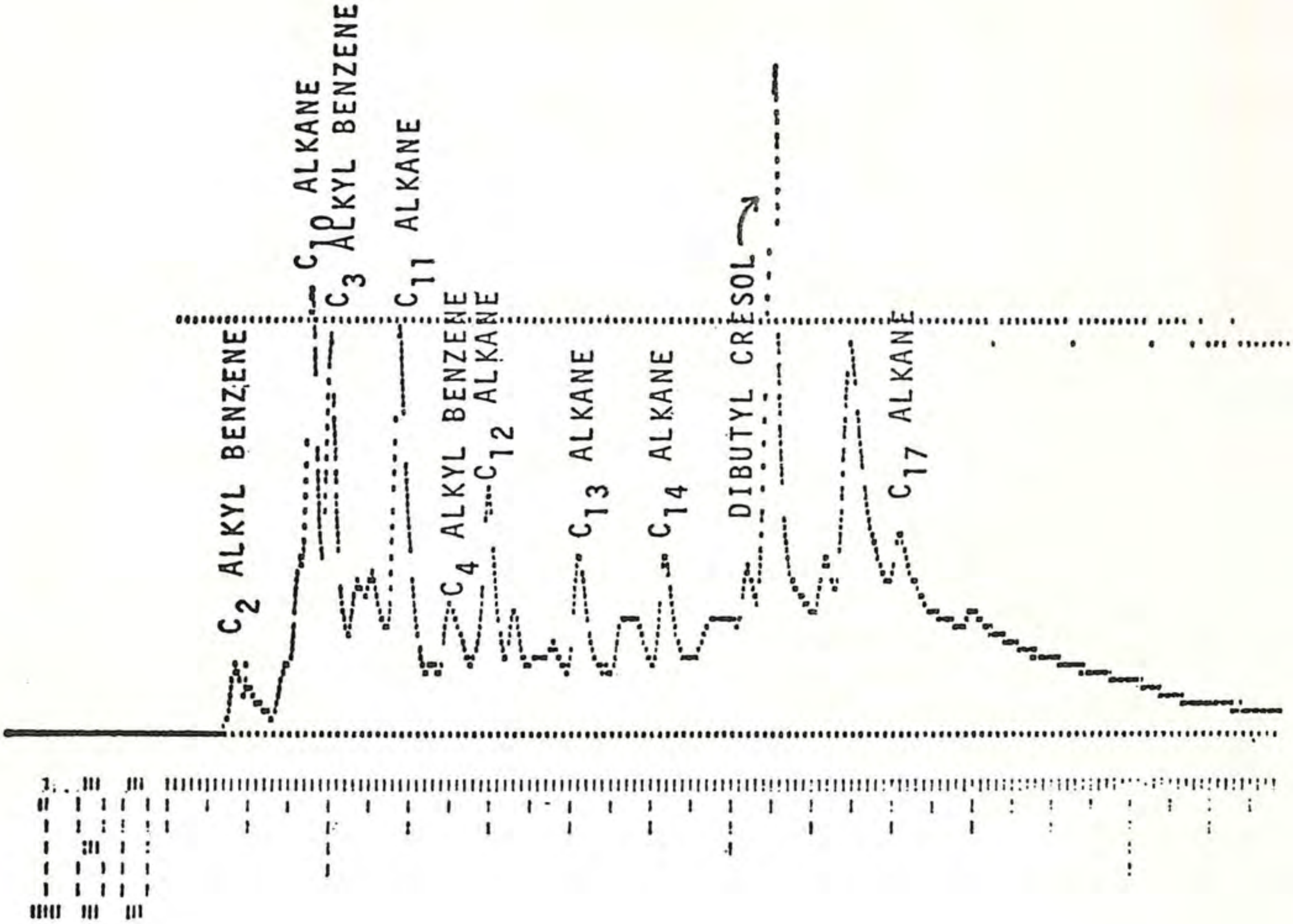

Figure 3. Mass Spectrometer Total Ion Monitor Chromatogram of Organic Components from Air in Automobile Interior.

Table I
Compound Classes Determined in Air in Vicinity of Manufacturing Sites

Compound Class	*No. of Compounds*	*Concentration range (mg/m^3)*
Phenols	*2*	*0.04 - 0.1*
Alcohols	*3*	*0.02 - 5*
Ketones	*2*	*.1 - .5*
Ethers	*2*	*.04 - .3*
Hydrocarbons	*>10*	*0.008- 10*
Disulfides	*1*	*5*
Sulfur Heterocycle	*1*	*0.4 - 7*
Aromatic amines	*2*	*0.02 - 0.1*
Phthalate ester	*1*	*>10*
Chlorinated Hydrocarbons	*6*	*.005- 6*
Totals	*>30*	*0.005- 10*

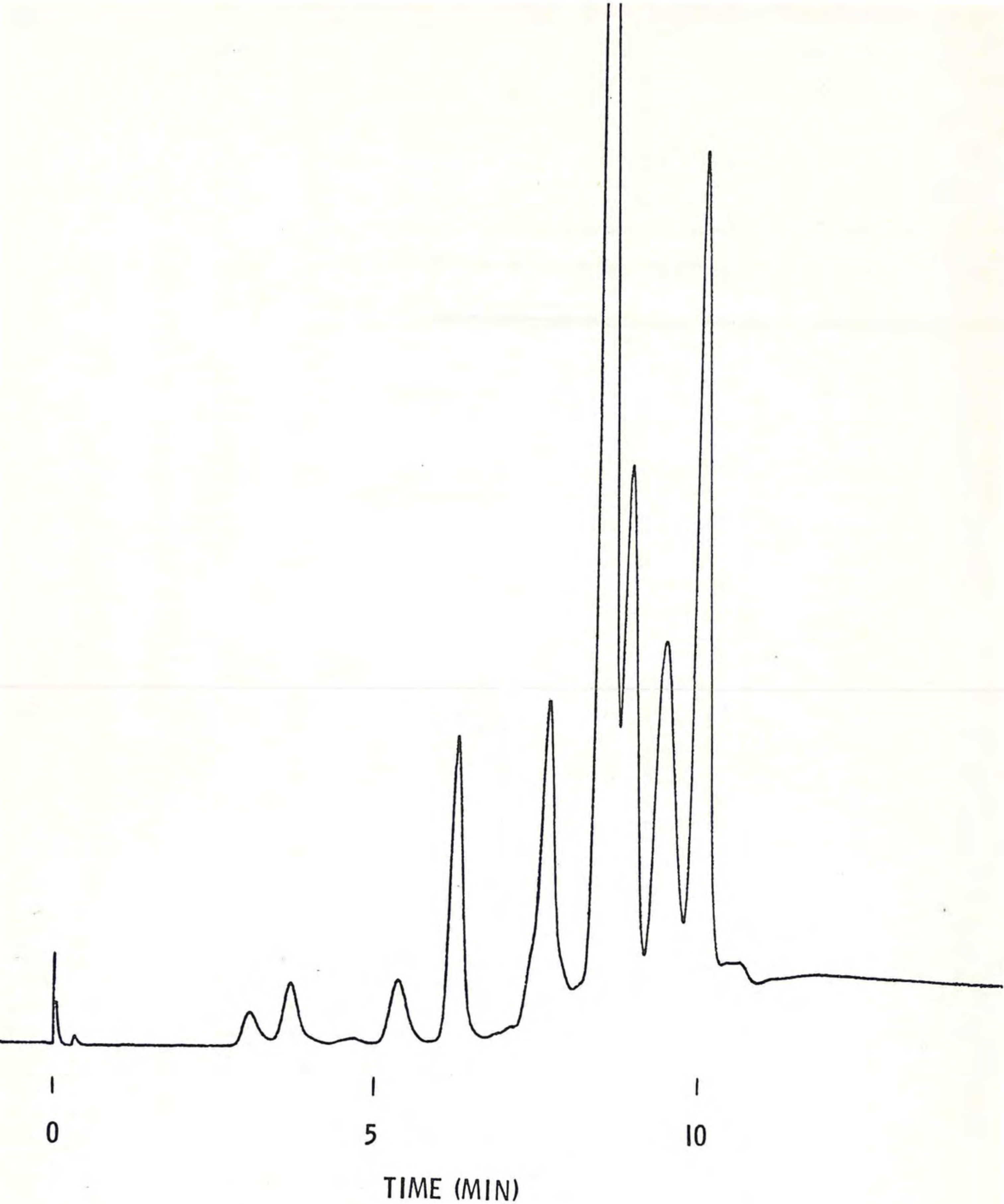

Figure 4. Organics from Ambient Air Chromatographed on a 1/8 in. o.d. X 6 ft. Packed Column.

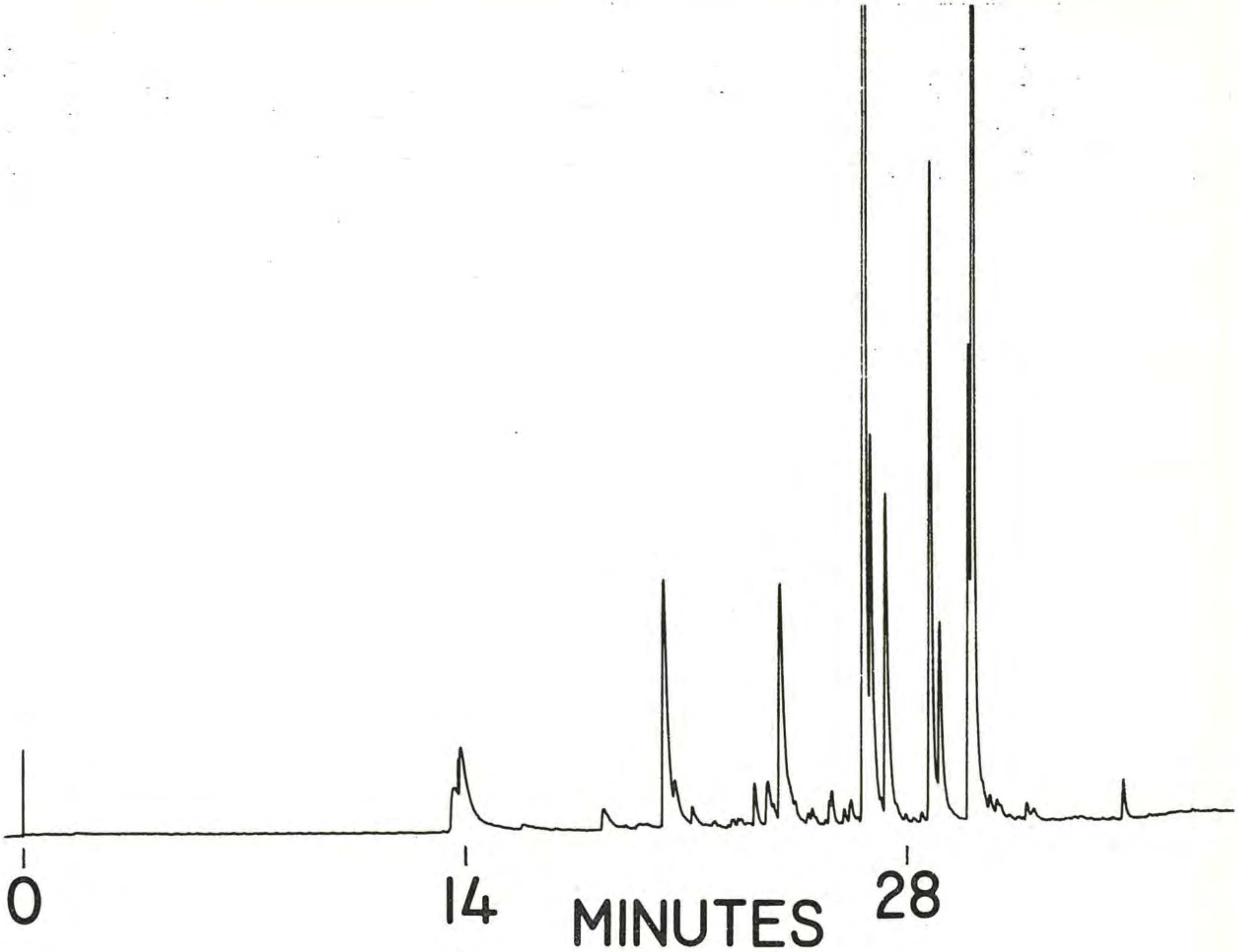

Figure 5. Organics from Ambient Air Chromatographed on a 0.02 in. X 100 ft. S.C.O.T. Column.

Odor Analysis - Coffee Beans

Figure 6 is a chromatogram of the aroma of freshly ground coffee beans. This is a packed column chromatogram of the organics obtained by sampling the head space above coffee. We were able, by mass spectrometry, to identify most of the major compounds in a two-hour experiment, including the spectral interpretation. I bring this up just to point out the utility of this technique for odor analysis. Odors are an obvious indication of the presence of volatile compounds, frequently organic. This type of procedure can be used to collect and identify odors.

Odor Analysis - Combination of Flame Ionization and Photometric Data

Attempting to identify odors can be frustrating, because strong odor bodies may have odor thresholds below the limit of chemical detectability. In addition, synergistic effects between odor and nonodor bodies can often alter the odor of a pure compound. In a complex chromatogram one does not know which components are odor bodies. In the case of sulfur compounds, this problem can be simplified by using a flame photometric detector as shown in Figure 7. The top trace is a flame ionization chromatogram; the bottom is a flame photometric trace using a filter specific for sulfur compounds. The flame photometric chromatogram shows that only the last peak contains sulfur and, hence, is suspect as being a possible odor body.

This procedure permits the analyst to concentrate odor bodies to aid in chemical or nasal identification. Besides providing the nasal identification capability, it offers at least two potential sample handling advantages over other techniques: First, the collected samples can be stored for weeks prior to analysis, and they can be shipped from site to site. Secondly, quantitative dilutions for odor threshold measurements are easily facilitated.

From the examples that I have shown here, both on odors and other organics in the air, I hope you can see the wide variety of compounds in air which can be determined by this technique. It offers several unique advantages without the need for elaborate equipment or extensive analyst training. Sample handling is simplified. Maximum sensitivity can be attained, because the total collected sample, rather than aliquots, is analyzed. Sample storage and shipment is convenient. Interference from water vapor is negligible. The major limitation is that the compounds to be determined must be amenable to gas chromatographic analysis.

Let me make a couple of comments on topics that have come up during the meeting or during lunch: First, sample columns of this type are regenerated during analysis, so they can be reused. This offers one potential advantage over some of the other techniques mentioned previously. Secondly, we have used Carbosieve B on one occasion where we were trying to measure a very low molecular weight material, a

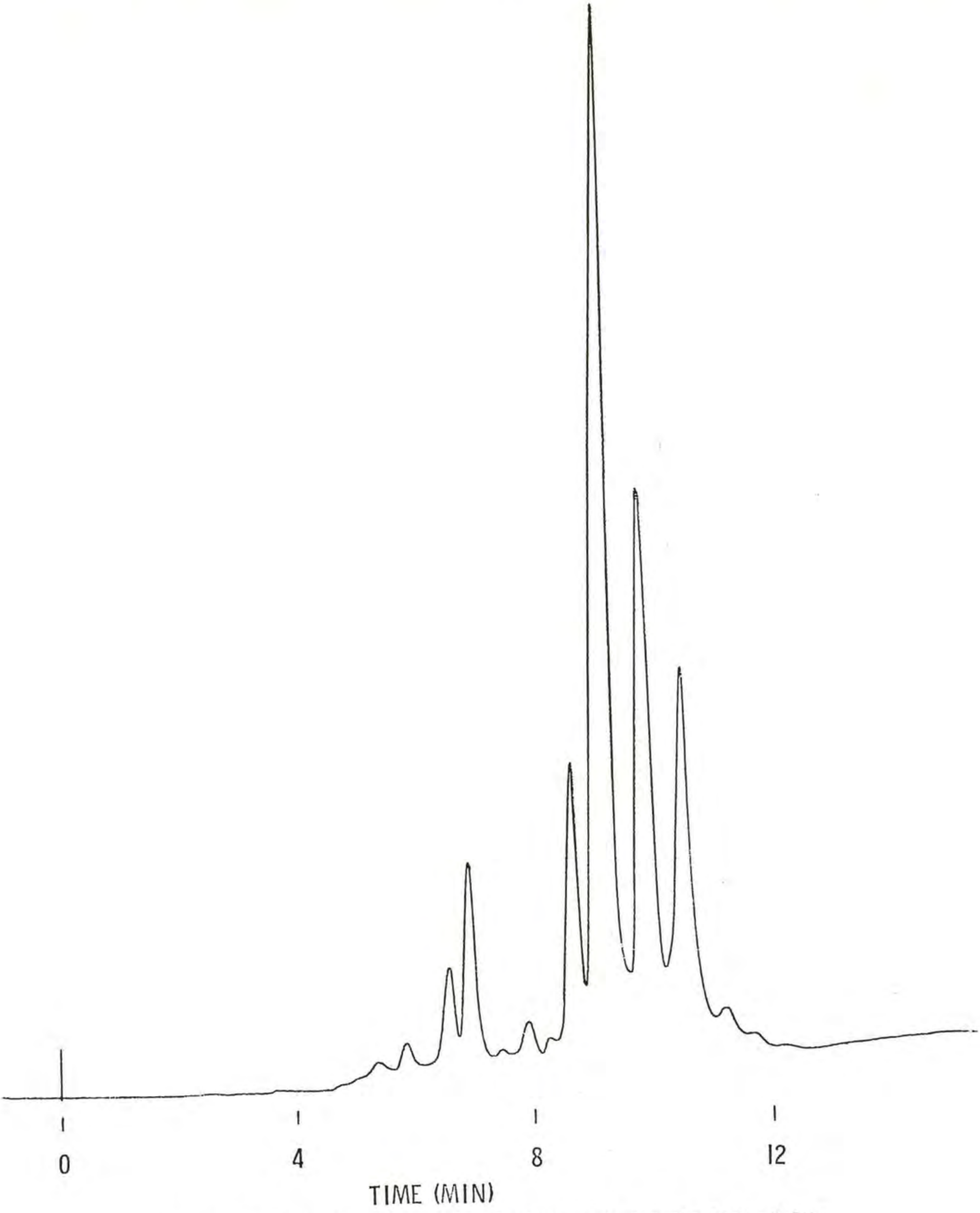

Figure 6. Chromatogram of Volatile Organic Components Evolved from Freshly Ground, Roasted Coffee Beans.

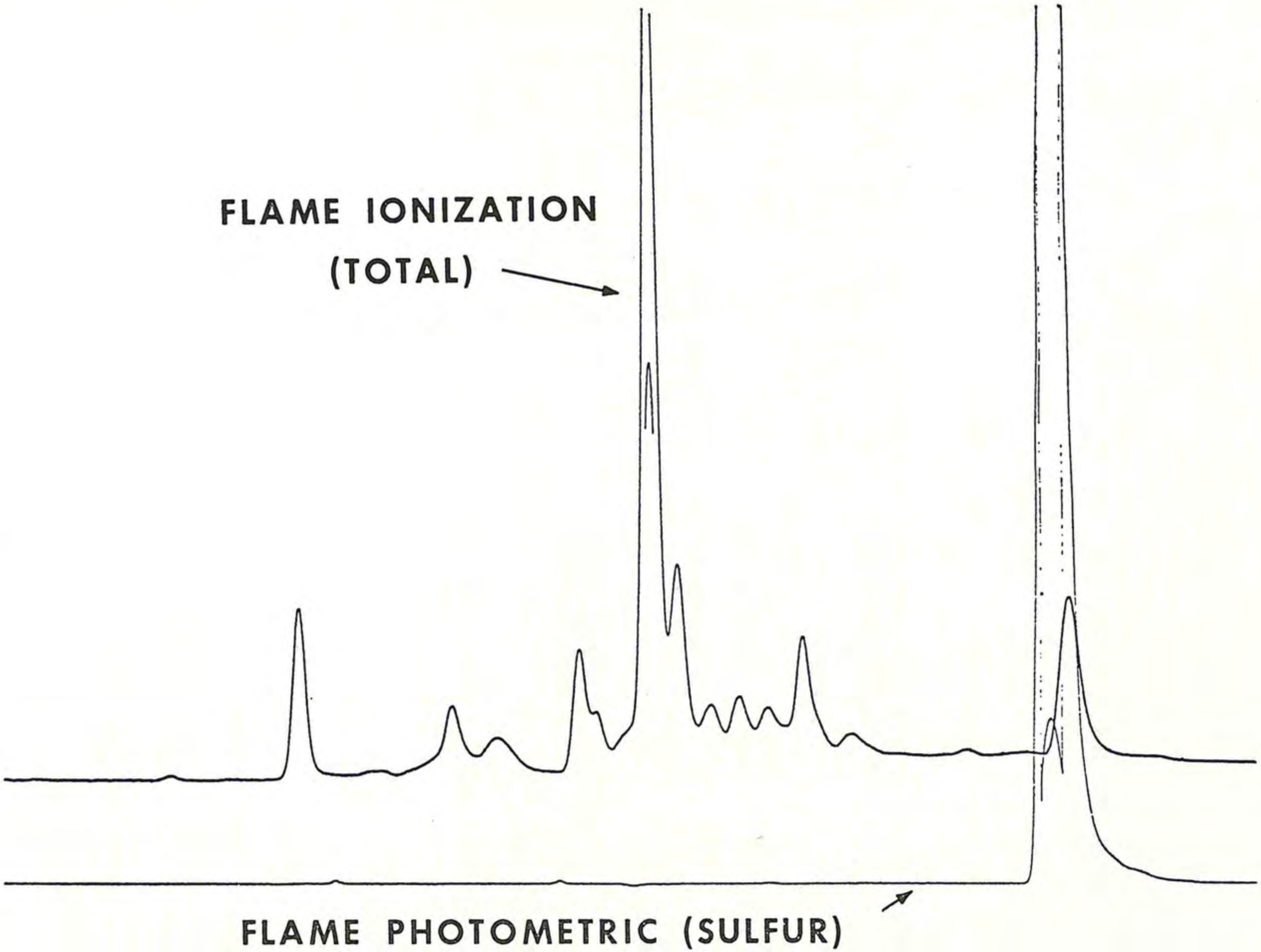

Figure 7. Flame Ionization and Flame Photometric Detector Responses to Identify Sulfur-containing Compounds.

molecular weight too low to be amenable to collection with a porous polymer bead column. Our experimentation was unsuccessful; a portion of the compound appeared to be irreversibly adsorbed on the packing.

Finally, one of the previously announced topics for discussion was thermal versus solvent desorption. Let me offer my opinion on that topic. I favor thermal desorption whenever possible, because no additional components, such as solvents, are introduced into the system. Secondly, since the entire collected sample is analyzed at once, thermal desorption directly into the gas chromatograph is inherently more sensitive than solvent desorption.

Discussion

Dr. Zlatkis: *On doing the* C_2 *benzenes that you had at those high flow rates, were they all retained quantitatively?*

Dr. Mieure: *I didn't go into as much detail in discussing that work as we actually undertook for the analysis. Quantitation of* C_2 *benzenes in the automobile was actually done at lower volumes. The 36 liters that I mentioned was the magnitude of air we had to sample to detect the low levels of phthalate esters that were present. We also did considerable work at lower volumes.*

To answer your question specifically, some of the alkylbenzenes would have been lost with those long sampling times.

Dr. Dravnieks: *I have a question. You said you tried Chromosorb 101, 105 and Tenax GC.*

Dr. Mieure: *Right.*

Dr. Dravnieks: *Is there some organic compound which you have tried with all three, and if so, what were the relative breakthrough volumes?*

Dr. Mieure: *I can give you relative numbers. I can't give you absolute numbers.*

Dr. Dravnieks: *Yes.*

Dr. Mieure: *The total volume which can be sampled without breakthrough is smallest with Tenax GC; next, Chromosorb 101, and we have found Chromosorb 105 to be most retentive. Remember that it has the highest surface area.*

Dr. Dravnieks: *Is there lots of difference between Tenax and Chromosorb 101?*

Dr. Mieure: As I recall, it is a factor of 2 or 3.

Dr. Dravnieks: What type of compounds are you talking about?

Dr. Mieure: We used alkylbenzenes as test compounds.

Dr. Wood: You made a general statement which I have heard before and I disagree with, and that is that the porous polymers do not retain water vapor. Some of them don't perhaps, but I think a general statement like that is not correct, because things like Porapak T do retain water.

Dr. Mieure: I have no experience with Porapak T. I meant to say the three porous polymer packings that we have used do not retain significant water. They all, of course, will retain some water. A certain amount is retained in transit through the column every time moist air is sampled.

Dr. Dravnieks: I think we can say that the polar porous polymer packings will retain water.

Dr. Mieure: Yes.

Dr. Klier: Sometimes even the hydrophobic polymers can be hydrophilic after exposure to the aggressive gases such as ozone. That happens with one of the Porapaks, I don't know which one. But before you have exposed them to nitric oxide the material is hydrophobic, but after you have exposed it to nitric oxide it is partially hydrophilic.

Dr. J. Taylor: Did you say the direction of analysis as compared with collection on your two types of columns?

Dr. Mieure: No, I don't believe I did. I concur with Dr. Zlatkis that a back-flushing type of analysis is preferred, although we have tried both ways to see what the effect would be. Using a programmed temperature analysis like we do, it doesn't make very much difference. But I would say in general that it is better to back-flush from the collection column.

Dr. J. Taylor: In the type that you are collecting, is it really necessary to have such a big tube? Couldn't that be greatly miniaturized for the applications that you talked about?

Dr. Mieure: Well, we wanted to be able to detect down to about 1 ppb, and with a very short sampling time. Hence we used a large column to get a high flow rate. The levels that I was talking about were well below the TLV values for most compounds. So if you are interested in the TLV values, then, yes, you could get by with much smaller columns because the volume sampled could be smaller.

Dr. Zlatkis: I might add as little as 10 millimeters of Tenax has been used to do an analysis.

Dr. Mieure: We used between 0.1 - 0.5 grams in our columns.

Dr. J. Taylor: I am a former microchemist, and I think small.

Dr. Teass: You say that you reuse these sampling tubes?

Dr. Mieure: Yes.

Dr. Teass: Do you notice on reuse that some of these properties change?

Dr. Mieure: We have noticed primary property changes during the first time the column is thermally conditioned. We have used them as many as 50 times without observing any apparent change after that. The flow characteristics will change somewhat during the conditioning period because of the shrinkage that Dr. Zlatkis referred to.

FLUIDIZED BED AND HIGH-HUMIDITY SAMPLING FOR AIR ANALYSIS

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Introduction

Presence of humidity in air complicates gas chromatographic analysis of air for small amounts of organic substances if efforts to pre-concentrate these prior to analysis do not include separation from the excess water. A pre-concentration with a simultaneous removal of water using non-polar sorbents solves this problem: only a small amount of water-vapor is collected, while organic substances collect efficiently.

Two collector designs are possible: fixed (packed) bed and fluidized bed. The fluidized bed design was used by us before we began utilizing high-capacity polymeric sorbents; it has some historic value, and merits a short characterization.

The collection of vapor by a typical GC stationary phase follows the equation:

$$W = KMC$$

where W is the amount collected, C is the concentration of the vapor in air, K is a coefficient related to the solubility of the vapor in the stationary phase, and M is the amount of the stationary phase used. The rate of collection depends on the rate at which vapors in air can reach the stationary phase. In packed beds, rate is limited by the pressure drop. The fluidized bed permits vapor to reach all of the stationary phase practically simultaneously; and since fast flow of air levitates and agitates the particles that carry the stationary phase, large amounts of air can be passed through the collector in a very short time.

Fluidized Bed Design

Figure I shows the fluidized bed design (1) Particles are Teflon, coated with either Apiezon L or a methylsilicone phase. Amounts of each organic vapor collected are maximum amounts permitted by the equation above; thus, this design fully utilized the collection capacity of the particular phase. Analysis involves transfer of the collected vapors by heating the bed to the highest temperature that the stationary phase can stand without trace decomposition, re-collecting vapors cryogenically, and injecting them into a gas-chromatograph by a special device described elsewhere (2).

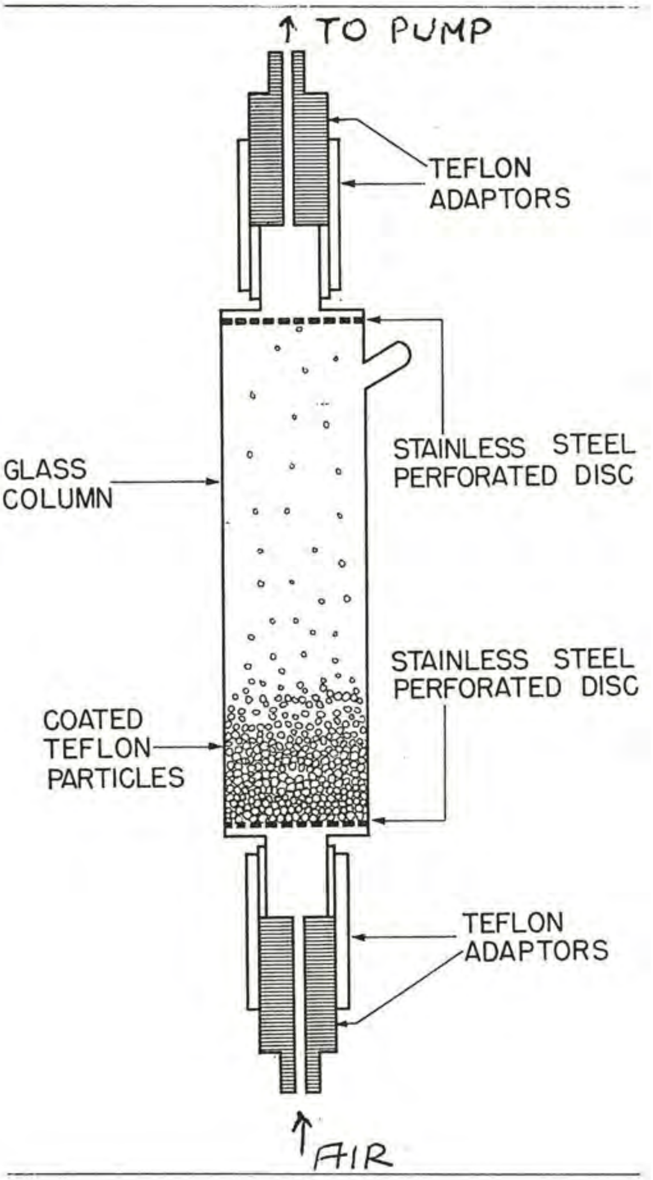


Figure 1. Fluidized Bed Collector (Ref. 1).

Two factors resulted in abandoning the fluidized bed design when high-surface-area organic polymers were introduced as the collecting media. First, these materials are much more efficient adsorbers, which in turn makes it more difficult to desorb the sample if the low-volatility components are distributed throughout the collector charge. Second, these materials do not fluidize easily, because of electrostatic charging through friction.

Fixed Bed Design

With organic polymeric collectors, the design shown in Figure 2 is used. Spring-loaded screen piston prevents powder from slushing around during transportation. Sampling is done with the spring upwards, and with air moving downwards, in the direction of gravity. In an earlier publication (2) we showed upward air flow; later it was found that such arrangement occasionally results, despite the spring pressure, in some powder movement and channeling at the faster air-flows; while with the direction of flow shown here this defect is eliminated. Sampling at rates of up to 5 l/min at tolerable pressure drops is possible.

Properties of Collector Phase

The collector phase should have the following properties. First, it must be non-polar, to minimize the co-collection of water. Second, it should have maximum possible surface. Third, the pore sizes should be sufficiently large to avoid specific effects (such as with molecular sieves) where molecules of vapor adsorb less efficiently if they do not fit into the pores. Fourth, the polymer should be sufficiently stable thermally.

Chromosorb 102, with a surface of 300-400 m^2 per gram, and 90 Å nominal pore size is one of the suitable collector phases. In actuality, the pores, in accordance with information from the polymer manufacturer, are snake-like with 30-Å diameter openings.

There is often a notion that in order to be a good collector, the polymer must be a good chromatographic phase--that is, to permit obtaining well-shaped GC peaks. This consideration is fallacious, since the only function of the collector is to collect as efficiently as possible. Broad peaks simply mean that the adsorption energy is not a relatively well-defined value, but a substantial range of values. "Tailing" means that in addition to the majority of adsorption sites there are many sites with a higher adsorption energy, thus better collecting than the average sites. Desorption prior to the analysis is a process that results in adequate removal of adsorbed vapors despite tailing and re-collection of these in a more compact form before injection into GC.

Sample Vapor Transfer and Injection

In the process which we use, vapors are then transferred to a cryogenically cooled 1/8 in. diameter empty stainless steel injector tube, while heating the collector to 120°C, Figure 3. The injector cooling

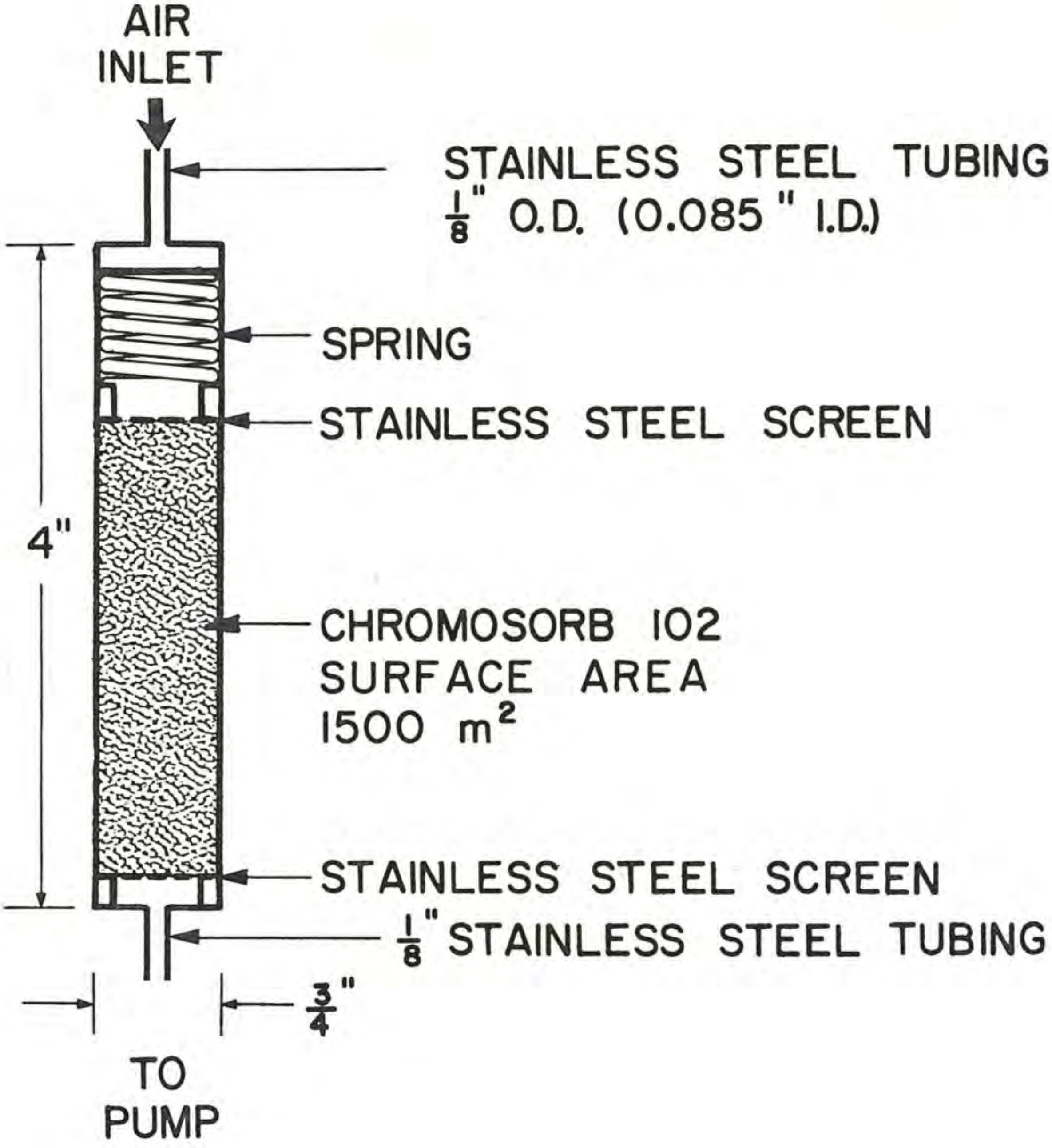


Figure 2. Fixed Bed High-Speed Collector (Ref. 2)

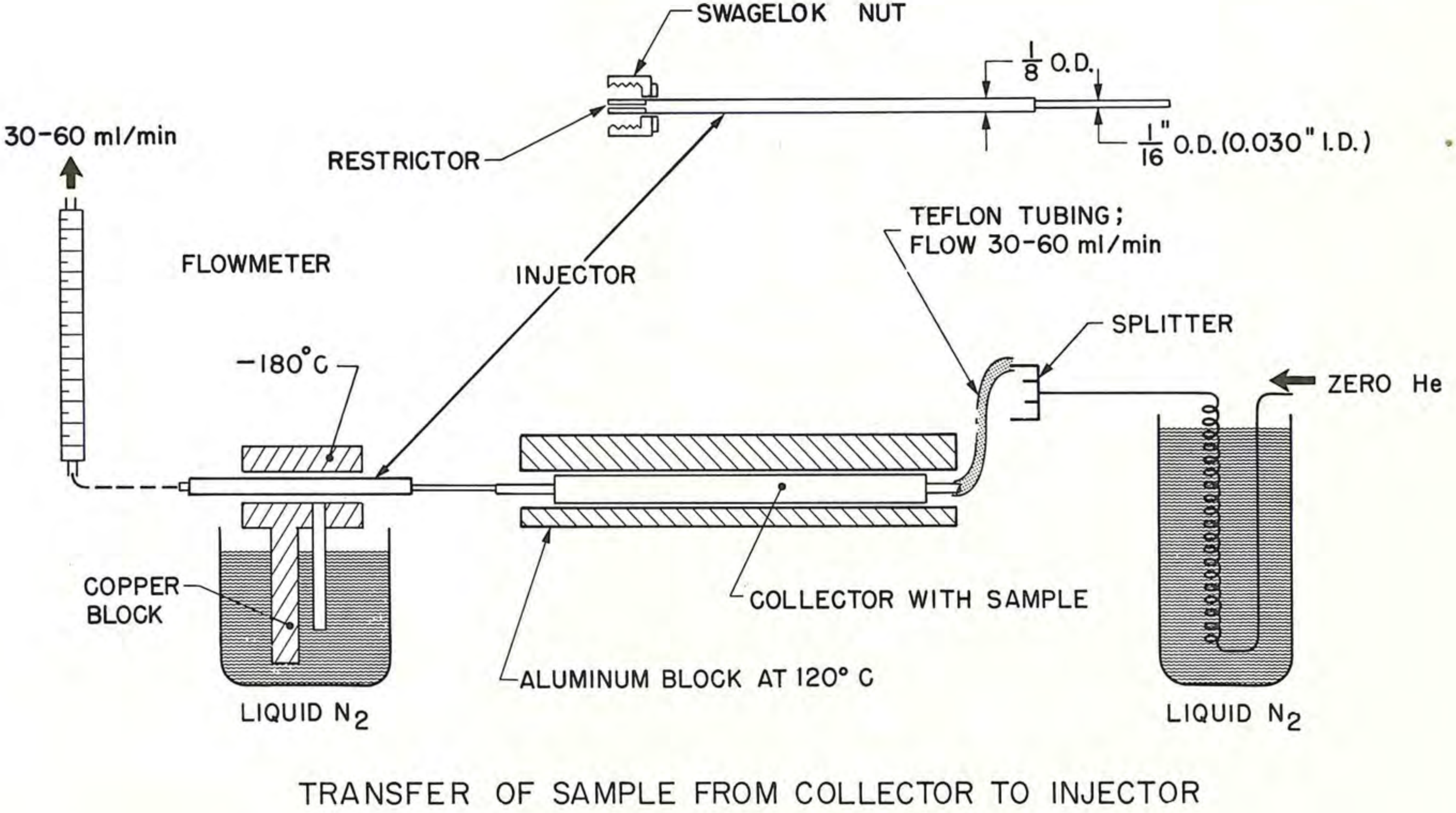


Figure 3. Sample Transfer from Collector to Injector (Ref. 2)

is accomplished by a copper block with a copper side bar immersed in liquid nitrogen. The injector is in a copper channel covered with a copper plate. A copper side tube connects this channel to the liquid nitrogen; small amounts of nitrogen boil in the tube and sweep the channel free of air to prevent ice formation around the injector. Ice would act as an insulator, interfering with the cooling.

Elution from the collector is in a direction reverse to that used during the collection from air. Otherwise, the less volatile materials would require too long a time to elute through the mass of the collector charge.

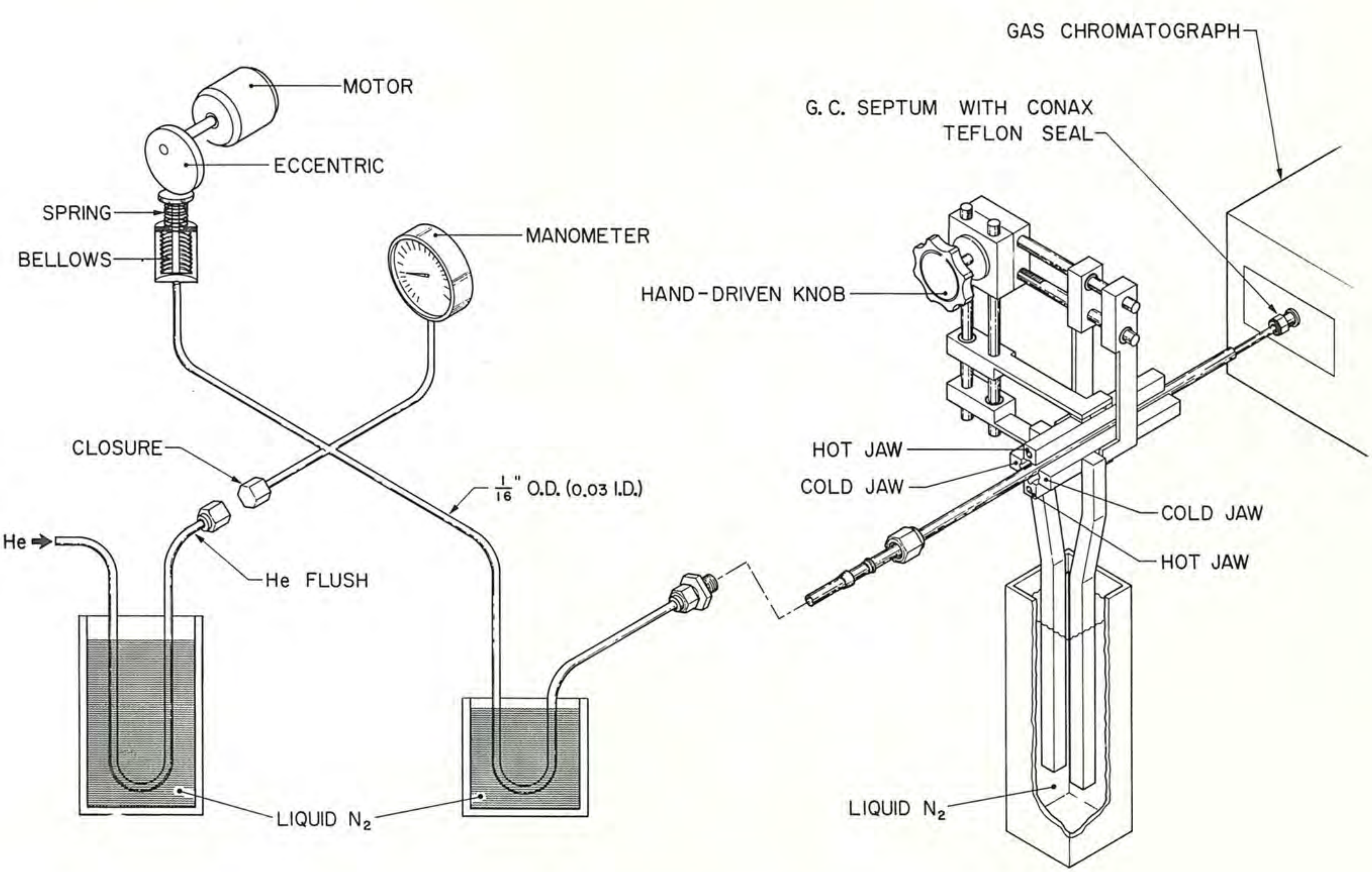
In Figure 4, the injector is shown connected to a chromatograph. Initially, the injector with the sample is still at cryogenic temperature, maintained by two copper-blocks with tails immersed in liquid nitrogen. The other end of the injector is connected by a stainless steel capillary to a bellows mechanism that can be operated by a motor-driven eccentric can. A pressure gauge serves to check for tightness of the connections. Before the injector is connected, the stainless steel capillary is backflushed with helium to prevent air impurities from entering the bellows system and air moisture from freezing in the cryogenically cooled loop of the capillary. This loop prevents impurities that cannot be gotten out of the bellows/manometer system from entering the chromatograph. When the injector needle is connected, the helium backflow is disconnected and the opening plugged (Swagelock). Finally, the bellows is operated to withdraw 1 ml of helium from the GC port. All these manipulations temporarily disturb GC flow and time is given for the pressures to stabilize.

To inject the sample, the device, operated by hand through a rack-and-pinion mechanism, moves cold copper blocks apart and moves two preheated (250°C) copper blocks to clasp the injector needle. Simultaneously, the bellows is operated to push helium through the injector, pick up the vaporized sample there, and push it into the GC. Thus, basically, since the moment the air sample entered the collector (Figure 2), the sample never passed through any valves, packing glands or other elements which introduce artifacts by trace contaminations that tend to linger in such locations.

A feature of the injector is a narrowing of the back-end. This prevents the sample vapors from backfiring toward the bellows system, since the flow resistance on the GC port side of injector is much less than through the narrow opening back. The procedure is lengthy, with two analyses per day pretty much a routine; sample collection, of course, is fast.

Characteristics of Samples Collected

Some properties of the collectors are low water pickup (water vapor in air samples begins to break through after passage of 0.2 liters of air) and good collection of organics from pentane (non-polar) or ethanol (a highly polar substance), breaking through after 12-14 liters of air



SAMPLE INJECTION INTO G. C. SEPTUM

Figure 4. Injection of Sample into Chromatograph (Ref. 2)

have passed. For each next higher homolog, the collection capacity increases approximately by a factor of 2.5. The collection capacity follows the same order as the retention volumes of organics by a typical non-polar silicone phase. This permits estimating that pesticides may be fully collected from a sample of several hundred liters of air; we have not tried to verify this for pesticides in actual experiments.

A typical blank from a collector is shown in Figure 5. It exhibits a few small peaks. The analysis of a Chicago air sample exhibits groups of peaks corresponding to gasoline and diesel fuel components. Analysis of air from a village near Chicago exhibits three solvent peaks characteristic of resin reactor effluent in a nearby resin plant; the peaks represent a dilution of the resin reactor effluent by a factor of 10^7 *before this chemical signal reaches the site in the village where people complain about the resin odor. Odor, of course, is not caused by these solvents but by some other substances co-present with the solvents in the reactor effluent.*

Automation of Collection and Analysis Process

The question arises if it is possible to automate and accelerate the collection and analysis process. In rating of grain for normal aroma by USDA inspectors, errors may occur as in any sensory evaluation. The USDA supported a project at our laboratorie, to investigate if grain odor classification may be feasible by a combination of GC and computerized pattern analysis methods, with a requirement that the evaluation of one sample should be possible within a reasonable number of minutes instead of the lengthy procedure just described. The cryogenic steps also had to be avoided.

Figure 6 illustrates the developed bench-top demonstration arrangement (3). The heart of the device is the adsorber F. It is thin-wall 3/8 inch diameter stainless steel tubing containing Chromosorb 105. This material has more surface per g than Chromosorb 102, but is also somewhat less thermally stable. By operating the appropriate solenoid valves, and operating the peristaltic pump, 1.5 liters of grain vapors are pulled into the adsorber and are collected there, except for water vapor. The grain container is then disconnected and the sampling port closed by a nut.

To analyze, the adsorber is heated by passage of 100A low-voltage current. A thermocouple monitors the adsorber temperature and controls it through a meter relay. The important feature of the adsorber design is balancing the sizes of lead wires, the thermocouple, and all connections to eliminate any cold spots in the adsorber-to-GC connections. Also, elution is through the upper end of the vertically placed adsorber. The upper end is hotter because of drift of hot air upward along the skin of the adsorber tube.

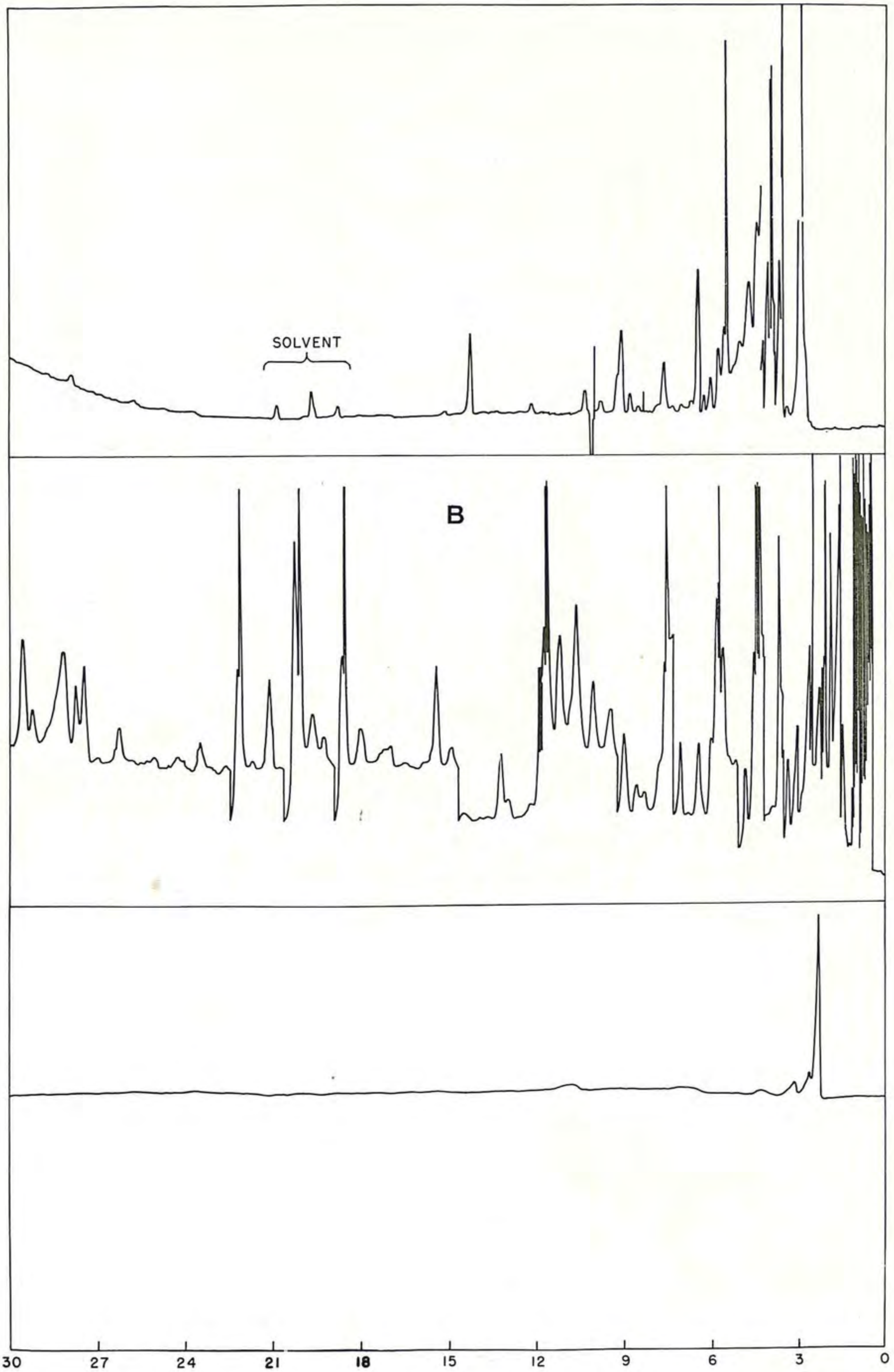


Figure 5. Typical GC Patterns.

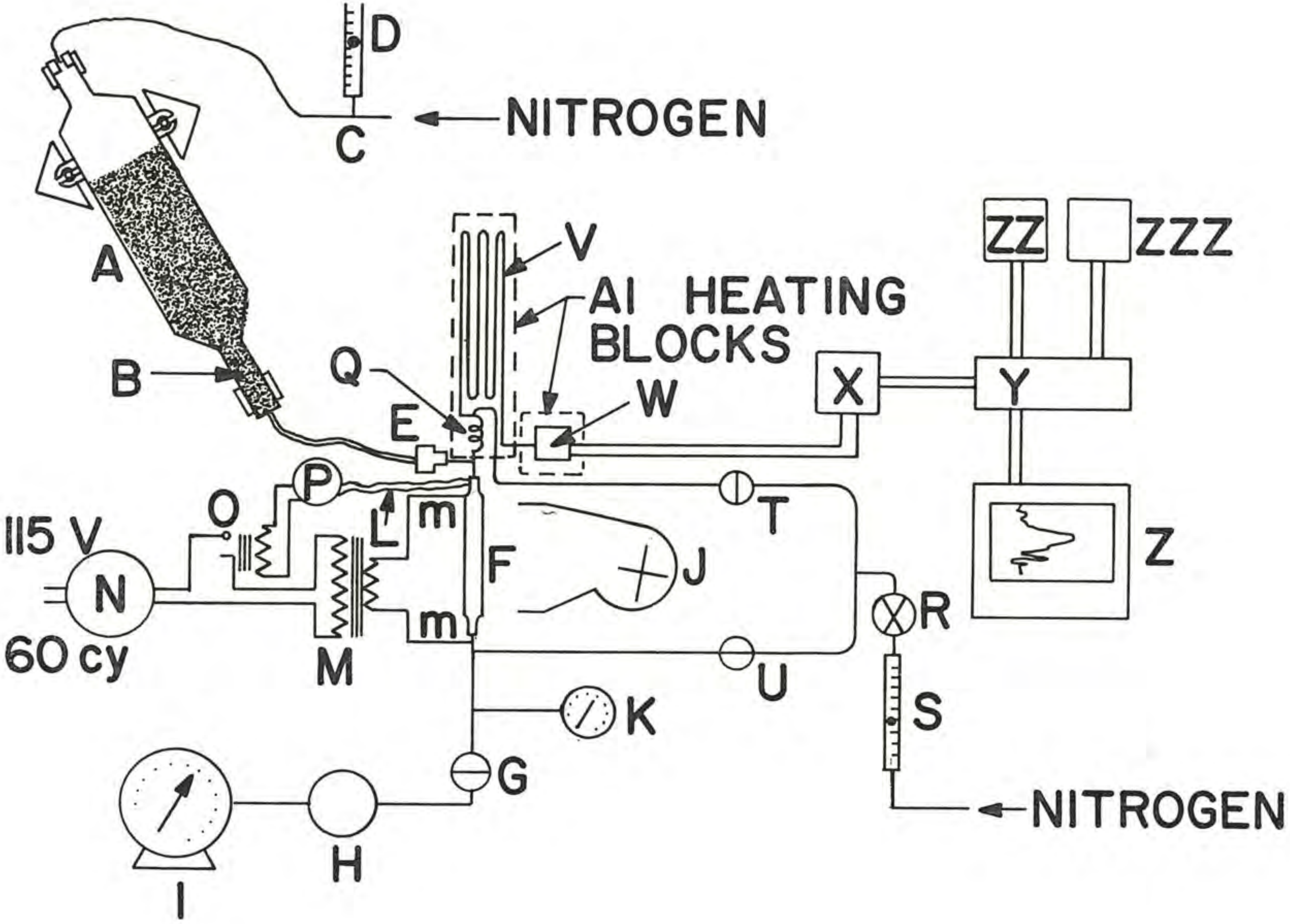


Figure 6. Apparatus for Non-Cryogenic Concentrative Air Sampling and GC Analysis (Ref. 3)

The GC column is 10% Sp-1000 on Supelcoport support, in a Teflon-clad (inside), stainless steel 1/8-inch diameter tube, 5 ft long. It is in an aluminum block at a constant temperature. All possible tubing connections, including column to adsorber, are silver-soldered, which proved essential in preventing leaks in cyclic operation.

A feature of the device is capillary tubing, Q, between the adsorber and the column. Its flow resistance is 10 times larger than that of the column. When the helium carrier gas is fed through the upper branch, T, during grain vapor sampling, most helium flows through the column while a small flow of helium through the capillary towards the adsorber protects the column from drift of the grain vapors. The column remains in good, stable condition.

When the adsorber is heated, the flow of helium is through the lower branch, U, so that the eluted sample vapors are now carried to the GC section. The fan, J, permits rapid cooling of the adsorber during turnaround for the next sample. Sampling time is 1.5 min.; elution and analysis time is 7.5 min. An additional few minutes are needed for cooling of the adsorber and a new sample attachment. Four to five analyses per hour are possible.

A computer was able to utilize GC data from such equipment to discriminate good aroma from off-aroma of grain at a reasonable statistical level of performance. Such a device can be easily automated and adapted to cyclic monitoring of air containing a large number of organic substances simultaneously.

Multistage Collectors

Finally, a few words on multistage collectors for the ambient temperature release of vapor. If elevated temperature is used for elution from sorbents, one desires sorbents with as much capacity as possible, so that more volatile substances can be adequately collected. Such sorbents would hold heavier vapors rather strongly, but at sufficiently high temperature would still release even these.

In studies of odors, it is desirable to be able to reconstitute the collected sample to its initial concentration in air. Thermal release is difficult because not all components are released simultaneously.

We have partially solved this problem using a three-stage sampler (Figure 7). Heavy vapors, e.g. phenol, collect in methylsilicone on Teflon packing, and are just as easily released by backwash at ambient temperature; high volatility compounds, such as NH_3 *or* H_2S*, easily pass through the methylsilicone and the medium layer (Chromosorb 101) but are adsorbed in the third layer, Chromosorb 105; they easily desorb from these in backflush; the center layer is for similar purposes for substances of intermediate volatility. Thus, strongly adsorbable substances do not reach the strong adsorbents.*

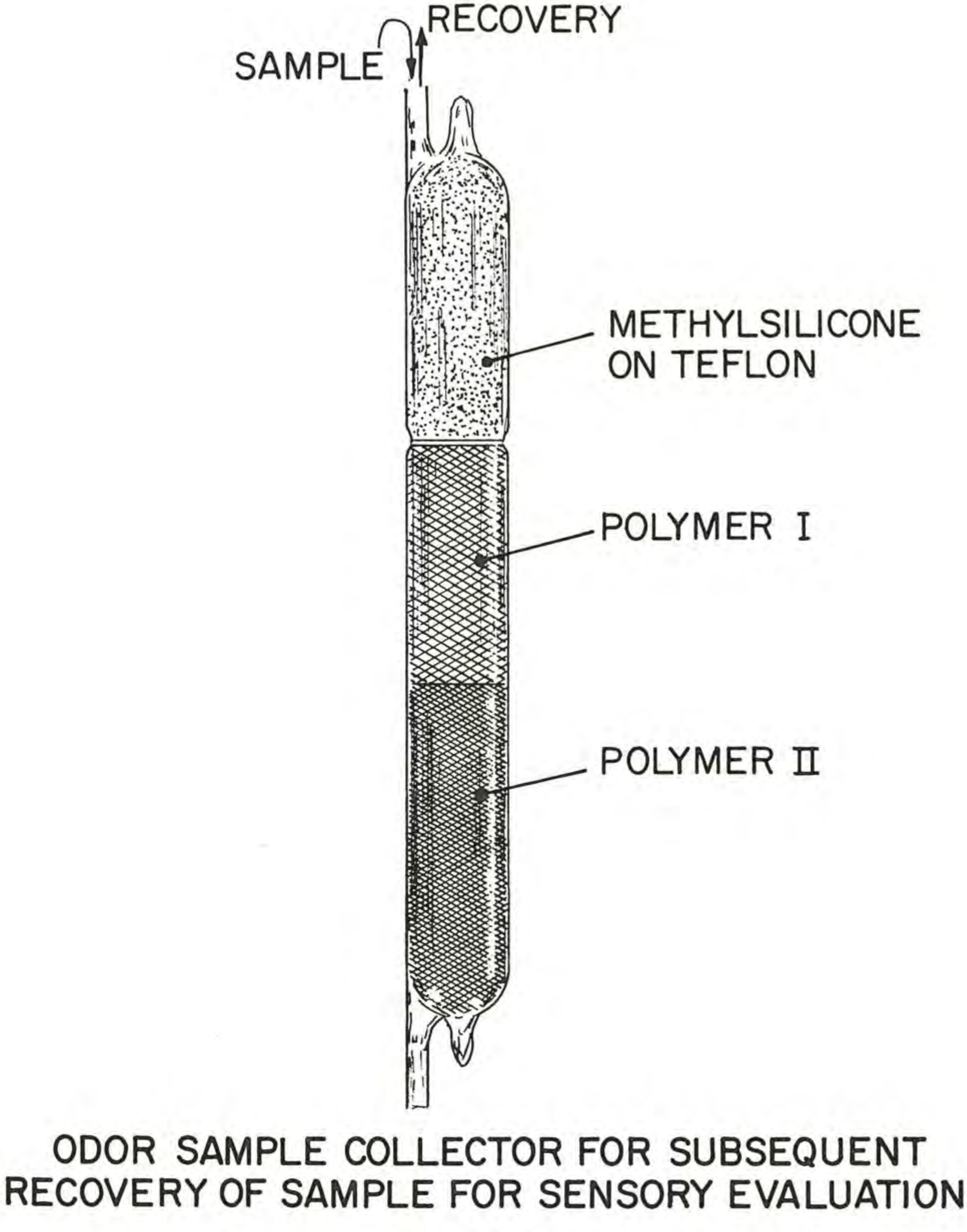


Figure 7. Three-Stage Vapor Collector.

When vapors of various odorants in air were measured for odorosity before collection and then collected and "played back" at the same temperature for another odor evaluation, essentially the same odorosities were observed; occasionally, over a day or two of storage, degradation for some components reached a factor of 2. For H_2S, tenfold degradation occurred. We suspect that H_2S in air oxidizes to water and S at the sorbent surfaces. Since H_2S is a significant odorant, we discontinued the use of such multi-stage collectors. Nevertheless, they may find use in some special tasks, and desorption may be assisted and reach a sufficient level if the temperature is only slightly increased.

References

1. *Dravnieks, A., and Krotoszynski, B. K., J. Gas Chrom. 6, 144 (1968).*

2. *Dravnieks, A., Krotoszynski, B. K , Whitfield, J., O'Donnell, A., and Burgwald, T., Env. Sci., & Techn. 5, 1221 (1971).*

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Discussion

Dr. Mieure: You mentioned degradation and low recovery of H_2S. Do you know if the porous polymer or methylsilicone or both were causing this?

Dr. Dravnieks: I really do not know for sure. When we used just methylsilicone, we did not observe a loss, but a small effect may not have been noticed. We suspect Chromosorb 105 to cause degradation of H_2S.

I would like to add a comment on the three-stage bed collector capacity, Figure 7. The collector contains 20 g of each of the 3 materials. However, 20 g of Chromosorb 105 permit collecting H_2S and NH_3 from not much more than 2 liters of air to "play" back at the initial concentrations of those trace components which did not degrade. Adsorption on walls, in valves etc. is much less important in loss causation since their surface is much less than that of the sorbents.

Dr. Ballou: Did you say there was a loss by a factor of 2 in the containment of aldehydes?

Dr. Dravnieks: Not quite in that way. I meant to say that if aldehydes are collected from air at ambient temperature, and then the odor is re-constituted by backflushing, again at ambient temperature, with air flow of order of 50-100 ml/min., the resulting concentration of valeraldehyde in air is about twice lower than in the original sample. That does *not mean that there is loss of 50 percent; simply, that the elution, e.g., at 50 ml/min, is too fast to permit equilibration with air flow. The total integrated recovery over longer time is probably much higher, but we have not studied it, since our concern was with the odor recovery at ambient temperature. Thermal recovery, with the collector, as shown in Figure 2, gives over 90% recovery.*

NBS RESEARCH RELATED TO THE DEVELOPMENT AND EVALUATION OF SOLID SORBENT ANALYTICAL SYSTEMS

by John K. Taylor

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Introduction

In the papers already presented, we have noted three areas of interest: research which is concerned with information basic to solid sorbent collector development; development of practical collection devices; and evaluation of devices in practical situations. At NBS, we have been largely concerned with the last area and to a limited extent with the first. However, we expect to be involved very soon in the middle area.

I would like to tell you about a program carried out during the past two years which has been jointly funded by NBS and NIOSH. I will discuss five subjects. One is the generation of defined test atmospheres which is basic for the development and evaluation of sorbents. Secondly, I will discuss the generation of mercury test atmospheres and the evaluation of a silver wool collection material. A third subject is a piezo-electric solid state detector in which the sorbent is an integral part of the analytical system. Fourthly, the development of SRM's (Standard Research Methods) for measurement of organic solvents in the atmosphere will be reviewed. Finally, I will outline some proposed work to develop some new types of collection devices.

Generation of Test Atmospheres

An extensive effort has been devoted to development of systems to produce test atmospheres of accurately defined composition. The simplest kind of test atmosphere is one contained in a pressurized cylinder which is available upon opening a valve. However, this approach is only useful for stable gas mixtures. Moreover, one may need such a variety of mixtures that it is not feasible to have individual test gases. Accordingly, we have directed attention to the dynamic generation of test mixtures at the time of need by gas dilution devices, both simple and complex.

A simple gas dilution device uses a pure gas or usually a relatively concentrated mixture and dilutes it quantitatively by measuring the flows of the material and the diluent. Accordingly, all mixtures between the two extremes can be produced and a dilution factor of 1:100 is well within the reliability range.

We have developed systems for preparing binary mixtures and one that mixes three components, one of which may be water vapor, which is essential for study of humidity effects.

Gas dilution devices for the preparation of unstable gas mixtures usually employ relatively concentrated bulk mixtures (several hundred parts per million) which will have reasonable stability and which can be analyzed occasionally prior to quantitative dilution to produce the desired gas mixture. Each system developed for NIOSH includes a means to verify the composition of the bulk mixture. Examples of such systems are those developed for ammonia and chlorine.

Another way to produce reactive mixtures is by component injection into the diluent stream. The permeation tube developed by A. E. O'Keeffe is an example. SO_2 permeation tubes are now distributed by NBS as SRM's and serve as bench marks for sulfur dioxide measurement in the ambient atmosphere. Mechanical injection of a gas mixture into a diluent stream is another means to produce gas mixtures although we have not had much experience with this.

A component of interest can be generated directly in the diluent stream. Thus, ozone mixtures are produced by ultraviolet irradiation of a diluent air stream. Chemical generation by a substitution reaction may be useful in some cases. For example, CO_2 may be reduced to the less stable CO. Also, certain mixtures may be produced by saturation of the gas stream with subsequent dilution to the desired concentration. The mercury system to be described later is a good example.

All told, systems for the generation of 23 different kinds of gas mixtures have been developed and performance tested for NIOSH. The concentration ranges produced vary from 0.5 to 5 times the TLV in each case. The following is a list of reports describing them.

NBSIR 73-255	System for Preparation of Known Concentrations of Methane in Air
NBSIR 73-257	A System for Producing Test Atmospheres Containing Hydrogen Cyanide
NBSIR 73-259	A Gas Dilution System for Methyl Bromide
NBSIR 73-260	A Gas Dilution System for Arsine-Air Mixtures
NBSIR 73-261	A Gas Dilution System for Hydrogen Fluoride-Air Mixtures
NBSIR 73-292	Gas Generation Systems for the Evaluation of Gas Detecting Devices Gas Systems described: CO, CO_2, C_6H_6, CCl_4, C_2HCl_3, C_2Cl_4, O_3, SO_2, H_2S, NO_2, NH_3, Cl_2

NBSIR 73-411 Development of Analytical Reference Materials and Contaminant Generation Systems -- Work Completed During Fiscal Year 1973.

Includes work on the development of generation systems for TDI, MDI, formaldehyde, phosgene, and sulfuric acid aerosol.

Mercury Vapor Generation System

The system developed for the generation of mercury vapor-air mixtures is of special interest. A stream of air is essentially super-saturated at a high temperature then passed through a condenser to obtain a saturated vapor. This saturated air can then be diluted to obtain the test concentration desired. The critical element of this system is the condenser in which the air stream first impinges on a pool of mercury held at constant temperature and then passes through a stainless steel heat exchanger over a tortuous path to achieve final equilibrium.

In evaluating this system we first evaluated a silver wool collector for mercury vapor in air. A collector of this type was developed by Long and associates at EPA (1). Essentially it consists of a tube packed with microchemical grade silver wool which has been given a prescribed heat treatment. Such a tube can be used to collect up to 4 μg of mercury which can be quantitatively liberated into a gas stream by a controlled heating cycle, and then measured by atomic absorption spectroscopy. A measured volume of mercury vapor can be withdrawn from the saturated atmosphere found above mercury in a suitable flask, for calibration purposes.

After verifying the efficiency of such collectors, they were used to measure the mercury concentration produced by the generator, which in turn could be calculated from the flow rates and pressure data. The agreement was within the uncertainty of the analytical data which is about 2 percent. Accordingly, the generator can be relied upon to produce concentrations in the range 0.005 to 0.500 mg/l. The following NBS report gives full details of this system.

NBSIR 73-254 A Mercury Vapor Generation and Dilution System

Piezo-electric Detector

We are interested in piezo-electric detectors since they give promise to combine a solid state collector used as a detector, together with an analytical system in a single unit. In principle, a quartz piezoelectric crystal is coated with a substance that selectively adsorbs or reacts with a component of interest, which changes its frequency *of oscillation. When calibrated with a standard gas mixture, it can function as an analytical instrument. In an alternate mode of operation, the component of interest might desorb a component of a coating, resulting in a decrease in mass of coating. There are obviously other modes of operation possible. A substance collected in an atmosphere of interest could be desorbed at a later time for remote analysis. Accordingly, one can envision field samples returned to the laboratory for analysis.*

A device has been successfully developed for monitoring mercury vapor in the atmosphere. In this case, the crystal is coated with a thin film of gold which serves as the collector-detector. Such a collector can be thermally reactivated for many cycles. Since the device is sensitive to about 10^{-12}*g of collected materials, it is very sensitive. Detectors for other substances of interest will depend upon the development of coatings of requisite selectivity for the component of interest. A paper describing the mercury detector will be presented (2).*

Charcoal Tube Reference Standards

Charcoal tubes in which known quantities of organic solvents are deposited to serve as SRM's have been under development during the past year. A gas stream containing a known concentration of the organic solvent of interest is passed through a manifold. A portion is withdrawn through a charcoal tube to which a critical orifice has been connected to control the rate of sampling. A system has been designed which permits the simultaneous preparation of 20 tubes. Research has continued to the point where it now appears to be possible to produce tubes that are accurate and reproducible to about 2 percent of the desired value.

In connection with this development work, some improvements in the analytical technique for determination of solvent content have been achieved. The reliability of the GC standards is increased by preparing them with micropipets, rather than microsyringes. Also, these standards are stored in glass vials with special Teflon plugs which can be pushed to expose a small hole for withdrawal of a portion for injection into the chromatograph, but kept tightly closed at other times. Such a technique reduces the loss of carbon disulfide by differential evaporation. Several other minor modifications of the analytical technique are described in NBSIR 73-292 cited above.

Development of Solid Sorbent Collection Systems

A program will be started early in 1974 to develop solid state collectors for the following substances: chlorine, fluorine, hydrogen fluoride, hydrogen cyanide, and phosphine. Because of the reactive nature of these substances, it seems unlikely that they can be physically adsorbed and subsequently desorbed. Rather, they may be trapped by a reactive mechanism and stripped by a chemical process for analysis.

The development of reactive processes would open the gates to a number of collection applications. The gas detector tubes now widely used are perhaps better collectors than indicators because the latter is limited by difficulties in reproducing packings, and personal errors in reading color boundaries, to mention several factors. Stripping of collected material, followed by measurement by suitable techniques, could solve some of these problems. We intend to take this approach, as well as to investigate other reactive collection techniques.

References

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Discussion

Mr. Crable: Any questions.

Dr. D. Taylor: I am interested in the piezo-electric detectors. How do you get selectivity?

Dr. J. Taylor: A film or coating is applied to the surface of the quartz crystal which may have a base coat of nickel, for example. In the case of mercury, an evaporated film of gold provides excellent selectivity. Perhaps conventional GC type materials could be applied to provide selectivity in certain cases.

Mr. O'Keeffe: It should be emphasized that the film cannot just stand on the crystal. It must be inertially bonded.

Dr. J. Taylor: Yes, and ordinarily it should be stable; it should preferably not evaporate. However, the system measures a change in frequency due to change in inertial loading of the crystal. If the film changes its mass with time, this may complicate the interpretation of the measurement. A second crystal, in a differential mode of operation might be used to compensate for non-analytical related changes of the coating however.

Dr. Mieure: John, you mentioned you would like to use this technique for water analysis.

Dr. J. Taylor: Yes, we hope to do so.

Dr. Mieure: You might consider electrochemical deposition on a crystal as a collection mechanism. Controlled potential electroanalysis could provide selectivity.

Dr. J. Taylor: This is a very practical approach which we expect to investigate. In the atmosphere, electrostatic precipitation may be useful for certain kinds of particulates. Clearly, one's imagination may be the limiting factor in developing collection techniques as well as selective coatings.

Dr. Hughes: I am interested in the problems concerned with dilution of NO to obtain sub-parts-per-million concentrations. What are the problems due to oxidation of NO?

Dr. J. Taylor: The rate of oxidation of NO at low concentrations is not as fast as one might think. In a dynamic dilution system, the residence time can be kept below that during which significant oxidation occurs, which illustrates the advantages of such a system. The main problem is to know the concentration of the bulk mixture used for blending.

Dr. Hughes: You mean that NO mixtures at the ppm level would require an hour for conversion to NO_2*?*

Dr. J. Taylor: Yes. I remember a paper appearing in the Journal of the Air Pollution Control Association which gives a half-life of 350 minutes for 10 ppm of NO in air and 3500 minutes for a 1 ppm mixture. In other words, the NO problem is one of long term stability. For mixtures of NO in nitrogen, containing only traces of oxygen, one would also expect long term stability but surface effects of the cylinder are also important. In general, one prefers oxygen-free nitrogen for the bulk gas and cylinder pretreatment is also required. However, once a stable mixture has been obtained, its dynamic dilution to yield lower concentrations offers no serious problems.

Dr. Dravnieks: In the mercury generation system, do you have any problems with aerosol formation on condensation of the supersaturated gas? This is a problem in organic solvents, for example. I did not see a trap to prevent aerosol carry over.

Dr. J. Taylor: This is a potential problem which we considered. However, the stainless steel wool heat exchanger seems to eliminate the problem, since our measurements show the output concentrations to be those expected and aerosol would have been trapped by our collection system, if present.

Mr. Behringer: John, as you know, we are interested in toxic agents in the atmosphere. We have considered piezo-electric sensors and have discussed them with Dr. Guilbault. However, interference from smoke and dust on a battlefield would seem to be a major problem.

Dr. J. Taylor: It is possible that filters could be devised or two crystals could be used in a differential mode to cancel out such problems. However, we have no specific experience at present to share with you on such problems. I am sure you know of Guilbault and Scheide's work with pesticides. Some of this might have relation to your interests.

Mr. Behringer: Was this in the same concentration range?

Dr. J. Taylor: I believe so, or perhaps even lower concentrations. At any rate, I want to emphasize the versatility and simplicity of the technique. Actually, specificity seems to be the major problem.

Dr. Klier: Modern spectroscopy can analyze adsorbed films on surfaces and the instrumentation is becoming relatively inexpensive.

Dr. J. Taylor: My colleagues at NBS have investigated some of these, ESCA for example. However, I understand the techniques are more research tools than analytical methods at the present time. These techniques are very sensitive, hence the original surface must be very clean.

Dr. Klier: The problem of clean surfaces applies to the techniques you are using?

Dr. J. Taylor: That is true. One must always use a blank and correct for the background.

Dr. Klier: This applies to the piezo-electric crystal as well?

Dr. J. Taylor: Yes. In this technique one measures a change in frequency due to collection of the component of interest. The original condition of the crystal - the blank - does not bother you. But what causes the change in frequency on exposure to the air stream is critical.

Dr. Hughes: How easy is it to obtain a selective surface?

Dr. J. Taylor: Perhaps I have glossed over the problem. It's very difficult. It's the heart of the problem. Some of the ideas presented at this Roundtable may lead to new approaches to the selectivity problem.

Dr. Hughes: With reference to mercury, the surface may become insensitive with use.

Dr. J. Taylor: Yes. Grease or oil might be adsorbed on the surface to decrease the adsorptive area. In other cases, moisture effects may cause problems. Such things must certainly be considered and minimized if the detector is to be useful.

Dr. D. Taylor: John, I asked my original question about selectivity thinking about such things as TDI, fluorine, and chlorine. If one uses a collector for fluorine, for example, and hydrogen fluoride was also collected, the fluoride ion selective electrode would not be able to discriminate between them in the analytical step. Similarly, the Mercali procedure for TDI does not discriminate free amine which would be a positive interference.

Dr. J. Taylor: Very true. In fact, from other work we have done on the TDI system, I wonder how much free TDI really exists in air and whether exposure to TDI has ever been measured.

A METHOD OF COMPARING SOLID SORBENTS FOR SPECIFIC ADSORPTION OF VAPORS

by Gerry O. Wood

Los Alamos Scientific Laboratory, Los Alamos, New Mexico

Objectives

The objectives of my talk this morning are fourfold: 1) to describe a test method which has been developed in our laboratory over the past few years; 2) to suggest an empirical classification of adsorptions that have been observed; 3) to present data for benzene and carbon tetrachloride on several batches of charcoal; and 4) to discuss some possible applications of the data from this test method.

The problem which we have attacked can be expressed by the questions, "Which of several materials is best for adsorbing vapors of a certain compound? What is a quantitative comparison?" The compound might be selected as representative of a certain class of compounds (for example, aniline for the aromatic amines), or it might be itself the one of interest.

Experimental

The test apparatus we used to explore these questions is shown in Figure 1. It is basically a gas chromatograph with some modifications. The sample is introduced by one of two methods: 1) a gas sampling valve may be used for gaseous samples of fixed volume; or 2) the injector of the gas chromatograph can be used for syringe injection of gases, liquids, or solutions. The liquids are vaporized in the hot injector.

For solutions, a chromatographic column can be used to retard the solvent and other unwanted compounds while allowing the test compound to elute. A valve is also included in the system for optional use of such a column, and to bypass the column before unwanted compounds elute. The carrier gas then transports the sample from the valve through the sorbent tube into the detector. Any detector that is linear in the range of interest is acceptable. The detector signal is recorded on a chart and, if possible, simultaneously integrated. An electronic digital integrator is very useful for this purpose.

The sorbent tubes are 6 mm O.D. by 60 millimeters long standard-wall Pyrex tubes. They are packed with a chosen volume of the sorbents to be tested, held in place with glass wool plugs. A constant volume is used instead of a constant weight, since densities may vary greatly among the sorbents. We usually use 25 cm^3, which gives a 20-mm long section.

The first step for a test is to prepare a sorbent tube and equilibrate it in the apparatus at the test temperature. Air is purged with the carrier gas flow. The compound to be tested is then injected or sampled with the gas sampling valve. If necessary, the test compound is separated from other compounds present by column separation and by valve switching. The amount of sample injected must be sufficient to overload the sorbent. A sharp peak with tailing is usually observed when this is the case. When baseline is re-established, the injection of the same amount of the sample on the same sorbent section is repeated. With fresh sections of the same sorbent, additional pairs of injections are made with larger or smaller amounts of the compound.

Interpretation of Injection Data

The purpose of the duplicate injections on the same sorbent section is to determine the fraction of the first sample which was adsorbed and not subsequently desorbed. Let us call this process irreversible adsorption. The fraction irreversibly adsorbed is the difference of peak areas divided by the area of the second peak. This assumes that all irreversible sites (at the experimental temperature) were occupied during the first injection. Carrier gas flow rate may need to be adjusted to make this assumption valid.

An alternate treatment of the data is a graphical plot of peak area versus sample size. When this linear plot is extrapolated to zero area, the intercept corresponds to the amount of compound irreversibly adsorbed, and this calculation can be used to confirm results from the area difference calculation.

Adsorption isotherms for the reversible adsorption can be calculated from the shapes of the peaks (1,2). The reversible adsorption may be due to a second layer of molecules on the sorbent surface or to weaker adsorption sites. The total equilibrium adsorption isotherm is obtained by combining reversible and irreversible adsorption results. Also, from adsorption measurements and isotherms at two or more different temperatures, heats of adsorption can be calculated.

Adsorption of Benzene on Charcoal

As an example of the types of information which this test method will yield, let us consider some experiments with benzene on charcoal from an MSA Organic Vapor respirator cartridge. Figure 2 shows tracings of peaks from two consecutive 75-µl injections of benzene on a 0.25-cm^3 *section of charcoal at 25°C.*

Irreversible Adsorption

The difference in peak areas, which is shaded, represents the amount of benzene irreversibly adsorbed after the first injection. Subsequent injections would give us a repeat of this second peak to indicate that, indeed, we had occupied all irreversible sites.

Figure 3 shows peaks obtained from four injections of different volumes of benzene. Each injection was on a fresh section of charcoal. Note that the 20-μl injection was completely adsorbed and there was no signal at the detector. Where the peaks overlap (on the tails), an equilibrium condition exists between adsorption and desorption.

In Figure 4 the areas of these peaks and others are plotted against the amount of benzene injected in microliters. Extrapolations of the data at 25°C. and 100°C. give intercepts of 25-μl and 5.3-μl, respectively, as the amounts of benzene irreversibly adsorbed. By calculation of the area difference, we get a slightly higher value of 27-μl at 25°C.

Equilibrium Isotherms

Equilibrium adsorption isotherms derived from peak shapes are shown in Figure 5. The nonzero intercepts are due to the irreversible adsorption. For air sampling of benzene, the range of interest is up to 50 parts per million, which is 5 times the Threshold Limit Value. For respirator cartridge work the range of interest is up to a thousand parts per million. If an equilibrium condition exists at these concentrations, the adsorption will be predominantly what I have been calling irreversible adsorption up to the point where all the irreversible adsorption sites are occupied. This may be considered a characteristic of a good sorbent.

Heats of Adsorption

Heats of adsorption can be calculated from the difference in the adsorption isotherms at a given vapor concentration. In this case the heat of adsorption is 4.55 kcal/mole at zero parts per million, which would presumably correspond to the irreversible sites, and 3.15 kilocalories per mole at 1000 parts per million.

Irreversible Adsorption Capacities of Various Charcoals

Irreversible adsorption capacities for benzene and carbon tetrachloride at 25°C. on 0.25-cm^3 of several batches of charcoal are given in Table I. The benzene results, and the carbon tetrachloride results in parentheses, were obtained by the area difference method. Most of the carbon tetrachloride data was obtained by area extrapolation. Note the agreements of the two methods for carbon tetrachloride, adsorption on

Charcoals 3 and 5. Also, note the wide ranges of capacities. Charcoal Number 5 (Barnebey Cheney petroleum charcoal) has the highest capacity for benzenes; Charcoal Number 2 (Barnebey Cheney coconut shell charcoal) has the highest capacity for carbon tetrachloride. However, for adsorption of both these compounds, Charcoal Number 3 (MSA coconut shell charcoal) is probably the best compromise.

Dr. Teass: What is the weight of the charcoal that corresponds to a quarter of a cm^3*?*

Dr. Wood: Approximately 80 mg.

Data Applications

Screening

Four applications of data from this test method are listed in Table II. Sorbent screening for adsorption capacity is illustrated by the data that have been shown for benzene and carbon tetrachloride on the charcoals. This is not limited to charcoals. At the present we are testing a variety of more than 50 sorbents for methylamine capacity. We have found that for such varied sorbents as silica gel, alumina, charcoal, and silicone OV-210 both irreversible and reversible adsorption have been observed for methylamine.

Desorption Efficiencies and Migration

The calculation of heats of adsorption has already been discussed. A possible application of this type of data is correlation with thermal or chemical desorption efficiencies. Also the problem of sample migration from a front to a back-up section of a sampling tube should also be related to the heat of adsorption of that vapor on the sorbent.

Specifications

The third suggested application is the establishment of specifications for sorbents. Breakthrough times of sampling tube or respirator cartridges should be very much dependent on adsorption capacities and heat of adsorption. One batch of sorbent could be selected as a standard. The adsorption capacity, heat of adsorption and breakthrough times for certain compounds on this standard sorbent would be measured. Then it could be assumed that any batch of the sorbent with the same or greater adsorption capacity and heat of adsorption would have the same or greater breakthrough times if tested. The advantage is that breakthrough times are often much more difficult and time-consuming to measure.

Interference Effects

The final application to be suggested is testing for interference effects, especially from water vapor. It would be necessary in this case to use a detector that will respond to the test compound but not to the interference compound. For example, a flame ionization detector will not respond significantly to water vapor. The interference compound could be introduced at a constant concentration in the carrier gas or as an injected amount following injection of the test compound. Effects of its presence, or amount of interference on adsorption capacity, retention, and heat of adsorption could be measured. It is our intention to continue to explore such applications of this test method at the Los Alamos Scientific Laboratory, as we develop methods for the sampling and analysis of toxic vapors in air.

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2. *Gregg, S. J., and Stock, R., "Gas Chromatography 1958", D. H. Desty, ed., Butterworth's, London, 1958, p. 80.*

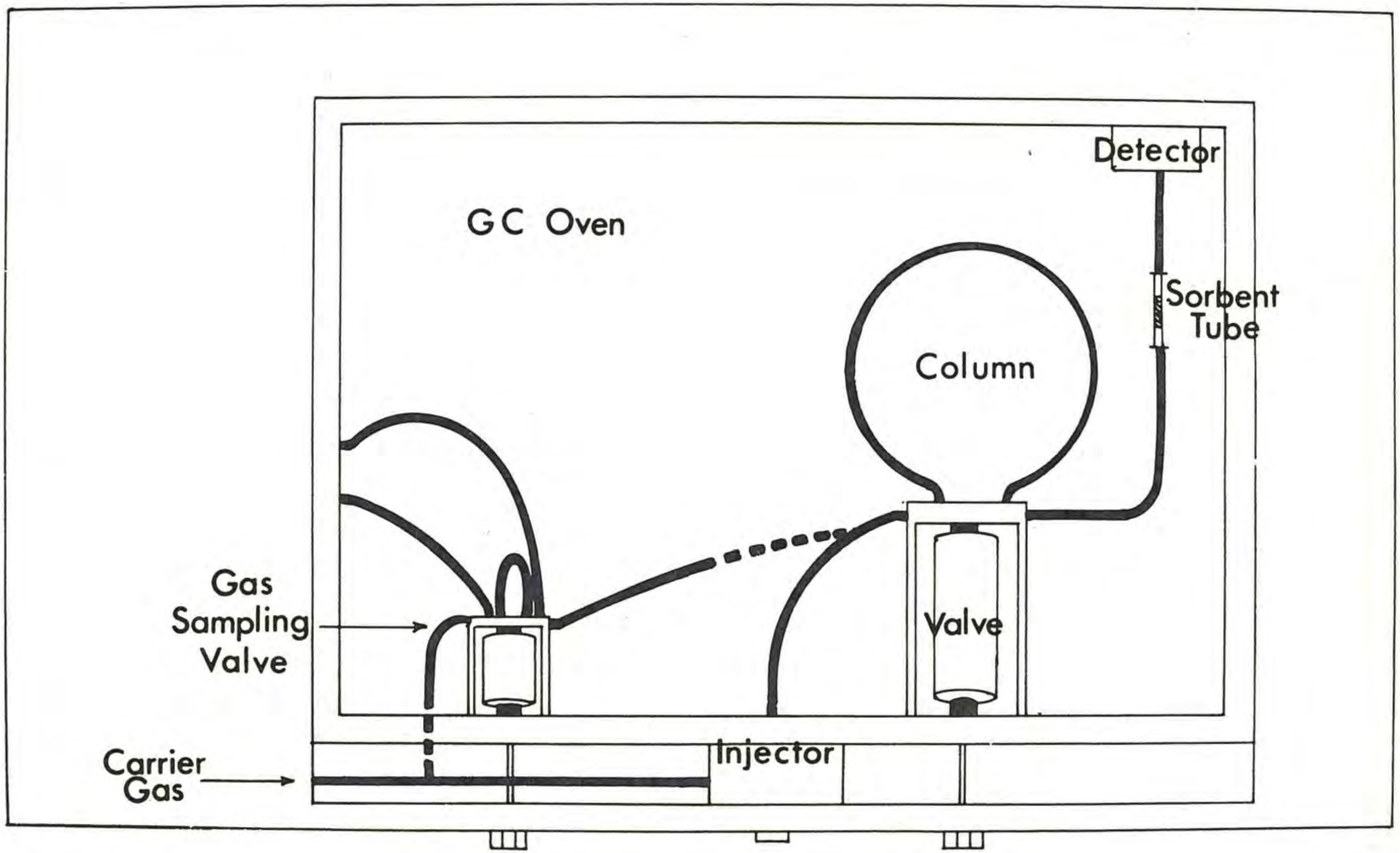

Figure 1. Apparatus for Testing and Comparing Solid Sorbents.

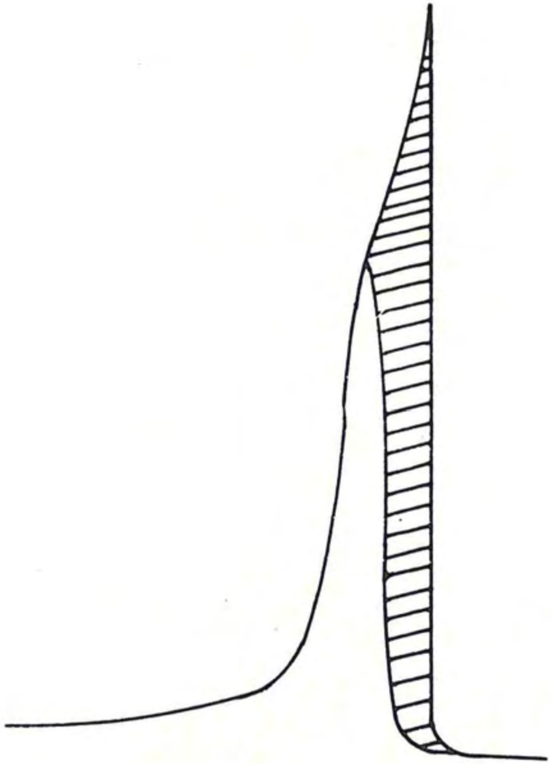

Figure 2. Peaks from Consecutive Injections of 75-µl Benzene on 0.25 cm^3 Charcoal.

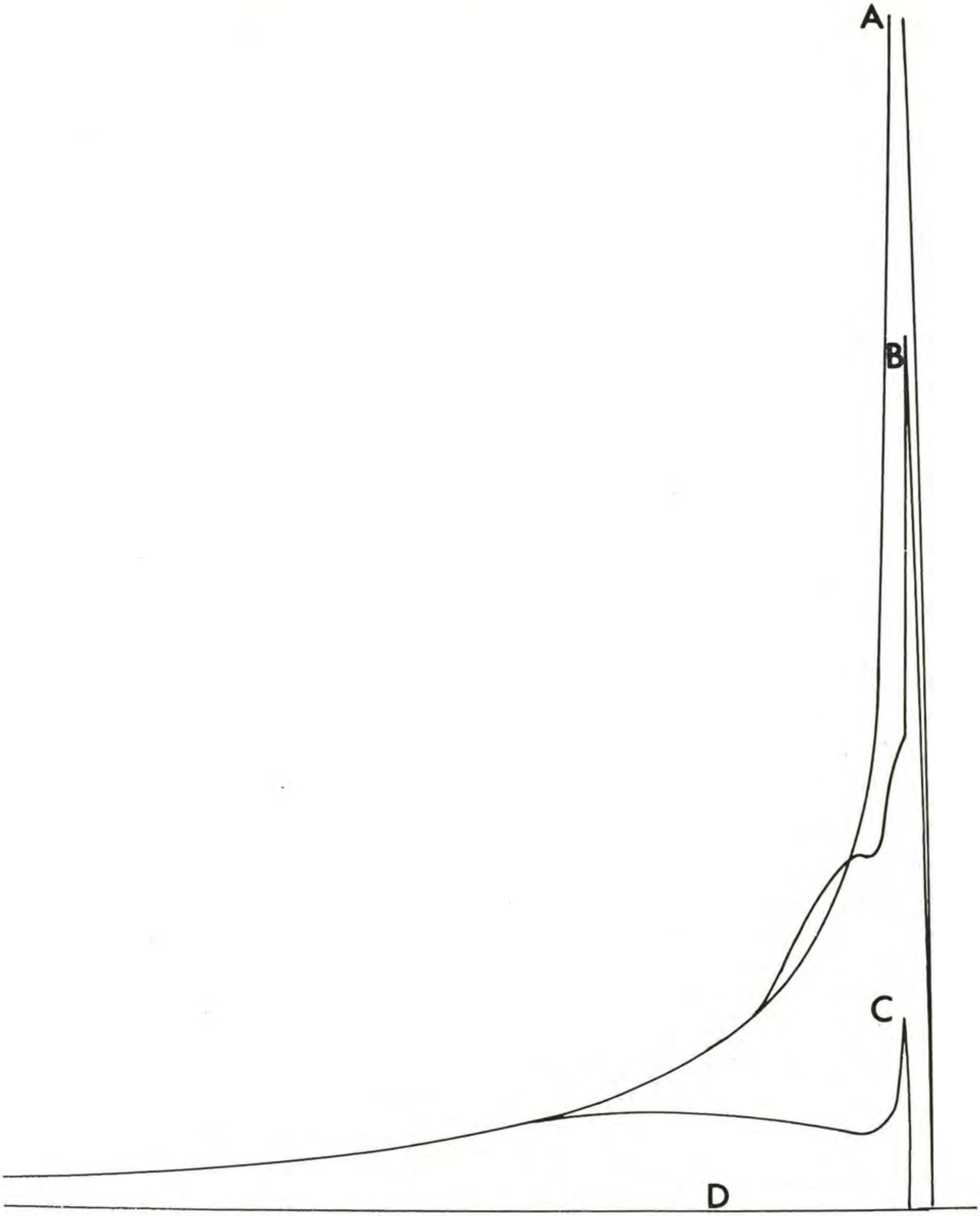

Figure 3. Peaks from Injections of Benzene onto 0.25 cm^3 Charcoal from an MSA Organic Vapor Cartridge Respirator.

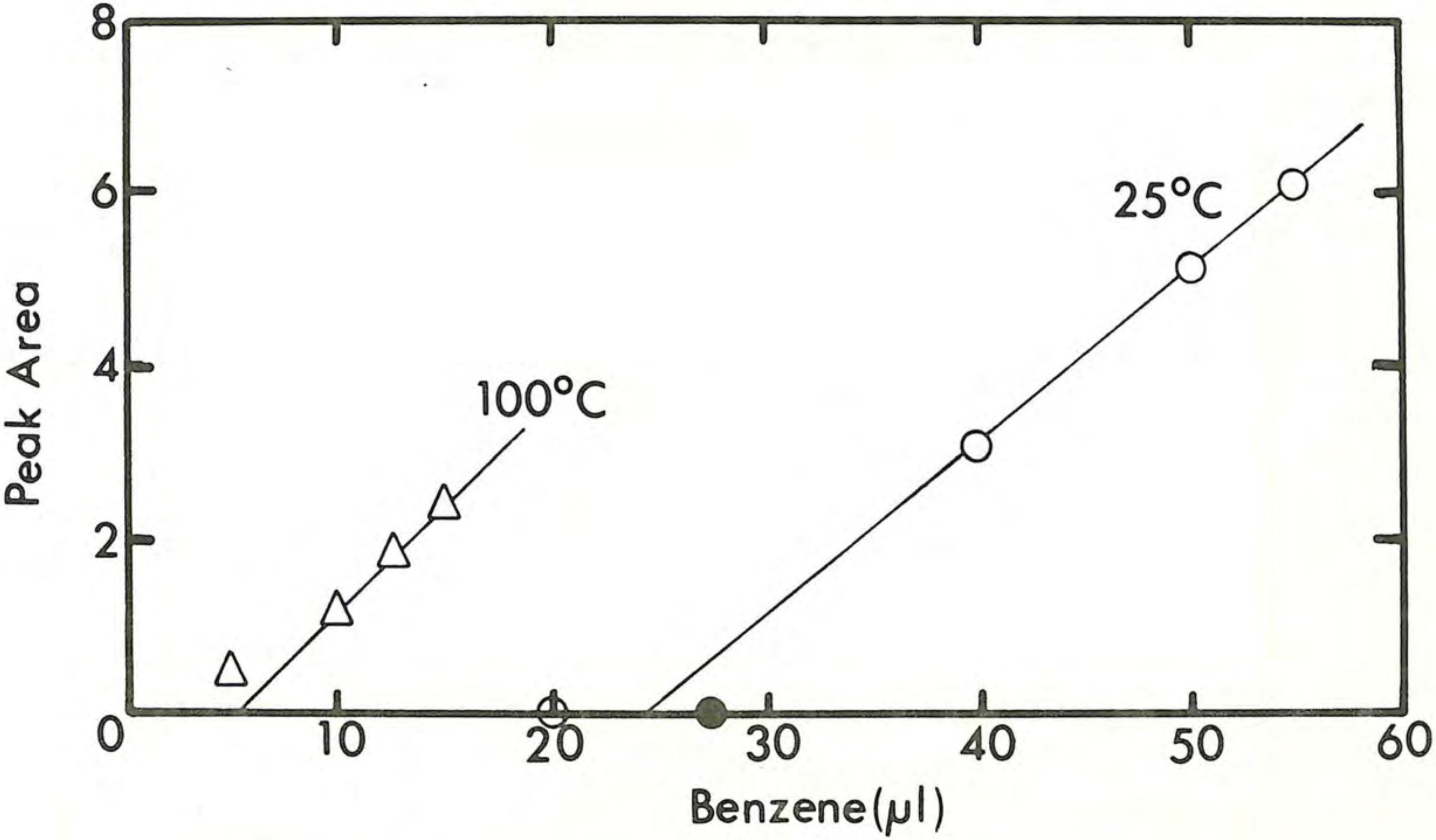

Figure 4. Plots and Extrapolations of Peak Areas from Benzene Injections onto Charcoal.

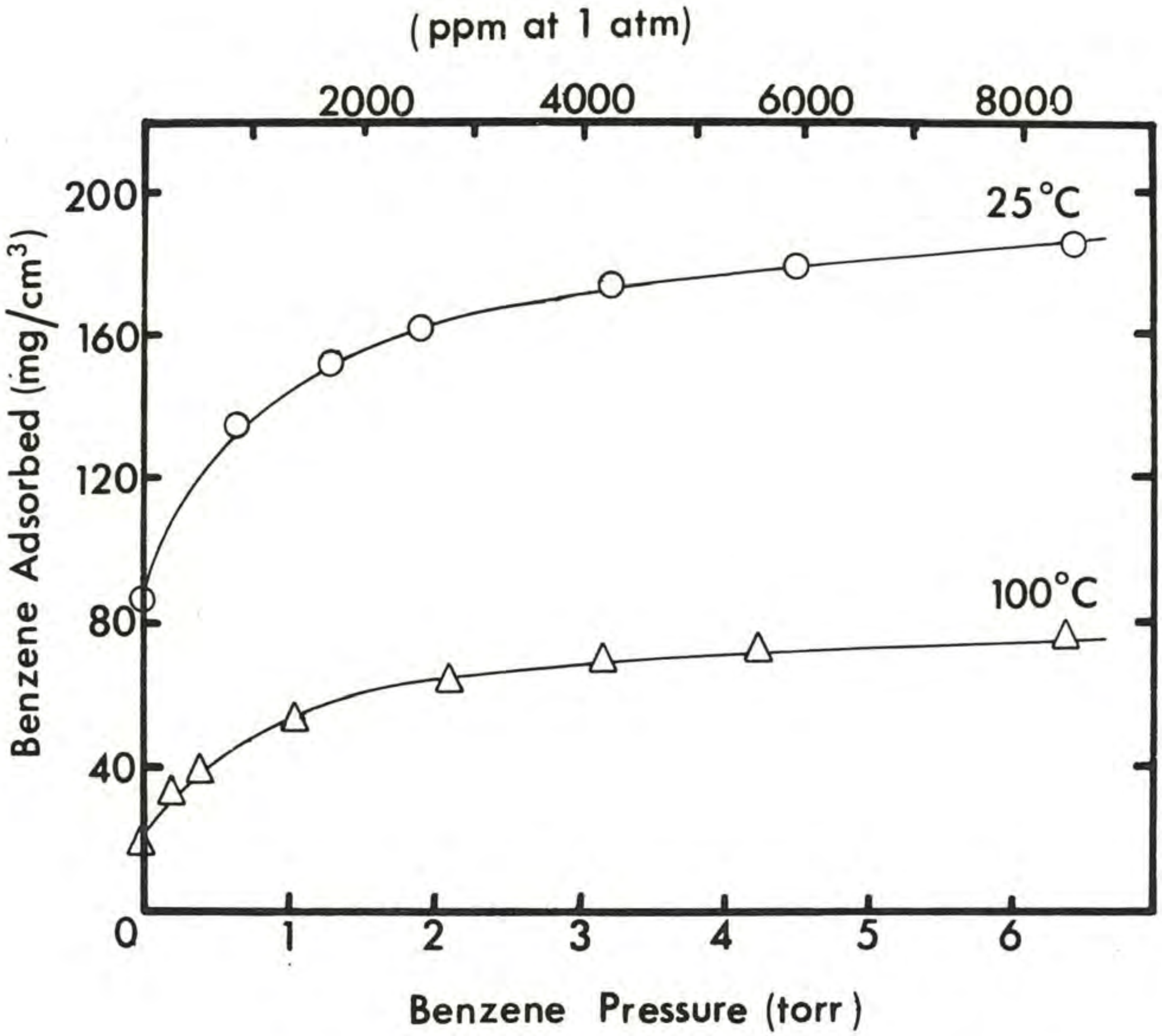

Figure 5. Equilibrium Adsorption Isotherms on Charcoal.

Table I. Irreversible Adsorption at 25°C.

Charcoal*	Benzene (mg)	CCl_4 (mg)
1	16.0 ± 0.5	46.9 ± 9.9
2	21.6 ± 1.2	64.9 ± 7.5
3	24.6 ± 0.3	54.2 ± 4.3 (53.6 ± 1.4)
4	16.4 ± 0.8	45.9 ± 2.7
5	26.0 ± 2.6	35.1 ± 7.2 (34.0 ± 0.5)
6	17.9 ± 0.8	33.8 ± 8.4

*0.25 cm^3 per sample

Table II. Applications

1. Sorbent screening for adsorption capacity
2. Heats of adsorption
3. Specifications for sorbents
4. Testing for interference effects

Discussion

Dr. Ballou: When you are calculating the heat of adsorption, this is normally the isosteric heat of adsorption, calculated from the isotherms at two different temperatures. This means you are comparing conditions for the same amount adsorbed on the same surface area. You are talking about comparing adsorption at the same vapor pressure. What does this lead to, or what type of heat of adsorption do you call this?

Dr. Wood: Well, I don't know. It is looking at it from the other side. However, I think it is a comparable number, and I think it's properly called the heat of adsorption. The only difference is that you are holding the vapor concentration constant, rather than the surface concentration constant.

Dr. Klier: I think this is legitimate, if you have a heat which is independent of surface coverage. Then, this is a legitimate method. You are reaching equilibrium at constant pressure. But, if the heat of adsorption does depend on surface coverage, then I think it would be possible to measure the isosteric case.

Dr. Wood: Right. This is an assumption that is in the calculations. It is also you might say, an average value that you get for surface coverage, and is only, perhaps, an empirical number. However, I think it is, in a sense, a heat of adsorption, and can be used as such.

Dr. Dravnieks: When you talk about irreversible adsorption, are you referring to your isothermal conditions?

Dr. Wood: Yes.

Dr. Dravnieks: Are you talking about adsorption so strong that carbon disulfide would not remove it?

Dr. Wood: No. I tried to find another term that would be better than "irreversible adsorption", but I didn't come up with one. It's not actually irreversibly adsorbed. If you heated it or eluted it, it would come off; but in this constant temperature, constant flow situation, it stays on there.

Dr. Dravnieks: It is more of a hysteresis effect?

Dr. Wood: Yes.

Dr. Dravieks: This heat of adsorption - I don't know exactly how it compares - but four kcal/mole doesn't seem enough heat of adsorption for an irreversible process.

Dr. Wood: Right.

Dr. Dravnieks: It seems that some of the adsorption is very easily reversed. It is low-grade physical adsorption, really.

Dr. Wood: As long as the temperature was 25°C., an amount stayed on the adsorbent. We followed the tailing peak until it came to the baseline, but if you raised the temperature it would come off. It is not that strong an adsorption.

Dr. Teass: Did you ever try to analyze the tubes after you did the experiment to see if your analytical results for the amount that remained on the tube agreed with your calculated amounts?

Dr. Wood: No, we haven't done this yet. I think that would be a good test.

Dr. Klier: What is the heat of condensation of benzene compared to this heat of adsorption? Which one is larger?

Dr. Wood: The heat of condensation of benzene is 8.1 kcal/mole at 25°C.

Dr. Dravnieks: The heat of adsorption is usually about twice the heat of condensation.

Dr. Klier: That is not a rule, but it should always be above.

Dr. Ballou: Does your term "irreversible" mean that the amount remaining adsorbed is in equilibrium with the vapor?

Dr. Wood: No, it means that a certain amount of material goes on to the adsorbent and does not come off under the conditions of the test.

Dr. Ballou: Do you mean the conditions of volume flow of the gas stream?

Dr. Wood: No, just the conditions of temperature.

Dr. Hughes: Doesn't the signal for the effluent stream fall to the baseline?

Mr. O'Keeffe: The signal comes down to zero concentration.

Dr. Teass: Does the "irreversibly" adsorbed material bleed out?

Dr. Wood: No, this would reduce the amount adsorbed, which is related to the capacity of the adsorbent. We are concerned with capacity rather than with the rate of going to the vapor phase from the adsorbent. The rate might be more related to the heat of adsorption than to the capacity.

Dr. Hughes: I don't think you are looking at the experiment long enough. I believe the apparently irreversibly adsorbed material would desorb if the experiment continued several days or months, because four kcal at room temperature is a very small heat of adsorption. I think the word "irreversible" is an unfortunate choice, as four kcal/mole does not denote an irreversible process.

What is the initial time for the experiment in which you adsorbed only 10-mg or µl or a very small amount, and saw nothing coming through in the effluent?

Dr. Wood: Usually an hour.

Dr. Hughes: Is that with a gas flow through the adsorber?

Dr. Wood: Yes, but a real difference is observed between the first and second injections. Something is going on the first time that is not going on the second time.

Dr. Mieure: If you do this with a porous polymer sorbent, you will find, depending on what material you use and the temperature, that you will later get a peak from the eluting material that you called irreversible adsorbed, just as in conventional chromatography. I don't know if this will be the case with the sorbents you are studying but it is overserved with porous polymer beads.

Dr. Wood: We haven't observed it. We have also used a porous polymer, and haven't observed any late signal.

Dr. Mieure: It takes a long time, hours for most compounds.

Dr. Teass: Do you mean that, after you inject, you get a peak of excess material coming off first, and, later, another peak?

Dr. Mieure: Yes, just as if you had injected onto a chromatographic column, which is what I consider these.

Dr. D. Taylor: Is this what you call ghosting?

Dr. Mieure: Yes.

Dr. Lonnes: This is the same effect we were trying to observe with porous polymers at ambient temperature. The retention times were inordinately long; so one way to shorten them was to go to very short columns. We did this with some of the Chromosorbs and Porapaks, and they did the same thing. We got an initial peak, which actually exceeded the capacity of the material in the column. It looked something like this - up, down. Later another bulge came out and we plotted the log of the volume desorbed vs. the reciprocal of absolute temperature and it fell on a linear plot.

Dr. Hughes: Is your effluent stream going directly into your detector? You are effectively putting 50 microliters into it.

Dr. Wood: Yes, we are using thermal conductivity detectors because we are at such high concentrations.

Dr. Hughes: Would you comment on your peak that did get through in a short period of time?

Dr. Wood: The retention time of the peak varies, depending on how good the adsorbent is. We haven't calculated sorbent isotherms for the reversible part of the adsorption, because the calculation is tedious and may not be necessary. The retention times vary, the shapes vary, and we have observed multiple peaks. However, the differences are on the same time scale, less than an hour, and usually overlapping.

Mr. Crable: Thank you, Gerry.

*HIGH VOLUME SORBENT SAMPLING FOR PESTICIDE ANALYSIS**

by Perry Lonnes

Interpoll Inc., St. Paul, Minnesota

Introduction

The primary objective of this study was to develop a low energy dry sampling system for the efficient collection of low concentrations of alkyl phophonates in the atmosphere, such that sufficient material could be collected in a short time for an infrared or mass spectrometric analysis. Inherent in this objective was the requirement that the sample also be easily recoverable once collected. The feasibility of accomplishing this objective had been verified theoretically, however, the success hinged on finding a collection substrate which on the one hand was strongly retentive, but not so retentive that the collected compounds could not be quantitatively recovered. Moreover, the collection substrate had to have the necessary physical characteristics such that it could be made with a low enough resistance to flow to meet the energy requirements.

The use of filter-like high volume adsorbent systems is not a new concept. Special filters fabricated from activated charcoal with a cellulosic binder have been successfully employed to adsorb iodine from the air to study radioactive iodine concentrations near nuclear reactors (1). A similar procedure was developed to collect ultra-micro concentrations of hydrogen fluoride in the air using a cellulose acetate filter impregnated with sodium formate (2).

Experimental

In the development of vapor sampling media or devices, it is necessary to evaluate the collection efficiency of these devices on a routine basis. This is normally accomplished by drawing gas with a known vapor concentration through the collection device at a known rate for a given length of time. The amount of material collected may be obtained by determining the amount of material collected in or on the sampling media or device, or by measuring the vapor concentration

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**This work was conducted by the author while he was at Environmental Research Corporation, St. Paul, Minnesota.*

in the downstream gas stream. The collection efficiency (ε) may then be calculated from one of the two expressions given below:

$$\varepsilon_a = \frac{100\ (C_1^i - C_2^i)}{C_1^i} \qquad [1]$$

$$\varepsilon_b = \frac{100\ m_i}{C_1^i\ Q\ \Delta t} \qquad [2]$$

where:

m_i = *amount of test compound i collected on (in) the sampling media or device*

C_1^i = *inlet vapor concentration of compound i*

C_2^i = *outlet vapor concentration of compound i*

Q = *volumetric flow of gas through sampler*

Δt = *sample time*

The use of equation (2) to calculate the collection efficiency is based on the assumption that all of the collected test compound is recovered for analysis. Thus, it can be seen that ε_b *is dependent on the degree of recovery affected in the analytical procedure. For the purposes of this work, it was desired to separate these two factors and study them independently. Thus, the first expression* (ε_a) *was used primarily to calculate collection efficiency.*

The degree of recovery (R) was defined for this study as that fraction or percentage of the test compound recovered from a test substrate and is merely the ratio of ε_b *and* ε_a*:*

$$R = \frac{100\,\varepsilon_b}{\varepsilon_a} = \frac{100 m_i}{Q\ \Delta t\ (C_1^i - C_2^i)} \qquad [3]$$

Gas chromatography was selected as the primary analytical technique on the basis of sensitivity, accuracy, and ease and speed of analysis. Originally it was planned to use an 8-port two-loop gas sampling valve (GSV) in the carrier gas flow system of a GC/AFID, such that the up and downstream vapor concentrations of test compound, which in this case was dimethyl methylphosphonate (DMMP), could be intermittently monitored by merely changing the position of the GSV and a three-port selector valve connecting the GSV to the up and downstream sampling *ports. This was not possible, however, as considerable or quantitative loss of DMMP occurred in all attempts to transport low concentrations of DMMP vapor samples. Stainless steel, glass and Teflon tubing transport lines gave equally bad results.*

Gas-tight glass and Teflon barrel syringes were then tested, however, similar wall losses were also encountered with these devices. An interesting observation was made during the evaluation of the syringes, when it was noted that the height of the corresponding GC peak correlated well with the number of times the syringe was flushed in the sample gas. Further investigation showed that practically all of the DMMP was adsorbed on the internal walls of the stainless steel needle and was not being injected.

Subsequently, a technique was worked out, the results of which correlated reasonably well with the results obtained using bubblers and a total phosphorous colorimetric method of analysis. The best correllation was obtained by withdrawing a sample with a Teflon barrel gas-tight syringe without flushing. The outside of the needle was then wiped clean of any DMMP with a tissue wetted with clean ethanol. When five samples were analyzed in this manner, the mean value of the GC analyses agreed quite well with the wet chemical technique.

The inconvenience of the above procedure, together with long-term changes observed in the AFID response after a number of air samples were injected, relegated this technique to a standby technique when instantaneous concentrations were required. A more convenient and reliable procedure was developed using ethyl alcohol as an absorbing agent.

In this procedure, a bubbler such as those used to sample nitrogen dioxide in the atmosphere was utilized. About 20-28 cc of absolute ethyl alcohol was placed in the bubbler and the bubbler placed in an ice-bath to minimize volatilization of alcohol. Inlet flow rates from 1-4 ℓpm could be employed with this procedure. The efficiency of adsorbtion was checked by placing a second bubbler in series with the first impinger and analyzing the contents of both bubblers by gas chromatography. Calculations showed the efficiency to be approximately 98 percent and independent of flow in this range.

The final experimental set-up used for evaluation of all collection substances is shown in Figure 1. A polycarbonate Nucleopore 47-mm filter holder was loaded with the collection substrate to be tested and attached to the bubbler by means of a piece of Teflon tubing. Approximately 25 cc of ethyl alcohol, the exact volume depending on the flow rate, was placed in the bubbler and the desired flow rate set by means of the working rotameter.

The appropriate setting on the working rotameter was established before the test by means of a secondary standard rotameter. This was accomplished by attaching the secondary standard rotameter to the inlet of the system by substituting an in-line filter holder for the

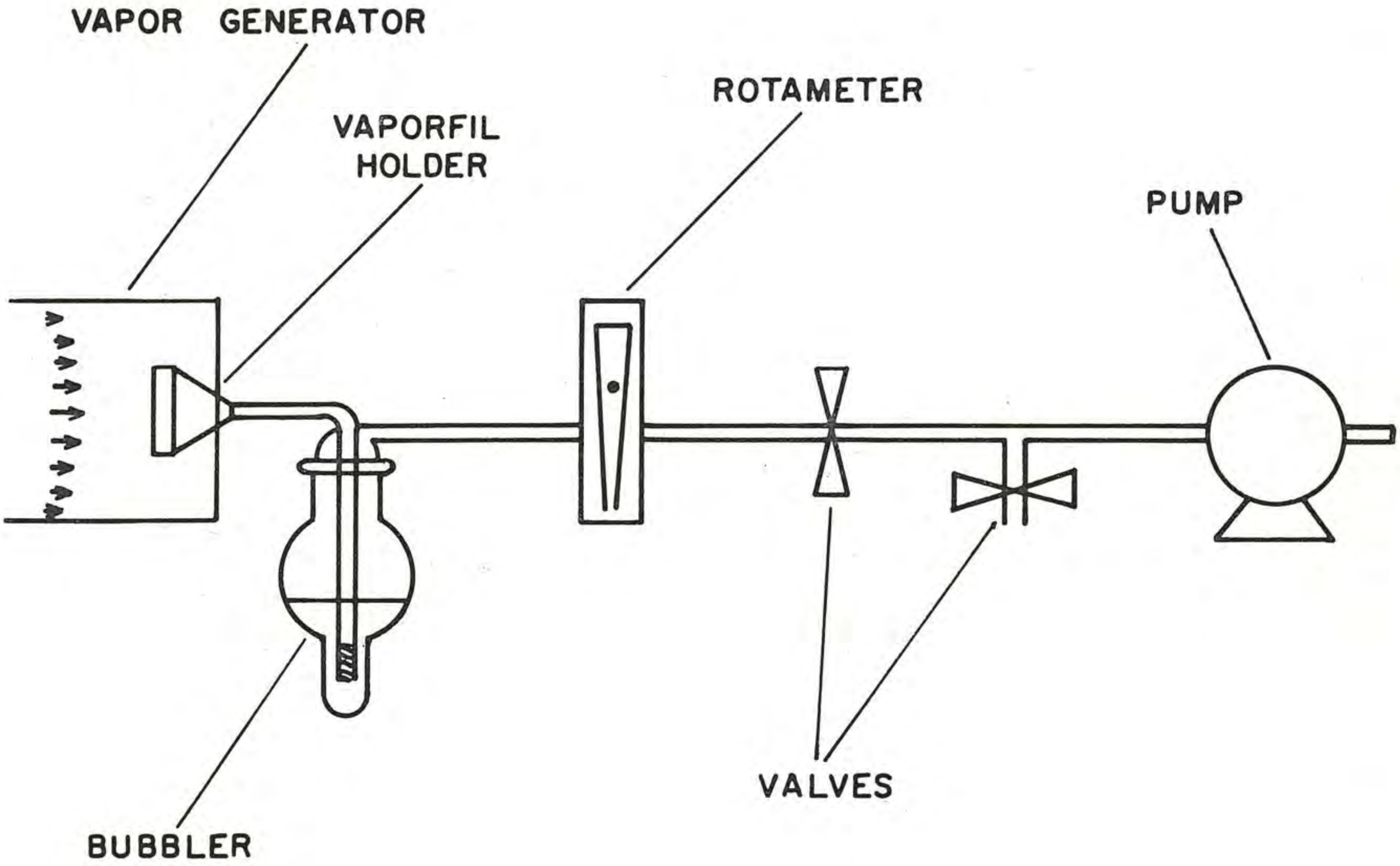

Figure 1. Final Experimental Set-Up Used for Evaluation of All Collection Substrates.

open-face filter holder. The pump was then energized and the flow adjusted until the desired flow as read from the secondary standard rotameter was obtained. The reading on the working rotameter was then noted and utilized to reproduce the correct flow during the experiment. This procedure was required, as the vapor volume of ethyl alcohol and the reduced pressure at the working rotameter result in a considerable correction factor.

The inlet vapor concentration was measured by means of another bubbler which was placed directly in the vapor generator outlet during the experiment. A critical orifice was employed to control the flow in this system, since it was not necessary to vary the flow from test to test for this determination. The exact inlet flow was also measured daily with the secondary standard rotameter to ensure against leaks and reduced pressure at the critical orifice.

Development and Evaluation

Collecting Agents

Three different approaches were originally conceived to include impregnated or coated filter systems, chemically bonded substrate filter systems similar to the so-called brushes in gas chromatography and porous polymer filter systems. These three collecting agents have one common requirement in that they all need some type of support matrix. Fluidization has been employed; however, it was felt that the electrical properties of some of these collecting materials were not suited for use in a fluidized bed.

It was decided that the simplest means of testing the suitability of these collecting agents was to apply the agents to the surface of a filter. A review of the commercially available filters was made and those filters selected which were considered to have some potential as a support matrix.

Filter Tests

A list of these filters is shown in Table 1. Since support effects are well documented in gas chromatography, each of the filters was tested to determine whether it might have some affinity for the test compound DMMP, and whether the test compound could be recovered from the filter once collected. Examination of the results show the Gelman glass fiber Type A to have the highest affinity for DMMP and also the best recoverability. The Millipore nylon filter proved to be the most inert of the various filtration media. The results of these tests point out the need for extreme caution in the selection and preparation of filters used ahead of gas sampling devices for particulate removal when dealing with polar substances at the sub-ppm level.

Table I: Collection Efficiencies of Untreated Filter Media and Recoverability

Filter Type	*Pore Size (μm)*	C_1 *(μg/ℓ)*	ε_a *(%)*	*R (%)*
Glass	*Micro-Fiber*	*0.63*	*46.8*	*94*
Cellulose esters	*5*	*0.48*	*18*	*43*
PVC	*2*	*0.50*	*7.8*	*51*
Teflon	*5-10*	*0.48*	*6.4*	*0*
Polypropylene	*10*	*0.59*	*5.5*	*72*
Nylon	*7*	*0.30*	*0*	*-*

The face velocity was 5 cm/sec and the DMMP concentration ranged from 60-120 ppb.

C_1 = *inlet vapor concentration*
ε_a = *Collection efficiency from equation [1]*
R = *degree of recovery from equation [3]*

Stationary Phase Tests

Gas-liquid stationary phases were investigated in the early stages of the study. Gas-liquid stationary phases are by definition high molecular weight liquids which exhibit differing partition coefficients for different compounds. A large number of GLC phases are known with widely varying chemical and physical properties. It was proposed to investigate a representative group of these compounds and determine whether one could be found which exhibited a high affinity for organophosphorus compounds at room temperature.

The search for such a substrate was complicated by the fact that most GLC phases exhibit considerably different retention properties at room temperature than at the temperatures employed for gas chromatography. The lower temperature actually favors partitioning or solution of vapors in the GLC phases, but most of the phases are solids or gases at room temperature, and the high viscosities of these generally amorphous solids greatly reduced mass transfer. Moreover, the mechanism of attraction or retention often changes from partitioning to adsorption at the freezing point. Thus, it was not possible to merely examine gas chromatographic retention data as a means of finding the best GLC phases. It was necessary to actually prepare filters impregnated with the prospective GLC phase and perform a collection efficiency test.

A representative group of GLC phases was assembled based on known gas chromatographic properties to include: SE 30, Apiezon L, Igepal CO-880, diethylene glycol succinate (DEGS), and Carbowax 20M.

Filter Preparation

Filters were prepared by dissolving the polymer in an appropriate solvent and wetting the filters with an aliquot of the solution. The solvent was then allowed to evaporate. The filter loading was determined by weight change. The initial collection efficiency tests were conducted on glass fiber filters coated with Igepal, DEGS, Apiezon L., SE-30 and Carbowax 20M.

Collection Efficiency Tests

The efficiency tests were conducted by drawing a known volume of test gas through a treated filter at a face velocity of about 5 cm/sec. The results of these initial tests are presented in Table 2. Apiezon L, Igepal and SE-30 exhibited low collection efficiency for DMMP. Carbowax 20 M exhibited varying collection efficiencies for the three different filter matrices upon which it was coated. DEGS, on the other hand, exhibited rather uniform collection efficiencies for the Teflon and glass matrices. As previously shown, the untreated filters exhibited a collection efficiency of 6.4, 5.5 and 46.8 percent for Teflon, polypropylene and glass fiber filters, respectively. Of the five GC phases

Table II. Results of DMMP Vapor Collection Efficiency Determinations of Filters Coated with Liquid GC Phases

Coating	Filter Type	L (%)	U (cm/sec)	C (μg/ℓ)	ε_a (%)
Apiezon L	g	22	5	0.63	11.5
SE-30	g	27	5	0.43	15.2
Igepal	g	21	5	0.48	15.5
Carbowax 20M	†	3.8	5	0.60	1.3
Carbowax 20M	P	7.0	5	0.60	11.3
Carbowax 20M	g	25	5	0.60	28.4
DEGS	†	2.0	5	0.63	32.7
DEGS	g	18.9	5	0.63	34.7
DEGS	g	18.0	5	0.48	38.8

g = glass
p = polypropylene
† = Teflon

tested, only DEGS appeared to have any potential for sampling purposes. The other substrates apparently act as coating agents which make the active sites on the untreated filters unavailable for interaction with the DMMP test molecules.

Dependence on Loading

The results obtained for DEGS indicated a complex dependence of collection efficiency on loading. In order to check this, a series of filters with different loadings of DEGS were prepared. The filters were coated by immersing them in acetone solutions of DEGS of varying concentrations and then volatilizing the acetone. The loadings were determined by the weight changes of the filters.

The filters were then tested to determine their collection efficiency for DMMP vapor. The results of these tests are shown in Figure 2. The efficiency of the coated glass fiber filters for DMMP falls off almost linearly for loadings less than 1 percent. The efficiency then plateaus between 2 and 4 percent, increases sharply after 5 percent, and finally falls off gradually after 7 percent. The results are best explained if DEGS is regarded as a relatively nonadsorptive material which covers the active glass surfaces, rendering them unavailable for interaction with the DMMP. Thus, as the loading is increased from zero to 1 percent, an ever increasing portion of the active glass surface is covered until all the surface is coated with a uniform film. As the loading is increased from 1 to 4 percent, the thickness of the layer merely increases.

At a loading of about 5 percent, the efficiency begins to recover. This must be due to some phenomenon which begins to occur in this loading region such as "puddling". Puddling is a well known phenomenon observed in the preparation of GLC packings. Once the loading exceeds some critical value, the coating no longer forms an evenly distributed film on the surface of the substrate, but forms little puddles of pure liquid at the points of contact of the support particles. If this occurs, bare regions of glass surface would once again be available for interaction with DMMP and higher efficiencies would be expected. To investigate whether such a phenomenon actually was occurring, microscope slides were dipped in various concentrations of DEGS in acetone and then set aside until the acetone had volatilized. For low concentrations, a uniform coating was obtained; however, at higher concentrations a speckled coating was obtained. Close examination of the coating showed regions of very large deposits of DEGS located adjacent to apparently bare regions.

At a loading of 7 percent, the efficiency once again shows a gradual decrease. This is probably attributable to the decrease in void space between the individual glass fibers, the effect of which would be to increase the actual linear velocity of air through the interstitial

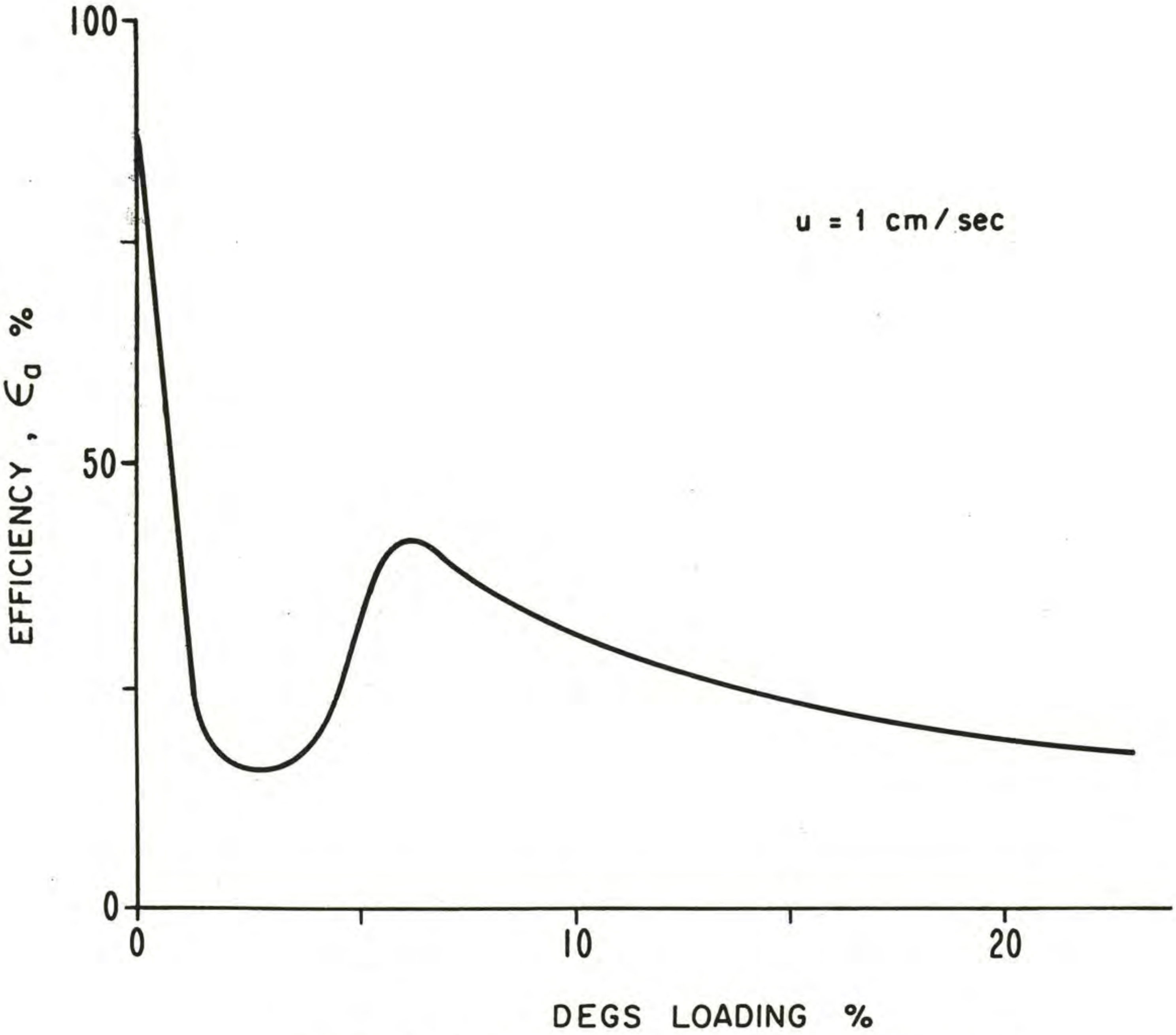

Figure 2. Collection Efficiency of Filters for DMMP Vapor.

area and reduce the mass transfer coefficient of DMMP. Thermal conditioning of the DEGS coated filters at 180°C under a nitrogen atmosphere decreased the collection efficiencies even more.

Breakthrough Determination

In order to determine whether breakthrough was occurring to any extent, the collection efficiency of a 5 percent DEGS filter for DMMP was tested at various times during a 30 minute sampling period. The "instantaneous" collection efficiencies were measured by drawing a 1 cc air sample upstream and downstream of the filter and analyzing them gas chromatographically. These tests indicated that DEGS has a low capacity for DMMP at room temperature and that its collection efficiency falls off very rapidly with time. Other substrates concurrently being tested exhibited much greater potential and further testing of DEGS was suspended. Several filters were also prepared for testing, where the GLC stationary phase was chemically bonded to the glass fiber filter instead of merely being applied as a coating. The procedure for preparing such substrates was time-consuming and efficiency tests of the resulting filters were so low that it was concluded that they did not warrant further testing.

Collection Efficiency of Untreated Glass Fiber Filters

On the basis of results from preliminary tests designed to shed light on the role that various filter matrices might play, it was concluded that the collection efficiency exhibited by the untreated glass fiber filter warranted further investigation. A series of tests were conducted to ascertain the relationship between collection efficiency, face velocity, and time sampled. This was accomplished by placing a clean glass fiber filter in the outlet of the vapor generator, establishing the desired face velocity, and measuring the concentration of uncollected DMMP vapor in the gas downstream of the filter after varying time intervals. The downstream concentration (C_2) *was determined by withdrawing a 1 cc sample with a gastight syringe and analyzing the DMMP vapor concentration in it gas chromatographically.*

Examination of Figure 3 shows that the collection efficiency of untreated glass fiber filters decreased with increasing linear velocity and time. Breakthrough occurred at 5 and 10 cm/sec, rather quickly, and shows the futility of sampling longer than 15 minutes at a face velocity of 10 cm/sec with the unmodified glass fiber substrate. An additional series of tests over a longer time period was conducted. The results of these tests are shown in Figure 4. It is apparent that the glass fiber filter is an effective collecting agent for DMMP if the linear velocity is 1 cm/sec or less.

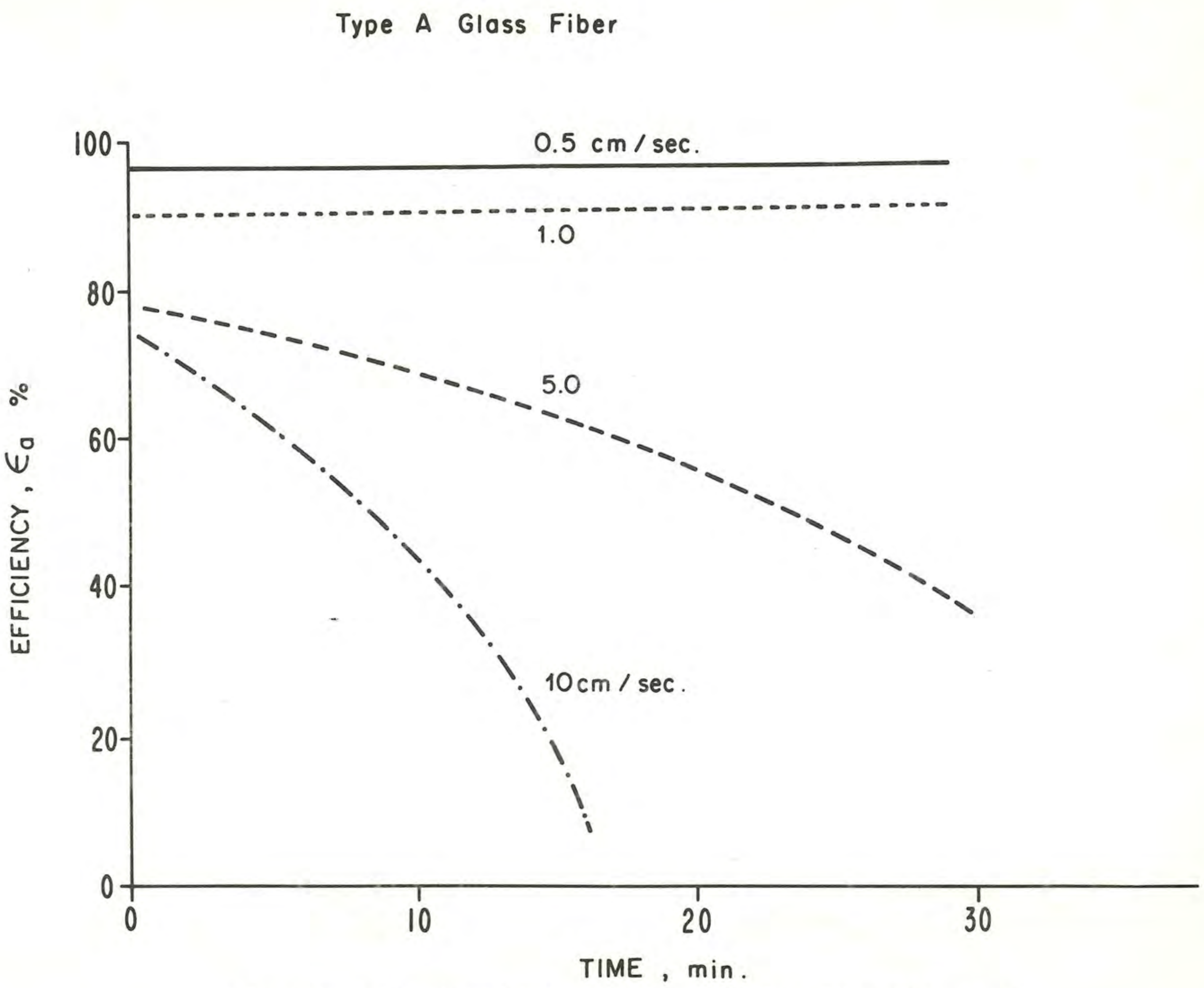

Figure 3. Collection Efficiency of Untreated Glass Fiber Filters as a Function of Linear Velocity and Time.

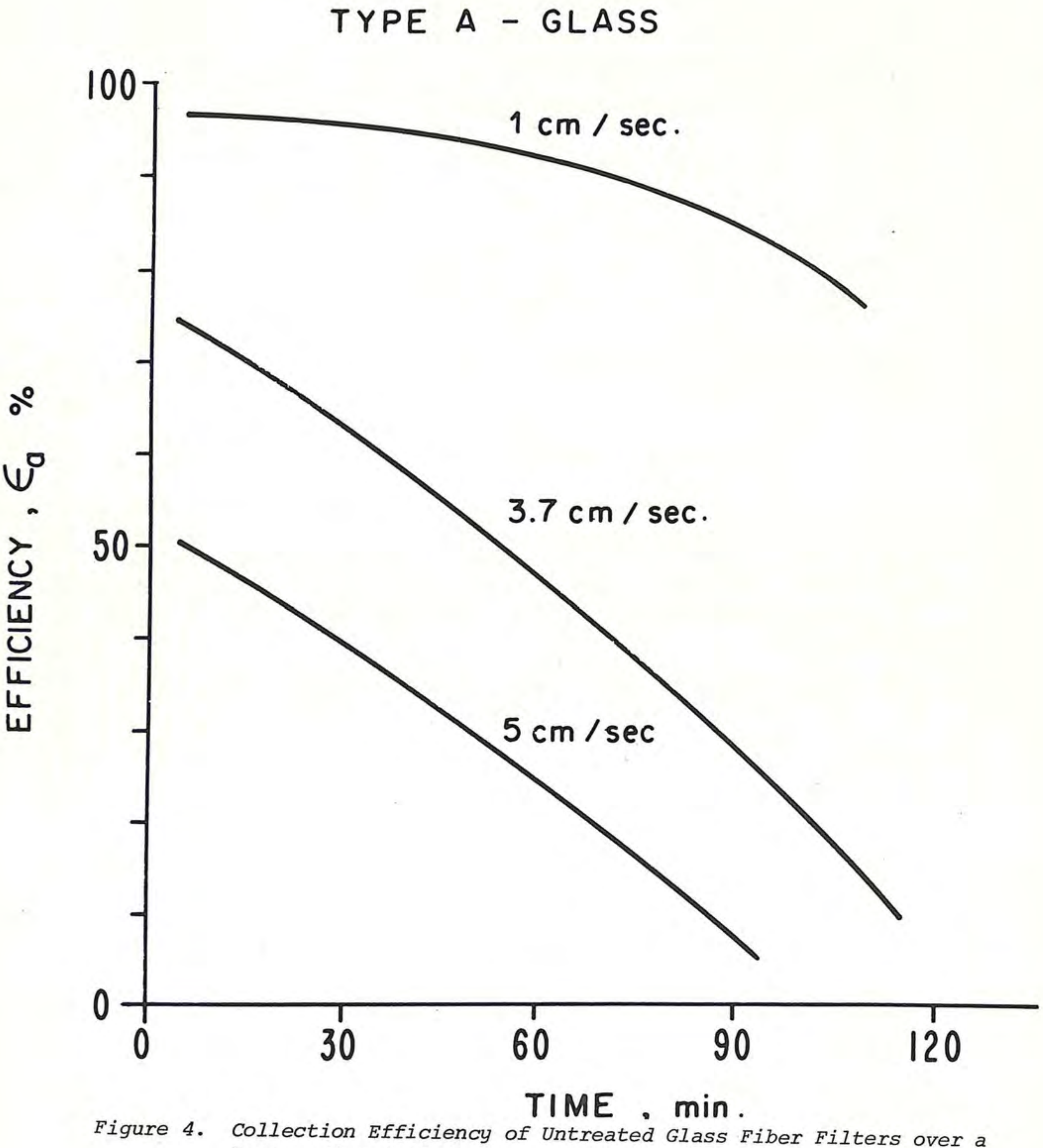

Figure 4. Collection Efficiency of Untreated Glass Fiber Filters over a Longer Time Period.

Glass fiber filters are available commercially with or without binders. Since the binder influences the physical properties of the filter, it was speculated that the addition of a binder would also influence the adsorptive properties of the filter. Previous tests were carried out using Gelman Type A filters which contain no binder system. Gelman, however, also manufactures a Type E filter which contains an acrylic binder. Identical samples of both types of filters were tested and the addition of the binder resulted in a reduction of collection efficiency for the first 30 minutes from 92 to 34 percent. The low efficiency of Type E filters suggest that the organic binder is blocking active sites on the glass fibers. This is not surprising in light of the results obtained with other organic polymers which have also reduced collection efficiency.

A review of all of the collection efficiency tests performed with the glass fiber filters together with a literature review of the surface structure of glass surfaces indicated that certain chemical properties of the glass surface might play a role in the attraction exhibited by glass filters for DMMP.

Glass surfaces contain numerous silanol groups. The silanol group is polar and has been found to be an active site for interaction with polar molecules (3).

Effect of Blocking of Silanol Groups

The role of silanol groups in the adsorption of DMMP was verified by chemically blocking the available silanol groups so they could not participate in hydrogen bonding. This is readily accomplished in the case of gas chromatographic supports by trimethyl silylating the support; i.e., substituting trimethyl silyl groups for active protons in the silanol groups.

Glass fibers can be trimethyl silylated in a similar manner and trimethyl silylated glass wool is presently available commercially. Such a filter would be expected to exhibit a considerably reduced collection efficiency for DMMP, if the silanol group actually played an important role in adsorption.

Silanization of a Type A glass fiber filter was accomplished by immersing a glass fiber filter in a 10 percent (v/v) solution of hexamethyldisilazane for 1-1/2 hours and then allowing the filter to air dry.

A drop of water failed to wet the silanized surface, indicating that a significant change in surface polarity had occurred. The collection efficiency of the silanized filter was then measured and found to be 39 percent at a linear velocity of 1 cm/sec, a reduction of approximately 50 percent.

The reaction of silica surfaces with methyl red has also been used as a test of the number of silanol groups per unit area. When a portion of the above-described silanized filter was tested with a benzene solution of methyl red, a slight positive result was obtained. Apparently *complete silanization did not occur and the observed residual collection efficiency for DMMP is probably due to the presence of unreacted silanol groups. It is also possible that some other sites which are not readily trimethyl-silylated are responsible for the residual activity exhibited by the fiber for DMMP.*

When heated, a glass surface can loose essential water to form siloxane bridges. These siloxane bridges are slow to rehydrate and due to the loss of sites for hydrogen bonding, the surfaces exhibit reduced adsorption for polar molecules. Gelman glass fiber filters are heat-treated at 900°F during manufacture (4). It was speculated that it should be possible to increase the collection efficiency of the heat-treated glass fibers by hydrolyzing these surface siloxane bridges to restore the silanol groups.

Regeneration of Silanol Groups

A series of tests was performed to verify this hypothesis. In the first test, a glass fiber filter was merely treated with 1M NaOH for ten minutes and washed with distilled water until the washes were neutral. The collection efficiency of this filter was essentially unchanged from the untreated filter. However, when a filter was treated for two hours with 1M sodium hydroxide solution, the collection efficiency increased significantly to 97 percent. See Figure 5. Additional filters were treated with 5M and 10M sodium hydroxide solutions for two-hour periods. Filters treated at these higher concentrations showed a decrease in collection efficiency to 82 and 85 percent, respectively. In the case of the prolonged exposures to concentrations of 5M and 10M alkali, serious etching of the glass surface occurred with concomitant loss of fiber surface. The increased efficiency observed for the filter treated with 1M alkali solution indicated that further activation of the glass fiber surface might be possible by an optimization study of alkali concentration and reaction time; however, this proved not to be the case.

Adsorption on Inorganic Salts

The adsorption of organophosphorus pesticides on simple inorganic salts has also been reported. Potassium nitrate, for example, has been shown to adsorb Vapona (5). The adsorption potential of inorganic surfaces for organophosphorus vapors was further substantiated by the adsorption losses encountered in this work with the test compound DMMP on glass and metal surfaces. Three different inorganic salts were originally selected and tested to determine their collection efficiency for DMMP. The results of these tests indicated that the affinity of the salt for water might be paralleled by its affinity for polar compounds such as DMMP. A list of a series of salts with differing affinities for water has been published by Kolthoff and Sandell (6).

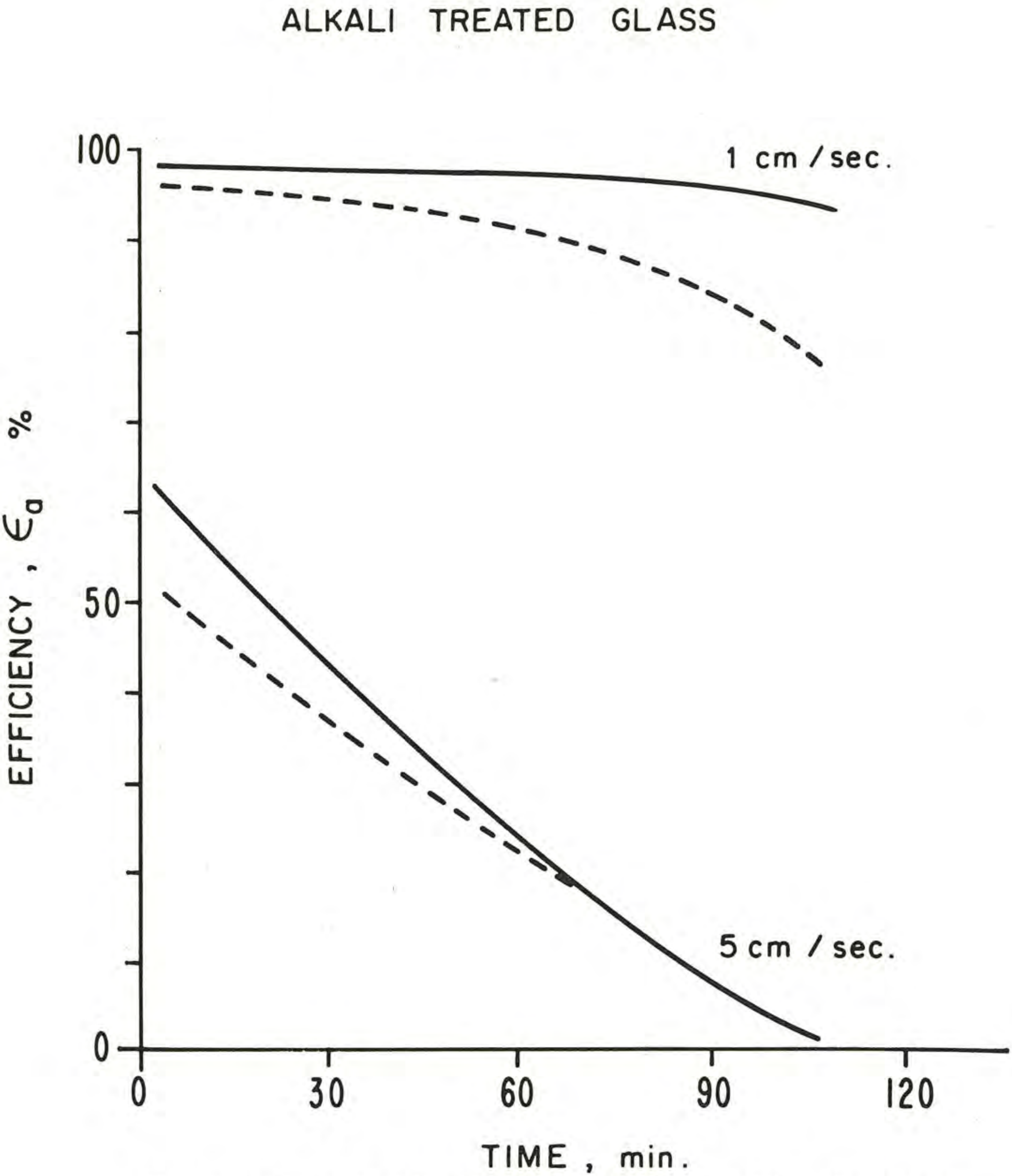

Figure 5. Change in Collection Efficiency of Glass Fiber Filters with Alkaline Etching.

The salts are ranked by the relative vapor tension exerted by mixtures of solid salts with saturated solutions of the salts. Salts which have low affinities for water do not appreciably reduce the vapor pressure of the system from that exhibited by pure water and thus have relative vapor tensions approaching one. Five salts of widely varying affinity for moisture were selected from this list and Type A glass fiber filters impregnated by immersing the filters in 13 mg/cm^3 aqueous solutions of the salts. The filters were obtained by drying in an oven at 110°C., cooling and weighing. The loadings of the filters were all about 10 percent dry salt.

The filters prepared in the above-described manner were then moisture-equilibrated with room air and tested to determine their collection efficiency for DMMP. The results of these tests together with the relative vapor tensions of the mixtures of solids with their saturated solutions in water are shown in Table 3.

Negative Correlation of Vapor Pressure and Collection Efficiency

Examination of these results indicated a negative correlation between the relative vapor pressure of saturated solutions of the salts and DMMP collection efficiency. The correlation coefficient for the data pairs was calculated and found to be -0.89. Thus, it appeared that those salts which have high affinities for water also exhibited high affinity for DMMP. It cannot be postulated from the above results whether the increased affinity results from the salt itself or the water associated with the salt in the form of a hydrate. The above results do, however, indicate that the collection efficiency of Gelman Type A glass fiber filters may be enhanced by the addition of some hygroscopic salt such as calcium chloride. Thus, several additional tests were conducted using calcium chloride to establish whether similarly high efficiencies were obtainable at higher linear velocities and also the effect of loading on collection efficiency.

Effect of Loading on Collection Efficiency

The first test was conducted in an identical manner to the earlier collection efficiency test of the calcium chloride impregnated filter, except that the linear velocity was changed from 1 cm/sec to 5 cm/sec. The 30-minute collection efficiency was almost 94 percent. On the basis of these encouraging results, a series of determinations were performed to ascertain the effect of loading on collection efficiency. The results of those tests are shown in Figure 5. The efficiency increases linearly for low concentrations, and after the surface is completely coated, the efficiency begins to decrease due to decreased porosity which results in reduced mass transfer. The efficiency attained a maximum of 98.9 percent at a loading of 2 percent.

Attempts to reproduce several points on the curve shown in Figure 6, however, gave inconsistent results and the available data appear to

Table III. collection Efficiency of Salt Impregnated Filters (u=1 cm/sec; C_1=0.15 μg/l)

Salt	Relative Vapor Pressure*	Collection Efficiency (%)
$CaBr_2$	0.15	91
$CaC\ell_2$	0.26	95
NH_4NO_3	0.57	90
Na_2SO_4	0.78	85
KNO_3	0.94	84

**Relative vapor pressure of mixtures of the solid salts with their saturated solutions in water at 30°C.*

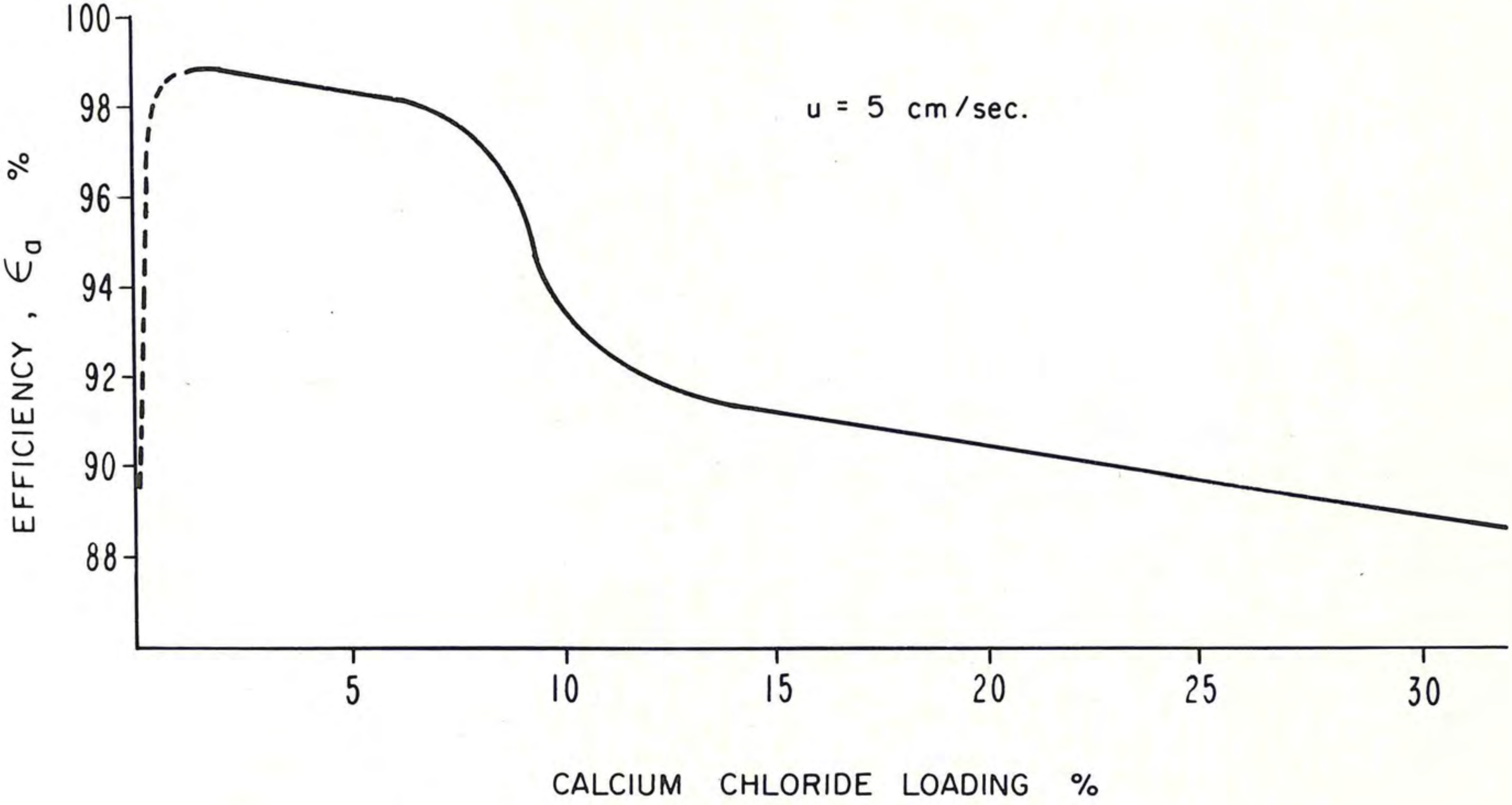

Figure 6. Effect of Loading on Collection Efficiency.

indicate some dependence on ambient relative humidity. Because of the experimental difficulties in generating large volumes of known DMMP vapor concentrations with given relative humidities, conclusive data were not obtainable.

Effect of Time on Collection Efficiency

A closer examination of the collection efficiency as a function of time, however, obviated the need for answering the above question, as the collection efficiency dropped off sharply after the first half hour. See Figure 7.

Preliminary collection efficiency tests of these materials were performed using two different preparation techniques. The first method was extremely crude and was designed merely to establish whether Chromosorb 102 exhibited enough potential to warrant further investigation. A mortar and pestle were used to grind 50/80 mesh Chromosorb 102 into a finer powder to increase the surface area to mass ratio. The resulting powder was then lightly pressed into a Teflon filter (Teflon was used to minimize the effect of the matrix). The resulting filter was then tested and the 30-minute average collection efficiency was found to be 43.5%. Visual inspection of the filter prepared by the above technique indicated that the distribution of porous polymer particles on the Teflon matrix was far from uniform.

On the basis of the above observation, a second method of supporting a porous polymer substrate (Porapak R) in a matrix was tested. Glass fiber filters were macerated in water in a blender. Porapak R (50/80 mesh) was added to the above mixture and mixed briefly. The resulting admixture was then poured onto a sintered glass frit and the water was removed by a mild vacuum. The resulting mat was dried at 100°C. before testing. This filter gave a collection efficiency for DMMP of 59.1 percent. Visual inspection of the filter mat indicated slightly more uniform distribution of substrate than that obtained with the first method, but it was felt that additional improvement was still required.

The initial collection efficiency results obtained with the crudely prepared porous polymer collecting substrates were promising. Previous results using Chromosorb 102 and Porapak R were not comparable, however, since the filters were not prepared in exactly the same manner.

A number of additional filters were prepared in this manner using a standardized technique so that the collection potential of the two different copolymers and several other similar polymers could be compared and the effect of higher linear velocities and sampling times on collection efficiency could be evaluated. Briefly summarized, these tests showed that Porapak R was best suited for collecting DMMP and established on a firm basis the need for a better means of preparing filter systems with higher and more uniform loadings.

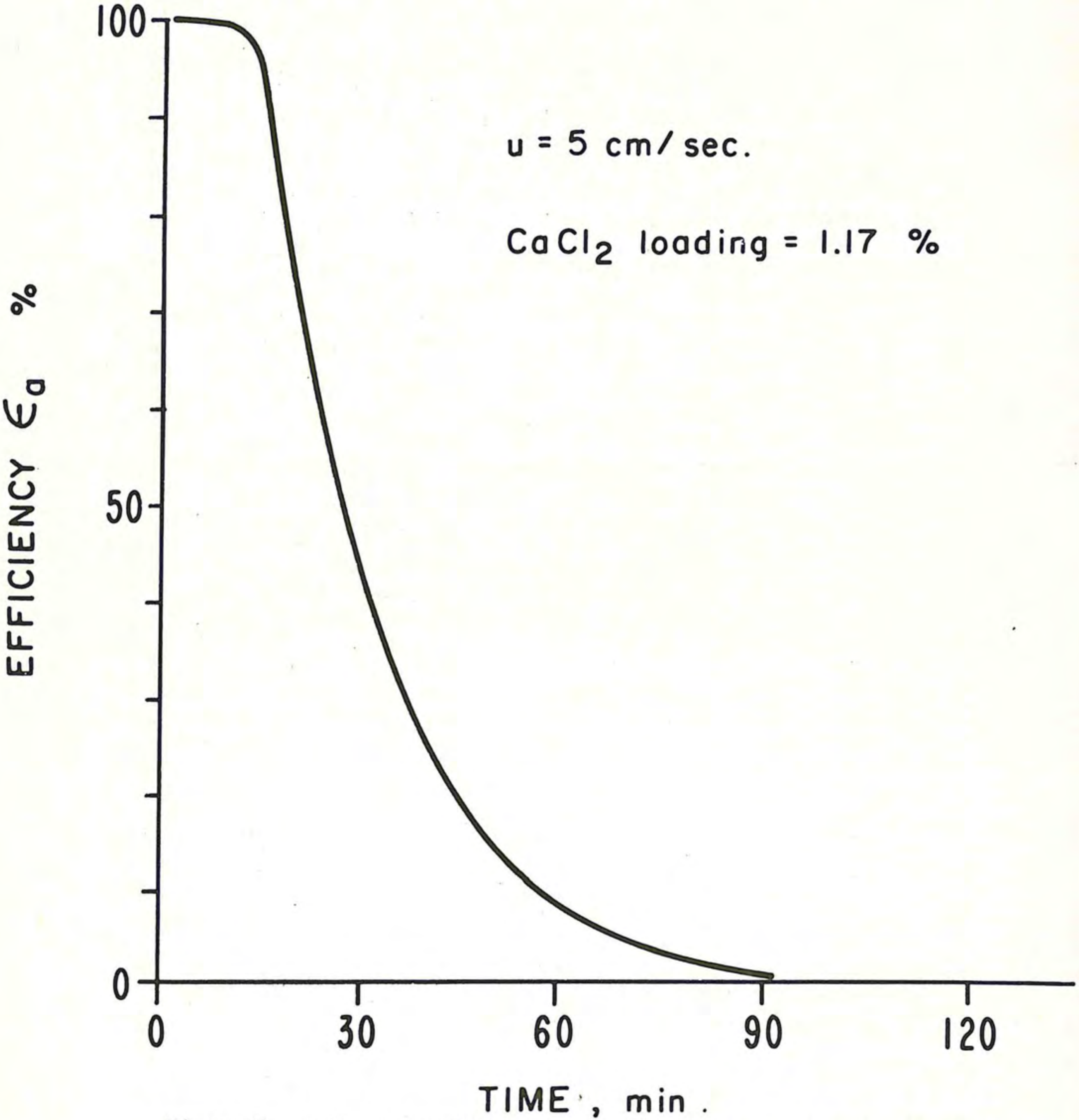

Figure 7. Collection Efficiency of Glass Fiber Filter as a Function of Time.

Thus, an effort was made to develop a procedure to prepare porous polymer filters. Filters is a misnomer for these substrates, since the sampling mechanism is not filtration but adsorption; thus, they will be referred to as vaporfils hereafter. These filters should be strong enough to withstand the handling which would normally be encountered in field sampling applications, and on the other hand, have a sufficient amount of porous polymer to provide the high collection efficiency required.

Consequently, an attempt was made to develop a technique for in situ synthesis of microspheroids of porous polymers so that a homogeneous concentration of similarly sized beads in a glass matrix might be obtained. These attempts, however, proved to be futile. Filters with high loadings exhibited extremely poor flow characteristics. Filters with low loadings and favorable flow characteristics exhibited poor collection efficiencies.

In situ polymerization was then dropped in favor of a slurry technique. In this method, an alcoholic slurry of porous polymer and bulk glass fiber is first prepared and a filter mat is then laid down by depositing the solid components in the form of a mat on a porous or sintered surface which serves to remove the liquid by means of a vacuum applied to the other side. The filter is then placed in a vacuum oven and activated at 120°C. This removes any residual alcohol. The first filter prepared in this manner was 50% glass fiber and 50% Porapak R. A collection efficiency test indicated that this type of "formed" filter exhibited far superior collection efficiency to the original Type A glass fiber filter and the filters where the copolymer was synthesized in situ as is apparent in Figure 8. A number of parameters, however, remained to be investigated to determine their effect on collection efficiency to include composition, test compound concentration, air flow direction, milling, drying or activation procedure, linear velocity and sample recovery.

On the basis of the strong dependency on linear velocity previously observed for other substrate collection efficiencies, a series of efficiency determinations were performed at 5 and 13.6 cm/sec to establish whether a similar dependency existed for the formed porous polymer vaporfils. These tests were carried out with DMMP at a vapor concentration of 36 ppb. The formed filters used in this test were prepared in the manner described above and were activated in a vacuum oven to remove any residual traces of ethanol. Sampling was carried out with the sample gas flow through the medium in the same direction as deposition during the preparation of the vaporfil. The results of the tests are shown graphically in Figure 9 and confirm that a strong dependency between ε_a and u exists for the formed filters. At the higher linear velocity, the collection efficiency falls off very rapidly in the second hour of sampling.

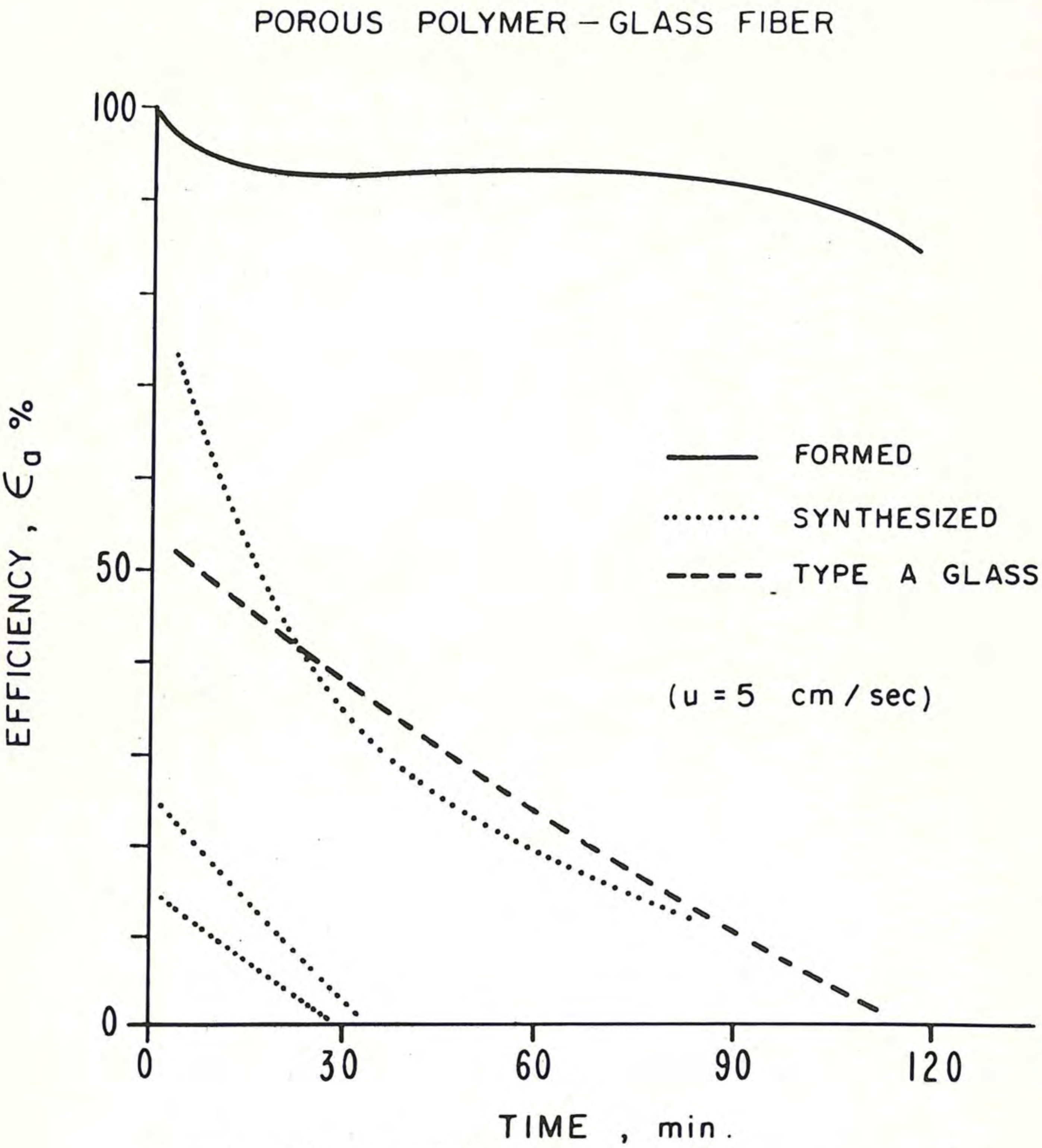

Figure 8. Collection Efficiency of Formed Filter as a Function of Time.

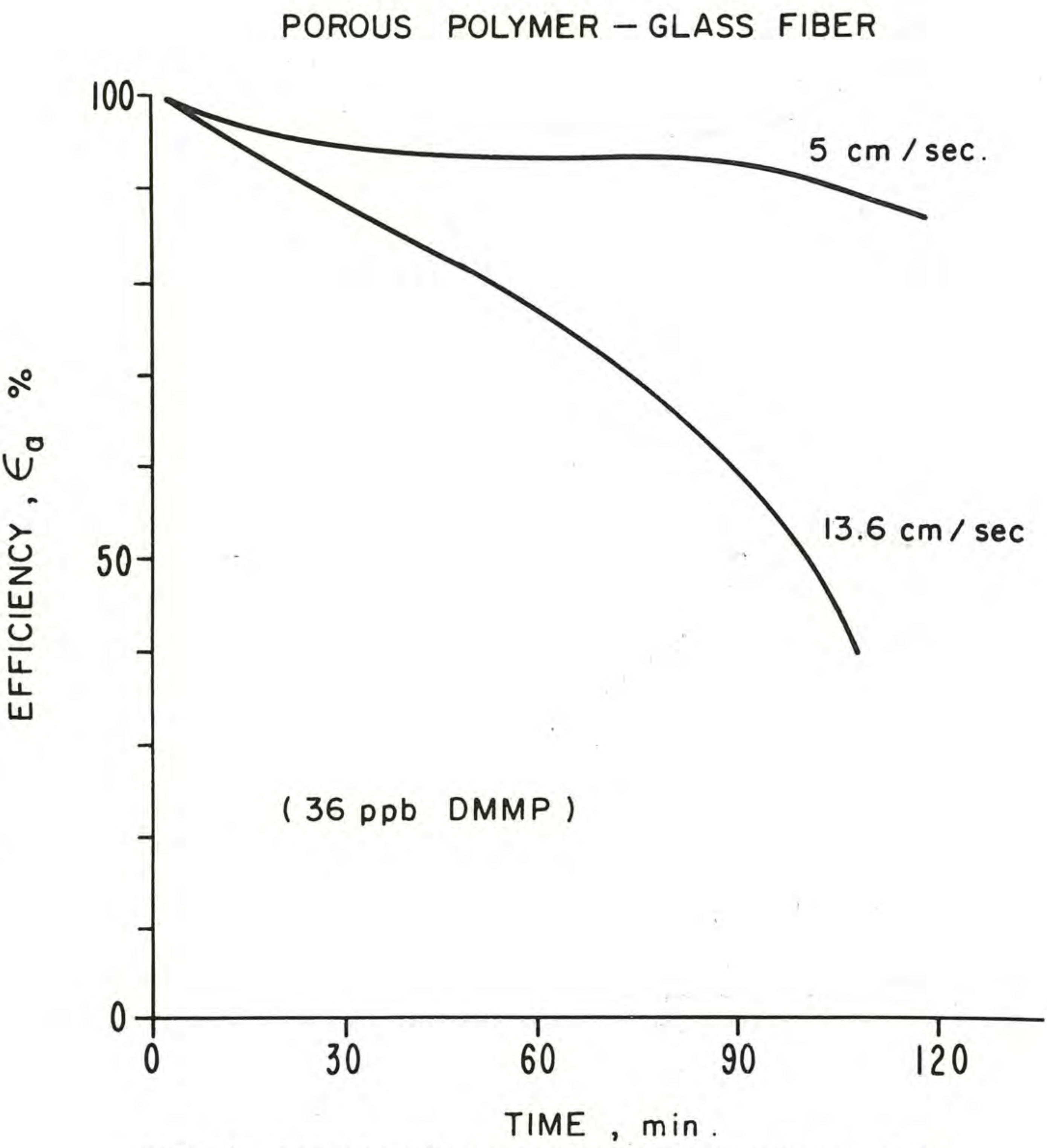

Figure 9. Collection Efficiency of Formed Filter at Various Linear Velocities.

During the formulation of the preparation procedure, it was decided, on the basis of previous experience with porous polymers, that they would require some type of treatment to remove residual adsorbed alcohol from the Porapak R. This was accomplished by evacuating the oven-dried vaporfils in a vacuum oven for one hour at 120°C.

The necessity of this step in the procedure was established in a series of tests at a linear velocity of 13.6 cm/sec with filters prepared in an analogous manner to those described above, except that some were not "activated" by the heating and evacuation procedure. It was found that activation had little effect on the collection efficiency when the simulant vapor concentration was high (36 ppb DMMP). At low concentrations (1 ppb), however, omission of the activation step resulted in a considerable reduction in collection efficiency (see Figures 10 and 11). Since the expected concentrations in this application were expected to be in the sub-ppb range, the necessity of activation is apparent and this step must be retained in the preparation procedure.

After the initial experiments with the formed 50 percent porous polymer-50 percent glass fiber substrates were completed, a question arose as to the effect of the direction of sample flow through the vaporfil. In preliminary experiments, the sample flow had always been in the same direction that the porous particles and the glass fibers were deposited from the slurry during preparation. Subsequent tests, the results of which are shown in Figure 12, indicated that a significantly higher collection efficiency is obtainable when the direction of flow is reversed as was the case for Curve A. Apparently, the overall mass transfer of DMMP vapor molecules is optimized when they encounter the large porous polymer particles and glass fiber first followed by finer and finer particles.

Next a series of tests was conducted to determine the effect of the particle sizes of the polymer. The results of these tests did not indicate any statistically significant difference over the particle size range from 20 μm up to 120 mesh.

The final parameter investigated was the mass ratio of Porapak R to glass fiber. The composition of the filters used for the experiments up to this point was 50 percent by mass of porous polymer and 50 percent glass fiber. This ratio was arbitrarily chosen as a good starting point with the knowledge that the optimum mass ratio would have to be determined experimentally after certain other parameters were investigated.

This was accomplished by preparing a series of samples (used milled polymer) in which the mass ratio of polymer to glass fiber was varied. The filters were then successively tested for efficiency with a vapor

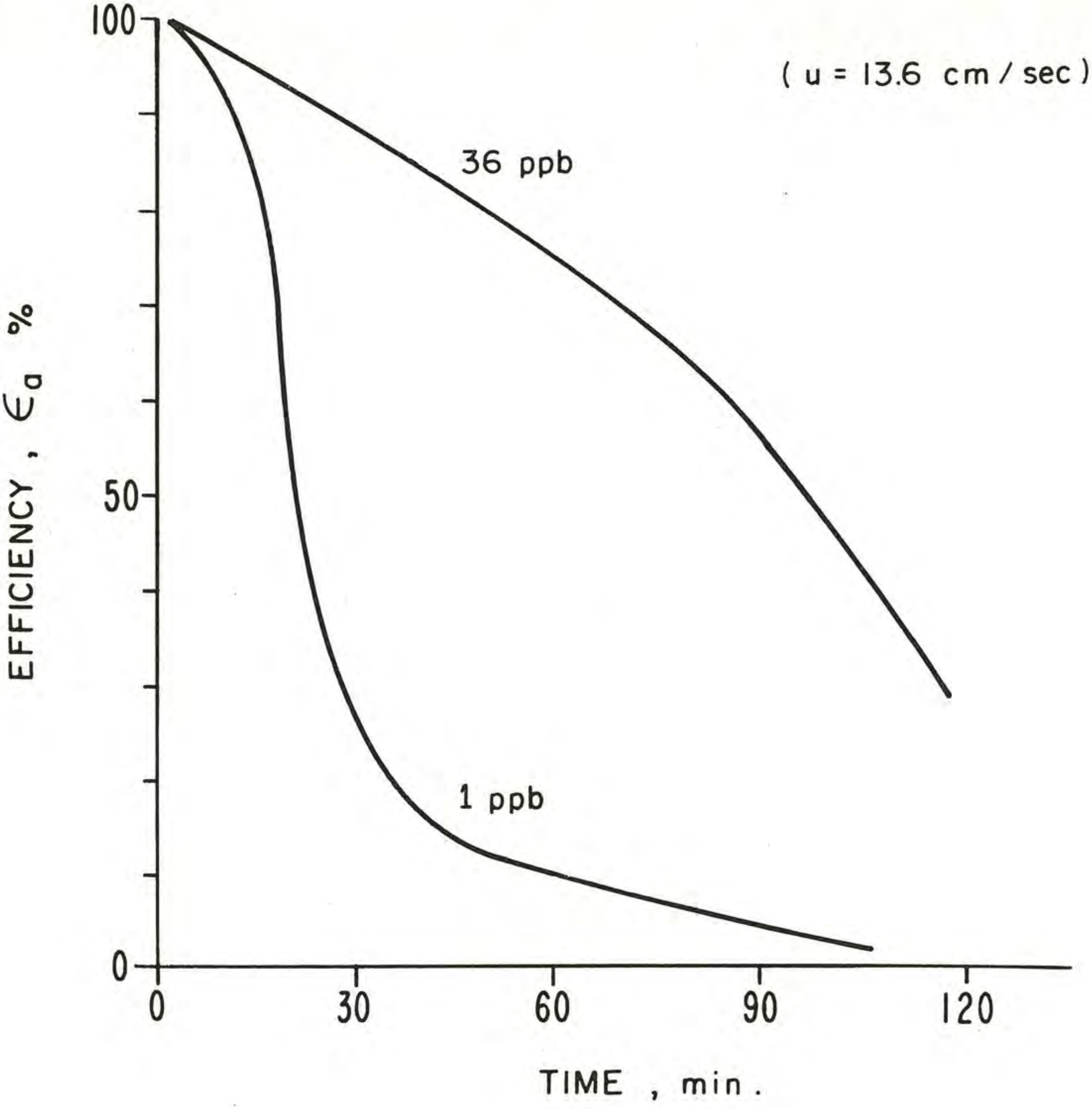

Figure 10. Collection Efficiency of Unactivated Porous Polymer - Glass Fiber Filter at High and Low Vapor Concentrations.

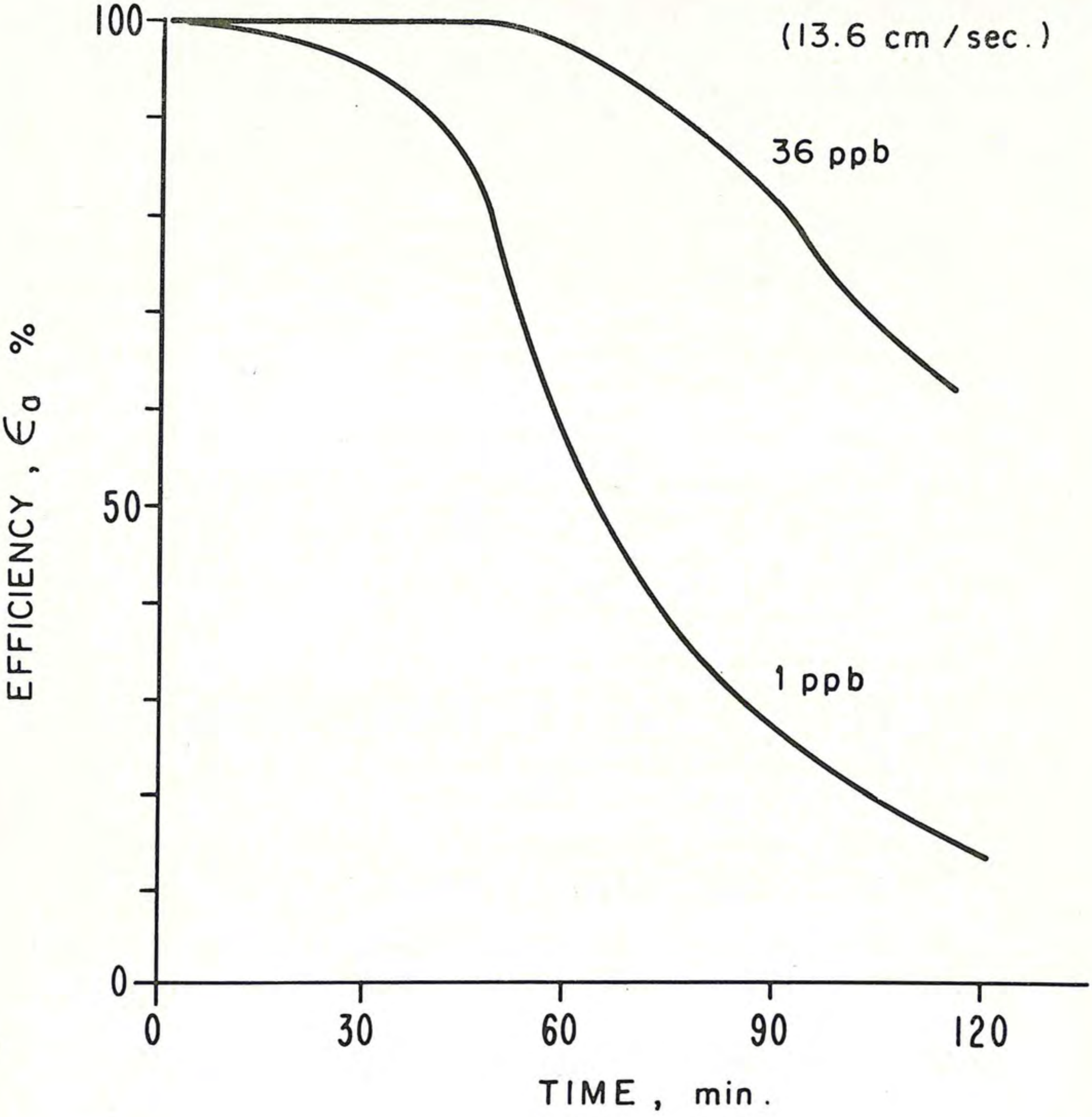

Figure 11. Collection Efficiency of Activated Porous Polymer - Glass Fiber Filter at High and Low Vapor Concentrations.

concentration of DMMP of approximately 1 ppb at a linear velocity of 13.6 cm/sec. The results of those tests are summarized in Figure 13. The upper curve (labeled 75:25) contained the highest mass ratio of porous polymer to glass fiber, 75:25. The two-hour average collection efficiency for this filter was 93.3 percent for DMMP.

The physical properties of the three filters, however, were reversed as might be expected. The vaporfil with the highest glass fiber content was the least susceptible to damage during manipulation (disjarring of porous polymer particles). However, the filter with the highest polymer content was still adequately durable for field sampling applications. Flow resistance of the formed filter as shown in Figure 14 is about 2.5 inches of Hg at 13.6 cm/sec.

Tests with DIMP

Up until this time, DMMP had been used entirely as the principal evaluative tool in developing a collection substrate for the application in hand. It was felt, however, that due to the similarity of DMMP to many of the members of the methylphosphonate family, that a collection substrate which would efficiently collect DMMP would also collect other members of this family efficiently.

This was partially verified by a test conducted with another simulant, DIMP (diisopropyl methyl phosphonate). A filter, prepared according to a procedure based on the results of the previous tests was tested with DIMP at 13.6 cm/sec at an inlet concentration of 4 ppb. The collection efficiency did not drop from 100% over a two hour test period.

Sample recoverability tests showed that a simple elution with ethyl alcohol gave a sample recovery which averaged 99.5% for DMMP. In the case of DIMP, several extractions are required to recover all of the sample. Sample extracts in the nanogram range were successfully concentrated from 300 cc down to 0.5 cc by means of a Kuderna Danish concentrator.

Conclusions

The sampling substrate developed in this work provides a means of efficiently sampling large volumes of air for organic vapors present at the parts-per-billion level. This technique was originally conceived for ambient air sampling to collect sufficiently large samples such that adequate compound would be available for subsequent physicochemical identification tests. It is possible, however, that this method could be modified such that it could have widespread application in industrial hygiene and occupational safety. Because of the relaxed sampling requirements for in-plant sampling (ppm concentrations and flow rates on the order of 1 ℓpm, a reduction in linear velocity from 13.6 cm/sec to approximately 0.1 cm/sec could be made which,

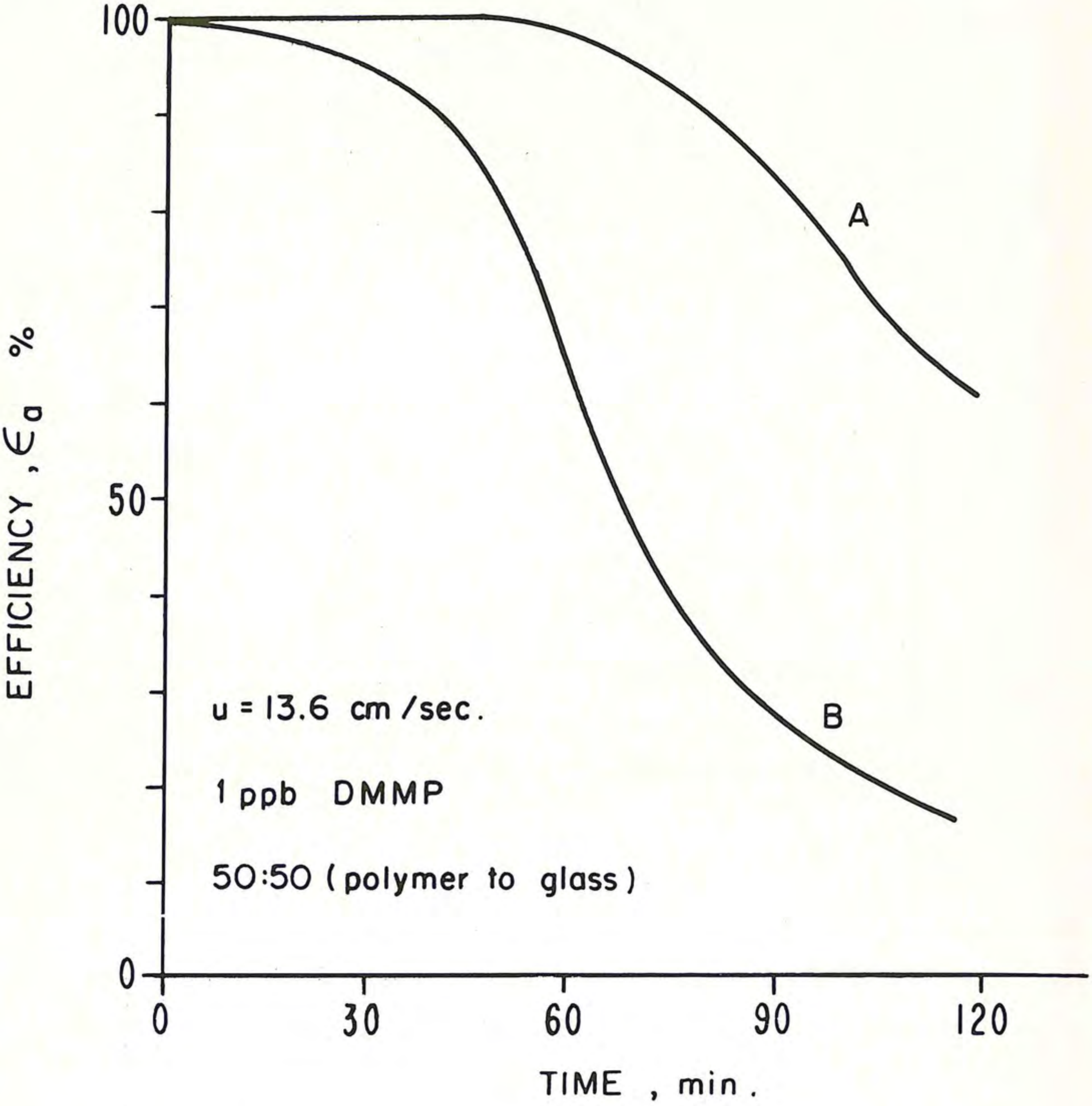

Figure 12. Effect of Flow Direction on Collection Efficiency.

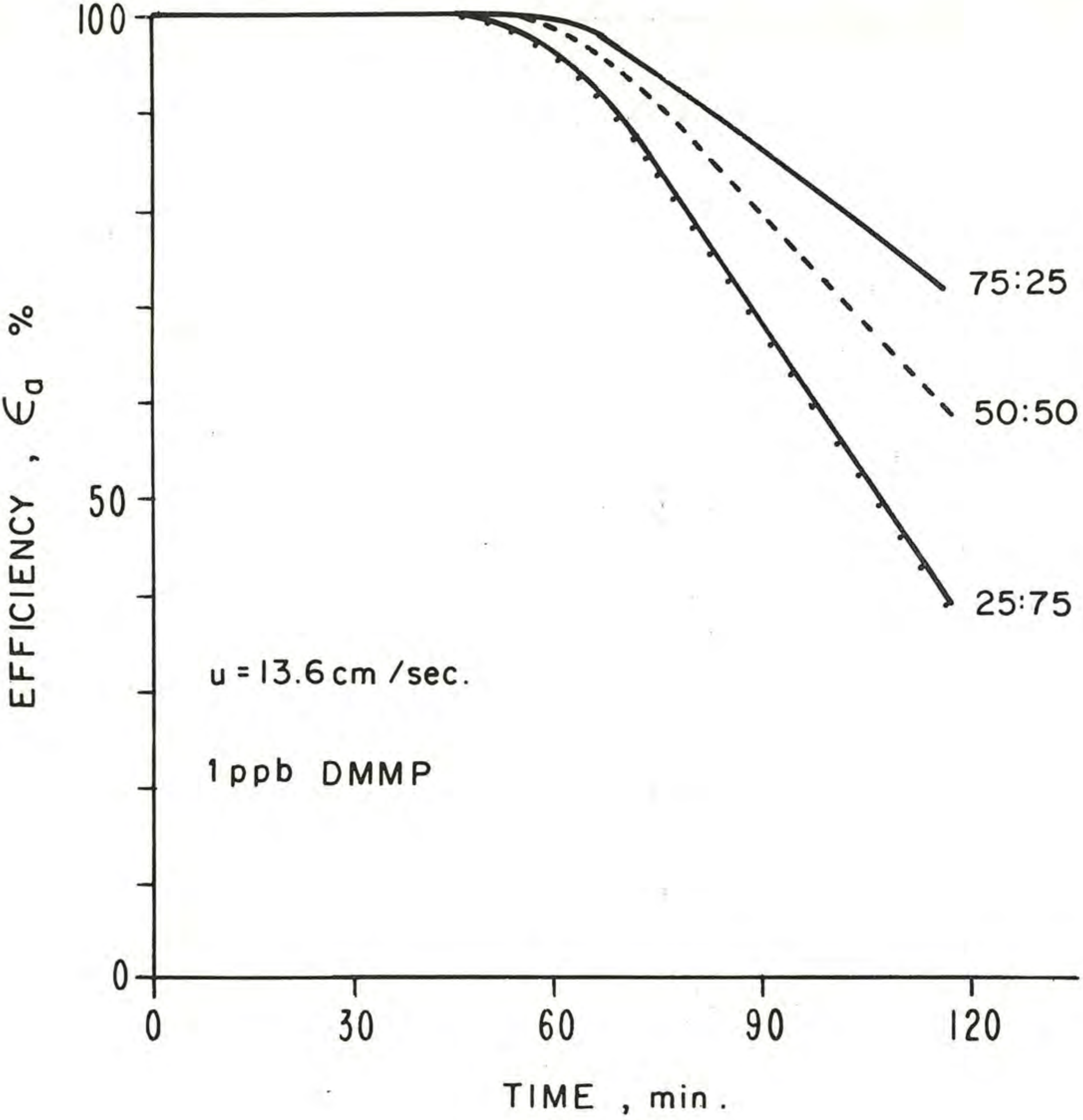

Figure 13. Effect of Filter Composition on Collection Efficiency.

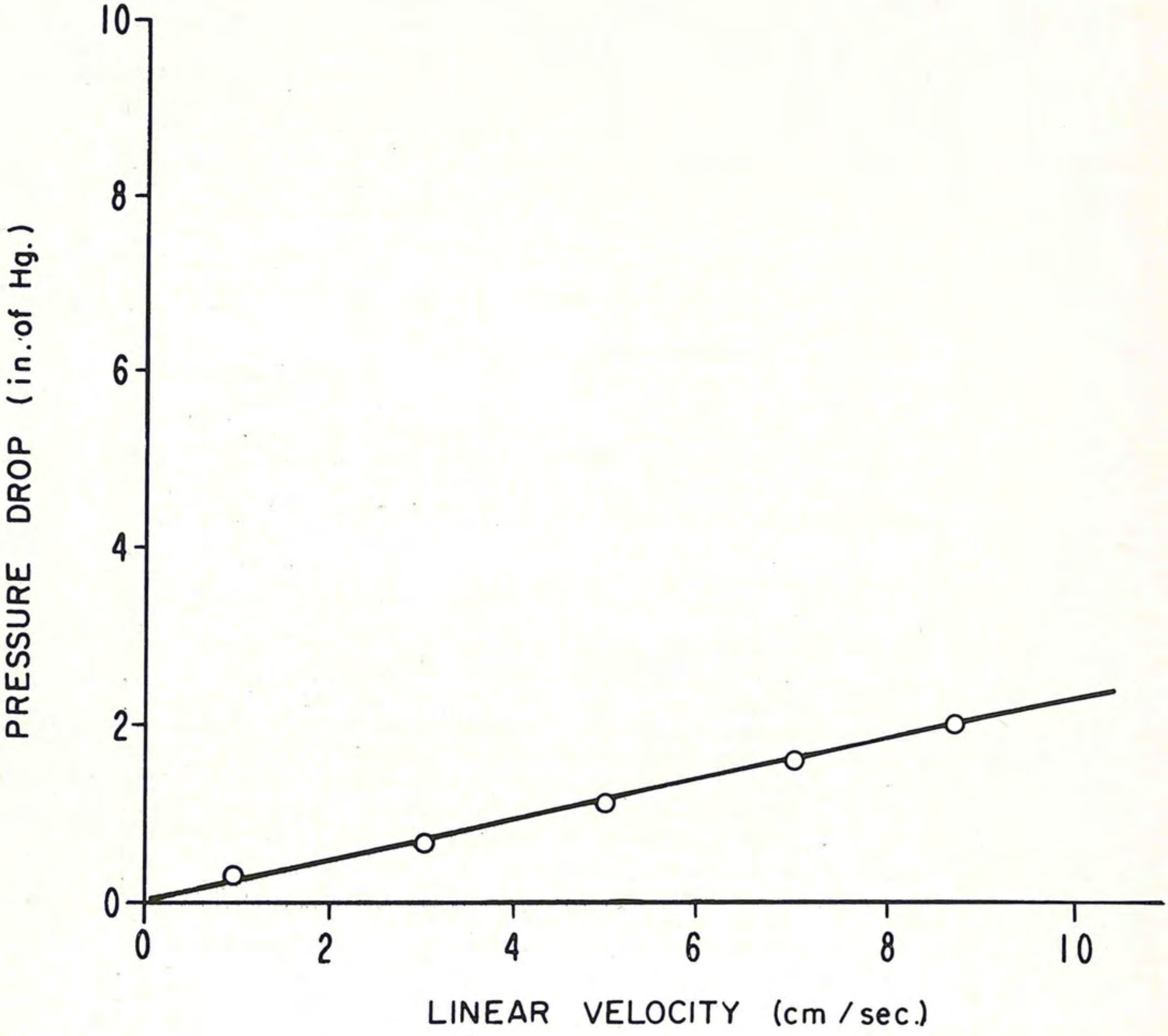

Figure 14. Flow Resistance Curve of Formed Filter.

based on the results of this study, would result in a significant increase in collection efficiency. The net effect would be to extend the application of this method to many of the volatile solvents encountered in the working environment. Should this prove to be the case, this would render vapor sampling simpler than particulate sampling, since isokinesis is not a necessary requirement for gas sampling. Further research is, of course, required to fully evaluate the feasibility of this proposed application.

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4. *Personal Communication, Gelman Instrument Company.*
5. *Heuser, S. G., and Scudamore, R. A., Chem. & Ind., 2093 (1966).*
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Discussion

Dr. Teass: In your work, would you say that a small glass tube filled with some porous polymer would be effective?

Dr. Lonnes: Yes, it would be extremely effective for sampling dimethyl methyl phosphonate or the organophosphorous compound which you are working with. I should add, however, that substantial pressure drop is required to draw sample gas through a packed column. Because of the large flow capacity and low energy requirements in this work, the use of a sampling column was not feasible. The sampling substrate which we designed and tested allows efficient sampling at high flow rates with a minimum energy expenditure.

PROGRESS IN THE DEVELOPMENT OF SAMPLING AND ANALYTICAL METHODS FOR ORGANIC MATERIALS

by William J. Barrett

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Birmingham, Alabama

This is a report on the sampling and analytical methods for four organic materials. These materials are phosgene; the combination of the nitrate esters, nitroglycerin and ethylene glycol dinitrate; acrylonitrile; and methyl chloride. The general idea is to develop methods basically similar to the method presently in use for a number of organic solvents using charcoal as a sorbent. The experimental effort consists of screening various solid sorbent materials for their efficiency in retaining the vapors; selecting the most suitable sorbent for each substance; determining the optimum conditions of use of the sorbent material in a sampling system that uses a personal sampling pump; devising a suitable method of desorbing the sample material from the sorbent; and evaluating analytical methods to select the most appropriate method for use by NIOSH. Finally, the selected methods and procedures are to be comprehensively evaluated to determine whether they meet the established criteria.

This report will include some background information and preliminary results for two of these materials - phosgene and the nitrate esters.

Phosgene

Phosgene is a chemically reactive compound and, especially in our applications, hydrolysis is an important reaction. The rate of hydrolysis of phosgene in the vapor form in humid air is fairly slow. In the atmosphere, however, in the presence of atmospheric particulate materials, the hydrolysis of phosgene appears to be accelerated.

The compound is primarily used in the manufacture of polyurethanes. There are 14 companies involved in production of phosgene. Only one of these makes the compound for sale, and the others make it for their own captive use in the synthesis of diisocyanates and other intermediates. Most of this production is in open plants, that is, not in enclosed buildings, so there is not much need for fixed installation, continuous monitoring for phosgene. The industry does have an interest in and is studying some commercial instrumentation that may be useful for monitoring phosgene in a plant area, but these instruments are not yet useful as personal monitors. One of them is based on development of a color on a reagent-impregnated tape, and another is based on an electrochemical sensing cell. The first one of these is manufactured in England by Universal Environmental Instruments and the second is a German instrument made by Hartmann and Braun.

To illustrate the real need for a personal monitoring technique, the Manufacturing Chemists Association's Task Force on Phosgene Safety is planning to sponsor during the next year a study attempting to correlate worker exposure with physiological effects. One of their problems is that they don't yet have a good way of measuring worker exposures.

For generating low concentrations of phosgene, we use a solution of liquid phosgene in hexane maintained in a dry ice bath. The generator is illustrated in Figure 1, which also shows the solid sorbent screening system. About 0.25 ml of liquid phosgene in 50 ml of hexane is placed in container B. This operation is performed under a nitrogen atmosphere to exclude moisture. Dry nitrogen is passed over the cold solution in a 100-ml flask at low flow rate and is diluted with dry air or with air of controlled relative humidity. By appropriate adjustment of flow rates, one can obtain in this way concentrations around the TLV value of 0.1 ppm.

We have used three different analytical methods. One is a spectrophotometric method based on the reaction of phosgene with 4-(4-nitrobenzyl)pyridine (NBP) and N-benzylaniline. This is the primary method to establish phosgene concentrations and to determine the output of the phosgene generator. Reagent solution consisting of the nitrobenzylpyridine and benzylaniline in diethyl phthalate is placed in a bubbler, the sample gas is bubbled through it, the solution is removed, and the concentration of the reaction product is determined spectrophotometrically. To calibrate this spectrophotometric method we prepared a solution of phosgene in diethyl phthalate and analyzed appropriate aliquots of that solution by hydrolyzing the phosgene to chloride and determining the chloride ion content. That is not, of course, a direct method of calibration.

Gas chromatography is useful for determining phosgene, and we have used it as a rapid method of checking the output of the generator.

The most useful method for continuous monitoring for phosgene is based on an electrochemical sensor that was developed for use by the Army for the detection of organic phosphorus compounds in air. The principle of that device is based upon the reaction of a class of organic compounds, acylating agents, of which phosgene may be considered an example-- with oximes having a certain structure. One of the products is hydrogen cyanide. The cyanide is detected in a galvanic cell with a silver anode and a platinum cathode. The readout is the measurement of a potential drop across an external resistor in the cell circuit. The response of this system to phosgene is illustrated in Figure 2.

Figure 1 also illustrates the system for monitoring breakthrough of phosgene in the screening of solid sorbent materials. The electrochemical phosgene detector cell I was calibrated by connecting it to the generator output (with the sorbent tube absent) and recording its response at one *or more phosgene concentration levels previously established by the NBP method. The recorder baseline was established by setting stopcock H to admit phosgene-free air of the same relative humidity as the sample air.*

The sorbent tube G was 5-mm i.d. and 70-mm long. It was packed with an appropriate amount of sorbent material, usually 25 to 200 mg, depending primarily on the particle size and the effect of particle size on resistance to airflow. In most experiments the flow rate was 1.0 ℓ/min and the amount of sorbent was selected to give a pressure differential not exceeding 1 in. of Hg.

Breakthrough time was defined as the time after sampling through the sorbent tube is begun until the time at which the cell exhibits a significant response. The cell gave a detectable response at a phosgene concentration of about 0.008 mg/m^3. Quantitative breakthrough was defined as the area under the recorded response-versus-time curve for the effluent from a sorbent tube divided by the area under the response-versus-time curve for an empty tube. It was expressed as percentage breakthrough.

Table I gives the results of screening tests conducted with the electrochemical method of monitoring the effluent from the sorption tubes. The electrochemical method provided a continuous recording of effluent phosgene concentrations. Thus, it was possible to determine breakthrough time and percent breakthrough. In some instances, breakthrough at low concentration was observed to occur immediately while percent breakthrough remained low throughout the period of exposure of the sorbent to phosgene. The time of exposure of the sorbent to the airstream containing phosgene was usually, but not always, 10 min. When significant breakthrough was observed immediately, the exposure was sometimes terminated in less than 10 min and the percent breakthrough was calculated for that period of exposure.

Figure 3 illustrates typical recorded breakthrough response curves. These curves are tracings from recorder charts showing the response of the electrochemical cell to phosgene at 2.0 mg/m^3 and responses to the effluents from four different sorbent tubes. The curves were selected to show the principal types of responses that were observed except for the zero response observed with a sorbent such as activated carbon that retained phosgene completely.

The conclusion to be drawn from the data in Table I is that the inorganic materials generally retained phosgene effectively while the organic materials, with some exceptions, did not.

Efforts to desorb phosgene from those sorbents that retained it were made by solvent extraction, usually with benzene, or by heating in a stream of nitrogen or air. Analyses of the solvent extracts by gas chromatography gave no evidence of the presence of phosgene and led to the conclusion that phosgene could not be effectively desorbed from any of *these sorbents by solvent extraction. The attempts to desorb phosgene by heating were also unsuccessful. No evolved phosgene could be detected by either the electrochemical method or the NBP method.*

In addition to the solid sorbents listed in Table I, a representative group of gas chromatographic packing materials consisting of a nonvolatile liquid phase on an inert solid support were screened for retention of phosgene. With most of these materials, breakthrough occurred almost immediately under the conditions used. The most retentive materials did not yield any detectable phosgene when efforts were made to desorb it by extraction or heating.

A sorbent consisting of a solution of the colorimetric NBP reagent in diethyl phthalate impregnated on an inert substrate was effective in retaining phosgene. On immediate extraction with chloroform and measurement of absorbance, recovery of 75 to 90% of the phosgene was observed. However, storage of the exposed sorbent tubes for 24 hours resulted in a substantial loss of the developed color and apparent recovery of only about 30%. Although this method of collecting phosgene by reaction was successful, the lack of stability of the reaction product precluded its practical use as a field method.

The general conclusion was that collection of phosgene on solid sorbents is not a satisfactory sampling method for industrial hygiene applications. The lack of success is attributable to the reactivity of phosgene, as evidenced by the inability to desorb it as the intact molecule and by the observation in many instances of the appearance of products of reaction on gas chromatograms.

Nitroglycerin and Ethylene Glycol Dinitrate

The nitrate esters usually occur together. Dynamite is most often made with an explosive oil, so-called in the industry, that is prepared by nitrating a mixture of glycerin and ethylene glycol. Sometimes, however, dynamite contains only ethylene glycol dinitrate (EGDN).

These nitrate esters are similar in chemical and physiological properties. The main practical difference between them with regard to our task is their difference in volatility. At 25°C nitroglycerin (NG) has a volatility of about 1.8 mg/m^3, and that of the ethylene glycol dinitrate is about 310 mg/m^3.

The threshold limit value is 0.4 ppm for either of these compounds, or for the total when they occur together, for continuous exposure. For intermittent exposures, the TLV is 0.02 ppm, which has been established because there seems to be some difference in physiological effects between continuous exposure and intermittent exposure.

We have used medicinal nitroglycerin tablets as the source of this compound. These tablets are manufactured under precise control and may be obtained from the manufacturers with a statement of the NG content as determined by their quality control laboratory. Ethylene glycol dinitrate was obtained in the form of dynamite that contained no NG, and for calibration we depended on the analysis supplied by the manufacturer for the EGDN content of the dynamite. The compound can also be obtained in the form of dilute solutions in ethanol.

Figure 4 is a sketch of the vapor generator that was used for the nitrate esters. The drying tower B contained 160 g of a mixture of 1 part of dynamite and 4 parts of 30/60-mesh Chromosorb P, or 20 g of a mixture of 1 part NG tablets and 9 parts of Chromosorb P. Dry nitrogen was passed through the tower at a flow rate of 1000 ml/min for NG and 10 ml/min for EGDN. Provision was made for dilution with dry air or air of high or intermediate relative humidity. The generator was set up in a room where the temperature was maintained at 25 ± 2°C. After mixing, a portion of the sample air was pumped through either a bubbler containing ethanol or a sorbent tube. The flow rate was fixed by a selected critical orifice. On occasion, air was sampled simultaneously through the sorbent tube and the bubbler. Before the beginning of an analysis or a test of a sorbent tube, the generator was allowed to operate for a length of time (usually 2 hours) sufficient to ensure that the nitrate ester vapor was in equilibrium with the surfaces and that the output concentration was constant.

Gas chromatography with electron capture detection was used for the determination of both compounds. Solid sorbents were extracted with ethanol for the GC analysis. Figure 5 represents a gas chromatogram of a mixture in ethanol.

Preliminary screening experiments showed that most solid sorbents retained both EGDN and NG. Generally, the most favorable results were obtained with Tenax GC. Table II shows retention data for EGDN with Tenax GC and with activated carbon (Mine Safety Applicances Company). Similar data were obtained for NG. The activated carbon appears to be an inefficient sorbent; however, other data show that the nitrate esters are not stable on activated carbon. Decomposition begins almost immediately after sorption and the amount of recoverable ester decreases gradually with time. For example, the amount of NG recovered from MSA carbon in one experiment was 64% after 4 hours, 18% after 24 hours, and 10% after 10 days. On the other hand, 100% of either NG or EGDN was recovered from Tenax GC after 24 days of storage at room temperature. The recovery of NG and EGDN from Tenax GC is also independent of relative humidity of the sample air over the range of 10% to 90% relative humidity. When Tenax GC was exposed to both compounds simultaneously, both were quantitatively recovered.

Thus, it was concluded that Tenax GC is a satisfactory solid sorbent for NG and EGDN, and that electron-capture gas chromatographic analysis of an ethanol extract of the sorbent is a satisfactory method of analysis.

There is one other incidental subject I want to bring up. I should have done this yesterday when we were talking about charcoal. I have a sample of what I believe is a rather interesting form of activated carbon. It was developed in our laboratory, and I thought I'd pass it around and let you look at it. As far as I know, activated carbon in the form of uniform spheres is not commercially available. This material was made from polyvinylidine chloride by a carefully controlled process of heating. Thermal decomposition, of course, causes HCl to be evolved, and the residue is carbon. Carbon made from this material, I am told, has a surface area of about 2500 m^2/g. *Other carbons are usually somewhat less than that. I don't know that it has any real potential application that would be particularly exciting. It does work about like the MSA carbon when it is used in the regular tubes for collecting solvent vapors such as benzene. One difference is that, for a given quantity of carbon, the spheres have less resistance to airflow.*

Discussion

Mr. Crable: Any questions? Comments?

Dr. Teass: How does a porous polymer compare to charcoal [with regard to surface area]?

Dr. Barrett: I don't have any information.

Dr. Dravnieks: May I make a comment?

Mr. Crable: Yes.

Dr. Dravnieks: Well, some years ago, we did work on some process for fast detection of low [levels of explosive vapors] in air. It is in connection with bomb detection possibilities, and we found that gold surface is very good adsorbent for nitro compounds, and also it seems to be able to release it upon gentle warming. Adsorption temperature was room temperature. It desorbed at 90°C, and at these levels one could get real regular adsorption and very complete desorption.

Table I. Results of Phosgene Breakthrough Measurements with the Electrochemical Cell Method of Detection

Sorbent	Amount of sorbent used, mg	Mesh size	Pressure drop[a] across sorbent tube, in. of H_2O	Breakthrough time, min	Time of measurement of percent breakthrough, min	Percent breakthrough
Empty tube	0	-	-	-	-	100
Glass wool plugs (2)	-	-	5	-	-	100
Activated carbon (Barneby-Chaney)	100	20/40	3	>10	10	0
Activated carbon (MSA, Lot No. 3)	100	20/40	3	>10	10	0
Activated carbon (MCB)	50	40/100	17	>10	10	0
Activated carbon (ASL)	25	60/80	10	>10	10	0
Carbosieve B (Supelco)	25	60/80	12	>10	10	0
CF-53 (SRI carbon fiber)	200	-	11	>10	10	0
CF-61 (SRI carbon fiber)	100	-	11	>10	10	0
Alumina, neutral (Fisher Scientific)	25	80/200	13	<0.2	6	20
Alumina, neutral (Fisher Scientific)	50	80/200	<22	<0.2	5	5
Alumina (Woelm)	100	80/100	20	>10	10	0
Alumina F-1 (Coast Engineering Laboratory)	100	60/80	16	>10	10	0
Silica gel (source unknown)	100	40/60	8	<0.2	8	90
Silica gel D-08 (Coast Engineering Laboratory)	100	60/80	12	<0.2	10	50

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[a] The flow rate of the gas from the phosgene generator was 1 ℓ/min through each sorbent tube.

Table I (Continued). Results of Phosgene Breakthrough Measurements with the Electrochemical Cell Method of Detection

Sorbent	Amount of sorbent used, mg	Mesh size	Pressure drop[a] across sorbent tube, in. of H_2O	Breakthrough time, min	Time of measurement of percent breakthrough, min	Percent breakthrough
Silica gel 60 (E. M. Reagents)	25	70/230	13	<0.2	5	90
Silica gel (Sargent)	100	40/80	>22	<0.2	4	90
Silica gel (Davison)	25	140/200	11	<0.2	3	90
Silica gel (Davison)	100	30/60	8	<0.2	4	90
Silicar CC-7 (Mallinckrodt)	25	60/200	19	<0.2	3	90
Deactigel (Supelco)	100	60/80	12	<0.2	4	95
Adsorbosil-CAB (ASL)	100	30/60	8	<0.2	7	75
Porasil A (Waters)	25	80/100	8	<0.2	10	95
Porasil A (Waters)	100	80/100	20	<0.2	10	95
Porasil F (Waters)	25	100/150	6	<2	10	40
Porasil F (Waters)	50	100/150	12	<4	10	20
Bio-Glas 2500 (Bio-Rad)	100	50/100	17	<0.2	4	90
Bio-Glas 200 (Bio-Rad)	100	50/100	22	<0.2	4	80
Cera Beads (Analabs)	100	40/50	6	<0.2	6	70
Florisil (Fisher Scientific)	100	60/100	17	>10	10	<5
Molecular Sieve 13X (Linde)	100	60/80	8	<1	10	5
Carbowax 4000 on Porasil S (Waters)	50	80/100	18	<0.2	10	50
Carbowax 400 on Porasil S (Waters)	50	80/100	11	<0.2	6	75
OPN on Porasil C (Waters)	50	80/100	12	<1	8	50

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[a] The flow rate of the gas from the phosgene generator was 1 ℓ/min through each sorbent tube.

Table I (Continued). Results of Phosgene Breakthrough Measurements with the Electrochemical Cell Method of Detection

Sorbent	*Amount of sorbent used, mg*	*Mesh size*	*Pressure drop[a] across sorbent tube, in. of H_2O*	*Breakthrough time, min*	*Time of measurement of percent breakthrough, min*	*Percent breakthrough*
Porapak P (Waters)	*100*	*50/80*	*22*	*<0.2*	*4*	*90*
Porapak P-S (Waters)	*100*	*50/80*	*22*	*<0.2*	*3*	*90*
Porapak Q (Waters)	*100*	*50/80*	*18*	*<0.2*	*3*	*90*
Porapak Q-S (Waters)	*50*	*100/120*	*14*	*<0.2*	*4*	*90*
Porapak R (Waters)	*100*	*50/80*	*19*	*<1*	*10*	*25*
Porapak R (Waters)	*50*	*50/80*	*12*	*<1*	*2*	*50*
Porapak S (Waters)	*100*	*50/80*	*18*	*<0.2*	*8*	*10*
Porapak S, dried (Waters)	*100*	*50/80*	*17*	*<0.2*	*6*	*5*
Porapak S, dried (Waters)	*100*	*50/80*	*16*	*<0.2*	*4*	*0*
Porapak S (Waters)	*50*	*80/100*	*20*	*>10*	*9*	*0*
Porapak N (Waters)	*100*	*50/80*	*17*	*<0.2*	*4*	*90*
Porapak N (Waters)	*200*	*50/80*	*22*	*<0.2*	*5*	*90*
Porapak T (Waters)	*100*	*50/80*	*14*	*<0.2*	*3*	*90*
Tenax GC (Enka N.V.)	*100*	*60/80*	*<22*	*<0.2*	*3*	*90*
Chromosorb 101 (Johns-Manville)	*100*	*80/100*	*22*	*<0.2*	*3*	*100*
Chromosorb 101 (Johns-Manville)	*100*	*80/100*	*22*	*<0.2*	*4*	*90*
Chromosorb 103 (Johns-Manville)	*200*	*60/80*	*22*	*<0.2*	*5*	*5*
Chromosorb 103 (Johns-Manville)	*100*	*60/80*	*12*	*<0.2*	*7*	*5*
Chromosorb 107 (Johns-Manville)	*100*	*60/80*	*11*	*<0.2*	*7*	*95*
Chromosorb 108 (Johns-Manville)	*100*	*60/80*	*16*	*<0.2*	*11*	*60*

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a. The flow rate of the gas from the phosgene generator was 1 ℓ/min through each sorbent tube.

Table I (Continued). Results of Phosgene Breakthrough Measurements with the Electrochemical Cell Method of Detection

Sorbent	Amount of sorbent used, mg	Mesh size	Pressure drop[a] across sorbent tube, in. of H_2O	Breakthrough time, min	Time of measurement of percent breakthrough, min	Percent breakthrough
Amberlite CG-50 (Rohm and Haas)	100	100/200	22	<0.2	3	100
Amberlite MB-1 (Rohm and Haas)	100	20/50	6	<0.2	4	90
Cellex CM (Bio-Rad)	25	b	22	<0.2	3	90
Dowex-1 (Dow)	100	20/50	5	<0.2	5	90
Ion-exchange resin AG1-X10 (Bio-Rad)	25	b	11	<0.2	3	100
Rexyn 201 (OH) (Fisher Scientific)	100	20/50	6	<0.2	10	50
Sephadex G-10 (Pharmacia Fine Chemicals)	25	b	15	<0.2	4	90
Stratabed 93 (Rohm and Haas)	100	20/50	5	>10	10	0

---

a. The flow rate of the gas from the phosgene generator was 1 ℓ/min through each sorbent tube.

b. These materials were finer than 200 mesh.

Table II. Retention of EGDN by Tenax GC and MSA Carbon

Sorbent[a]	Concentration of EGDN in sample air, mg/m^3	Flow rate, l/min	Time of exposure of sorbent to EGDN, min	EGDN retained by sorbent, %
Tenax GC (35/60 mesh)	0.27	0.40	60	100
	0.61	0.26	90	119
	0.61	0.26	90	95
	1.77	0.40	60	103
	1.77	0.40	60	105
	3.93	0.40	60	106
	3.93	0.40	30	99
Average	-	-	-	104
MSA activated carbon (Lot No. 3)	0.61	0.26	90	59
	0.61	0.26	90	84
	0.72	0.40	60	57
	0.72	0.40	71	71
	0.72	0.40	60	76
	0.72	0.17	60	72
	0.72	0.17	71	69
	0.72	0.17	60	74
	1.56	0.40	60	93
	3.93	0.40	30	87
Average	-	-	-	74

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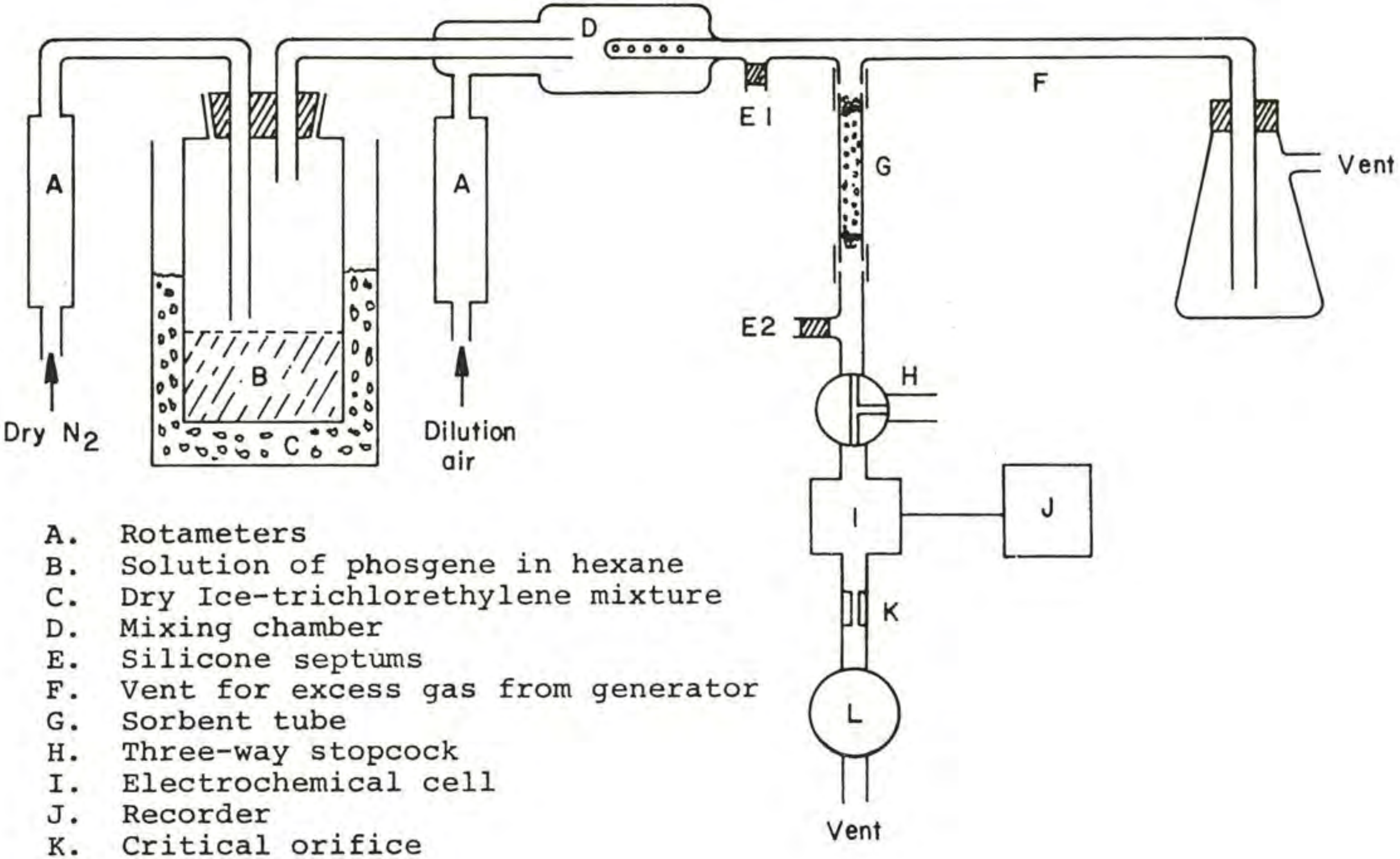
[a] The amount of sorbent used was 100 mg.



A. Rotameters
B. Solution of phosgene in hexane
C. Dry Ice-trichlorethylene mixture
D. Mixing chamber
E. Silicone septums
F. Vent for excess gas from generator
G. Sorbent tube
H. Three-way stopcock
I. Electrochemical cell
J. Recorder
K. Critical orifice
L. Pump

Figure 1. Phosgene Generator and Solid Sorbent Screening System.

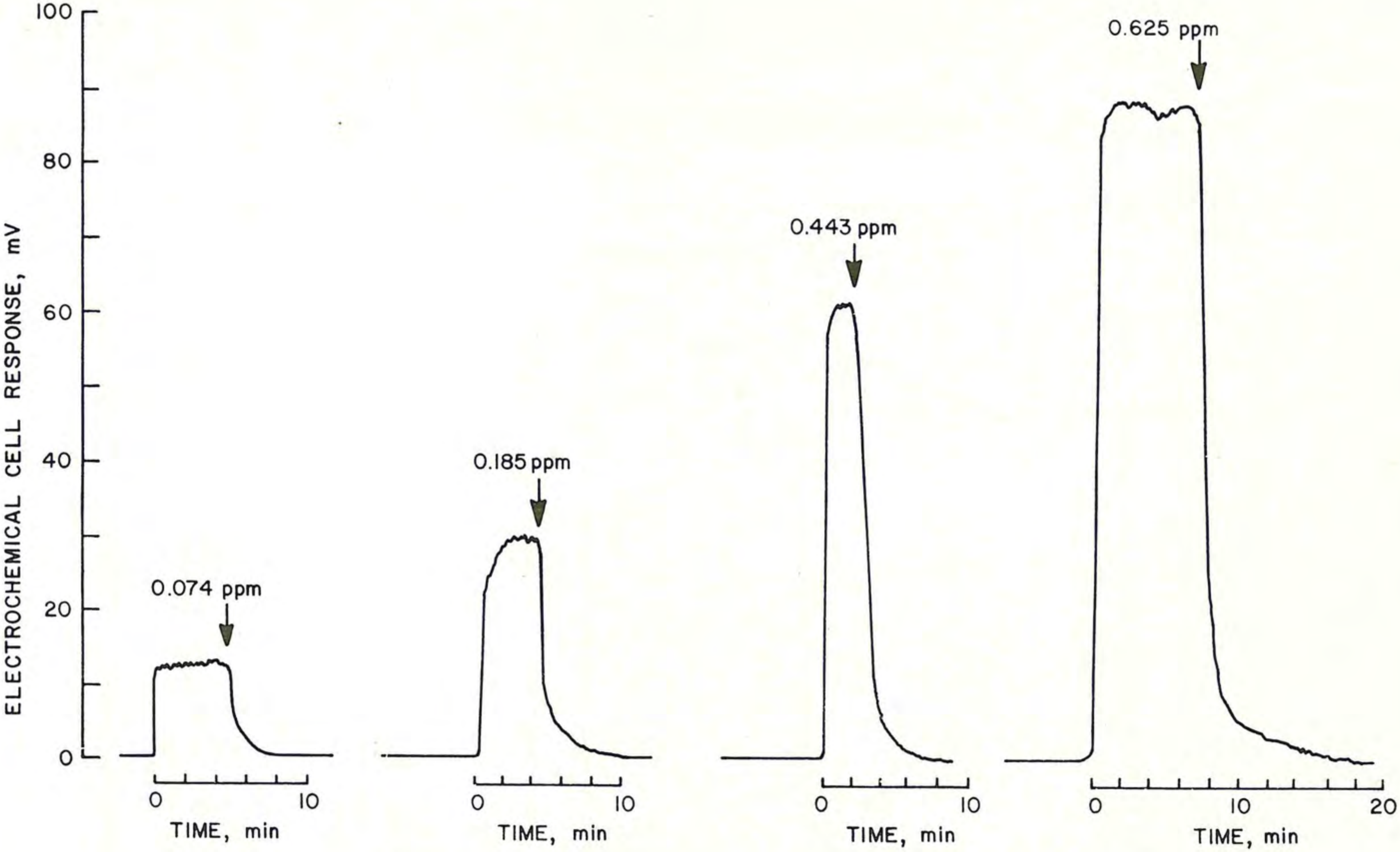


Figure 2. Electrochemical Cell Response to Phosgene.

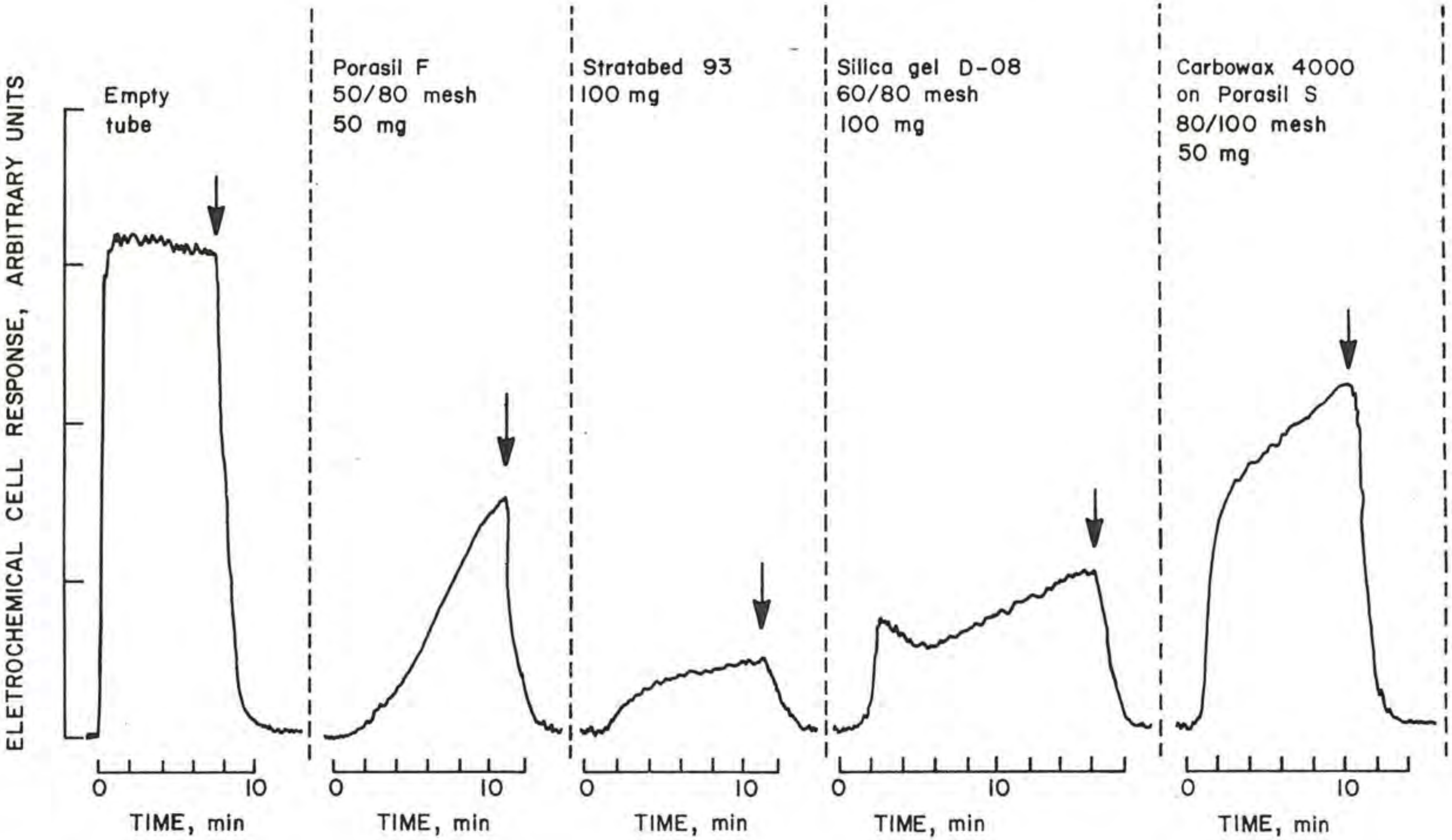
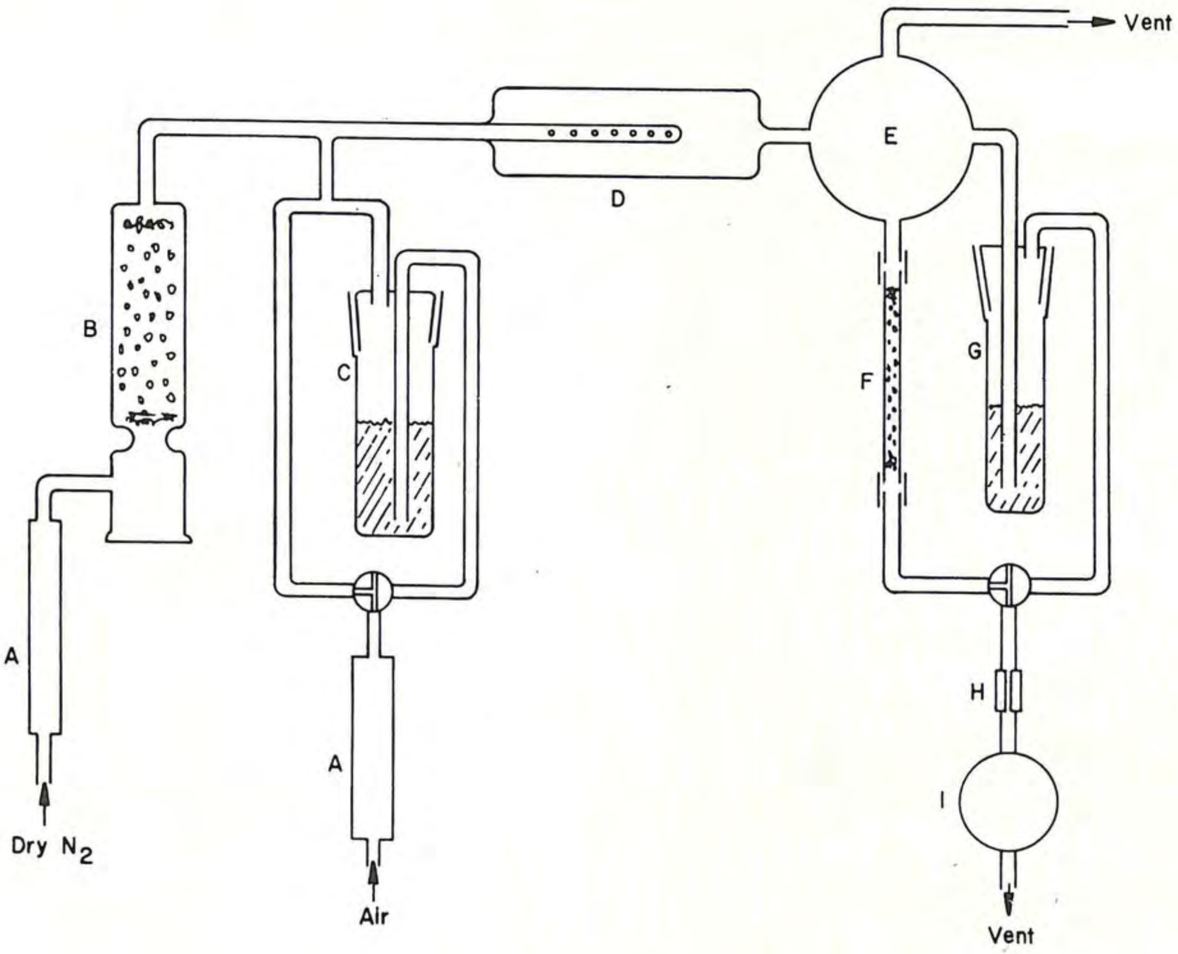


Figure 3. Typical Breakthrough Curves.



A. Flowmeters
B. Nitrate ester—
Chromosorb P mixture
C. Humidifier
D. Mixing Chamber
E. Flask
F. Sorbent tube
G. Ethanol bubbler
H. Critical orifice
I. Pump

Figure 4. Vapor Generator and Sorbent Screening System for NG and EGDN.

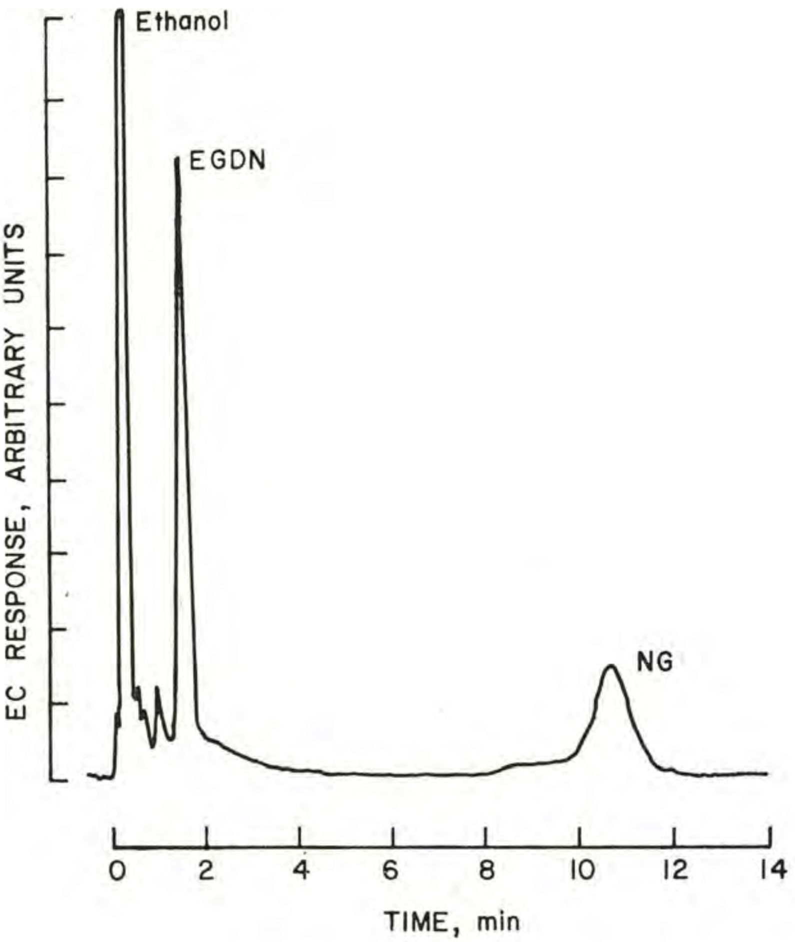


Figure 5. Chromatogram of Mixture of EGDN and NG in Ethanol.

Column: 10% OV-17 on 60/80-mesh Gas Chrom Q,
2.5 ft by 0.25 in.
Carrier gas: Helium, 100 ml/min
Purge gas: Argon/methane, 125 ml/min
Column temperature: 130°C
Injection port temperature: 160°C
Detector temperature: 280°C

SOLID SORBENTS AS GO/NO-GO MONITORS IN TOXIC GASEOUS ENVIRONMENTS

by Donald C. Behringer

Development and Engineering Directorate, Aberdeen Proving Grounds, Maryland

Introduction

I am from Edgewood, that is, Aberdeen Proving Grounds. Edgewood, for administrative purposes, is under Aberdeen; but we still maintain our identity for the work we do at Edgewood.

I think you are familiar with the present extensive laboratories in biochemical and medical research, as well as developmental laboratories doing work in protective equipment, clothing, and face masks. I am working quite a bit with charcoal materials, automatic detection (which I will be talking about today), and also, I am doing some work on remission of toxic agents. I have been working for Chemical Warfare Region "N", and now I am getting into air pollution and water pollution studies. The objective of our work is the automatic detection of low concentrations of organic phosphorous compounds that might be present in the air.

Portable Detector

We are in the development end, and so we are developing finished hardware. It has to be portable equipment. It has to operate unattended for 12 hour periods. It is used by the field soldier; so characteristics like ruggedness, reliability, and maintainability are very important along with high sensitivity and specificity. The concentrations we are trying to detect in the air are about 0.1 mg/m^3.

This becomes a go/no-go alarm; that is, our alarm sounds when certain concentrations are exceeded. We don't try to measure how much it is, whether it is 1 mg/m^3 or 100. It exceeds 0.1; that's all we know. We developed such an alarm for the field soldier, and it is a type classified "in production" right now.

What I wanted to talk about today was some applications of that alarm which required us to look into some solid sorbent materials. The problem came about when they wanted to mount the alarm inside a pressurized vehicle and use long sampling lines from the outside to the detector inside the vehicle. We found that quite a bit of material was lost in the sampling line. We went into a program to develop the laboratory plumbing from outside to a sensor inside the vehicle and then to detect the required concentrations.

Let me start with the detector Dr. Barrett was talking about, which is a field alarm. It is the alarm we developed for the field, and it has a sensitivity of a 0.1 mg/m^3.

Sampling Probe

Sampling from the outside is through an insulated sampling line, operated at 200°F. We drop the temperature to 90°F. and bring it into the engine compartment to the solid sorbent material system, which we developed. From the sample concentration system, the air goes down to the detector. Air is being drawn in from the outside by a series of two pumps: the detector pulling air at 1 liter/min and an auxiliary pump which is pulling 2 liters air/min. So a total of 3 liters/min is coming in through the 200°F. line and the filter chamber.

Concentration Column

One liter/min is diverted to the detector, and 2 liters/min to the concentration column, which is a small chromatographic column containing 4 mg Ampak N. This comes on for 8 min, exhausting to an auxiliary air pump, and out as waste.

The reason for the concentration column is that, if you have just a bare minimum detectable concentration (0.1 g/liter) in the sampled air, you never get 0.1 g/liter at the detector; you have considerably less. We have a line by-passing the concentrator when you have a high concentration out there, such as 1, 2, or 10 g/liter. Then, you could not wait for up to 8 min for this detector, so you have a by-pass line giving you 10 liters flow. The sorbent material we used was Porapak N.

Discussion

Dr. J. Taylor: What material is the case?

Mr. Behringer: It is Teflon.

Dr. Hughes: Are you using nitron gas for a detector, or what sort of a detector are you using?

Mr. Behringer: I am using a liquid alarm system, based on the principle Dr. Barrett mentioned, and a solution which gives cyanide detection by silver and platinum. I further point out, that in this particular module, as an overall part of the entire combat vehicle alarm system, we put almost all the electronics for the system. Miniaturization and reliability of equipment is a crucial item in something like this. To heat the column we developed, we raised the temperature to 175°C. This is a small glass tube *with Nichrome wire inside, and polymer beads located below at ambient temperature. If you collected sample for 8 min when the valve was switched on and the air was purged down, this would heat up; and the heat drives the collected agent off the column so it can be detected. Here is a breadboard model of a straight concentrator. We had this packed with 10 mg of Porapak material.*

Just a few things about the Porapak material. I didn't bring along any curves or graphs of agent desorption, but maybe just a few words. We found that after the repeated cycling of this material - 8 min collection, 2 min heat, repreated time and time again - for thousands of temperature cycles, they could collect the organophosphorous compounds and get it desorbed again. The collection was almost 100% efficient for collection and almost 100% efficient for eluting. A very good material for our applications.

And as far as interferences go, if one had started collecting interferences - the interference for the innate alarm, which might, of course, be cyanide - you would start getting purges in high concentrations of that and you would be building yourself a false alarm, which is what we do not want. This material either doesn't adsorb it, or, if it does adsorb it, doesn't give it back up. It was an irreversible thing, because we do have specificity for organic compounds.

One of the disadvantages is that it appears to go through a sort of conditioning period when we first get started with the material. When we first put one of these gadgets together and go through the first few, maybe 10 or 15 cycles, we are getting fairly high effusion of burn-off material. Sometimes pre-purging the column with dry nitrogen gives you a column that works fine right from the word "go", and sometimes it doesn't work. But after you have a stable column, if you stop for a couple of weeks and start back up again, then you have to recondition the column. That's about the main disadvantage of the material we have.

In order to calibrate our equipment, we have to know what we are generating. So we use a small portable generator which works at 110 volts. We can generate the very low concentrations of toxic materials that we need to expose to our detector. In this bubbler we put 0.1 cc of our compound and 25-30 cc of ethylene glycol. For the small pump, a low amount of air is diluted over this line. We have a very controllable concentration coming out.

There was discussion the last day or so about pumps, and how small pumps are needed. This pump housing has a single motor which pushes 2 pumps. The peristaltic pump, driven by the same motor, is off the same shaft. That is, of course, a 24 volt motor. We developed it.

Dr. Dravnieks: *How fast does it move air?*

Mr. Behringer: *1 liter/min. After you have finished concentrating through the column, and switch valves to purge the column, you get a pressure drop of approximately 7 or 8 inches of water through the column.*

GENERAL DISCUSSION

- Afternoon Session -

Suggested topics:

a) Evaluation of Sorbent Materials for Operational Reliability

b) Prediction of Sorbent Materials Use for Other Chemicals

c) Chemical vs. Thermal Desorption

Mr. Crable: Dr. Mieure has a topic that came up yesterday, and I thought we'd let him start the discussion.

Dr. Mieure: In a lot of our work, we tried to sample quantitatively and were not getting breakthrough of the components of interest to us. Some work has been done in Europe, where they have deliberately sampled large volumes for long periods of time so that they got complete breakthrough of the adsorption tubes for every component that they were trying to measure, and then they analyzed the adsorption tubes for the amount of material in the tubes. This is still a concentration-related value, but you don't have to worry about loss of material because of exceeding the breakthrough volumes.

There are some other problems with this method. For one, I think you have to standardize for each component.

Dr. Dravnieks: In considering fluidized beds, all these vapors get at each particle. One bed does not remove anything substantially. 99 percent of the vapor goes through, only 1 percent gets caught gradually, and, after a while, whatever amount goes in is exactly what goes out. About 20 minutes is enough to equilibrate each particle. You have to calibrate with these vapors, and that's essentially the same as continuing a test on a solid sorbent bed until materials start breaking through.

Mr. Crable: Dr. Ballou, do you have a comment?

Dr. Ballou: In order to predict the amount adsorbed for a single component, you have to know the isotherm on that adsorbent. When the adsorption of multiple components is to be predicted, you have to know the isotherms for the particular mixture of components; or else the isotherms of the individual components and, in addition, a suitable theoretical framework to predict blocking or enhancement in mixed adsorption.

Dr. Dravnieks: It depends on what vapor concentrations you work with. If it's concentrations of the order of trace contaminants in air, the vapors do not influence each other very much.

Dr. Ballou: That is a good point. At very low concentrations, multiple vapor species can be adsorbed without interfering with each other. However, it is primarily the concentrations of components on the surface of the adsorbent, rather than in the vapor phase, that must be considered in multiple species interaction. This will be determined by the adsorption potential of the species, the surface area of the adsorbent bed, the vapor flow rate, and the length of time of vapor flow, as well as the concentrations of adsorbable vapors in the influent gas phase.

Dr. Barrett: I wonder if this theoretical material applies to a porous polymer like Porapak, as distinguished from sorbents that consist of liquid films and inert solid substrates.

Dr. Mieure: I can see how the principle could apply. I don't say whether it does or not.

Mr. Crable: Dr. Wood, do you want to comment?

Dr. Wood: I would think this method would only be valid if the concentration was constant throughout the sampling period. If there were variations, this would not be a valid method of determining adsorbent capacity.

Dr. Mieure: It would still reflect the concentration change, but it might not reflect it in a way which could be interpreted analytically.

Dr. Hughes: I think the method would only be applicable to a liquid coated support, because, in a porous polymer, there are sites available for adsorption on the solid surface. The dynamic equilibrium between liquid phase and gas phase, that you have on the liquid coated support, is not present.

Dr. Barrett: You have liquid solvent and the solid phase confused. You don't have diffusion in the same manner with a single substance, a solid polymer.

Dr. Mieure: But still, if you sample on a solid sorbent, (say, porous polymer beads) until the compound has broken through, the amount of material on the column is in proportion to the concentration that is coming into the column. If you do not wish to exceed the retention volume of the components and prefer trying to collect quantitatively, there is an alternate way of doing it.

Dr. Dravnieks: Fixed polymer beds are used to sample fluorides, and, if there are very many different types of vapors present, a potential problem develops. In order to determine whether formaldehyde, for example, is breaking through from a 10-liter sample of mixed gases, we have to know which species are breaking through after equilibration with the polymer. For these species, the concentration in the effluent stream will not increase any more with duration of sampling. The amount collected would not increase, but would be proportional to the influent vapor concentration. For other compounds, which have not broken through yet, the collection is complete. As the vapor sample size is increased, more and more components break through.

With Chromosorb 102, for instance, you can predict what is going to break through from the tables of adsorption coefficients for various substances. If you know pentane breaks through at 14 liters, for example, then substances with a higher adsorption coefficient from a non-polar phase, would be retained better than pentane.

Mr. Crable: Dr. Klier, did you have some comments you wanted to make?

Dr. Klier: I would like to understand the phenomenom of breakthrough. Is it something that happens after the surface is saturated with the adsorbate in the influent gas phase?

Dr. Dravnieks: It indicates equilibration.

Dr. Teass: It apparently involves equilibration, because if you saturate the adsorption tube, the amount that remains on the adsorbent in the tube is dependent on the concentration, or the partial pressure of the adsorbate above the charcoal bed during equilibration.

Dr. Klier: In other words, this refers to reversible adsorption.

Dr. Dravnieks: Not totally reversible, because you need a little heat to complete desorption in a reasonable time.

Dr. Klier: The question I have is, whether the sensitivity of the analytical method would need to be the same on a column in which the adsorbate had broken through, and on a sample equilibrated in the same system without breakthrough. It seems to me the conditions of reversible equilibrium might not be different.

Mr. Crable: Dr. Teass, would you like to give us a rundown on the way our laboratory evaluates charcoal adsorbents?

Dr. Teass: Currently we evaluate the adsorptive properties of activated charcoal, in the sampling tubes OSHA purchases, only by determining the percent of desorption of selected compounds upon treatment with carbon disulfide. We are investigating the possibility of also using breakthrough data. We would then determine the effective capacity of 100 mg beds of charcoal for selected compounds at concentrations of interest, say one to three times the threshold limit value of the contaminant.

Dr. Ballou: Have you made a decision as to whether the adsorbent tube capacity should be twice the TLV for 8 hours, or three times, or some other limiting capacity? Is there any guideline for required capacity for a particular species?

Dr. Teass: We haven't obtained enough data to fix the desired capacity, because the capacity changes with the concentration of the vapor in the influent stream.

Dr. Ballou: In enforcement of the toxic limit in workplace environments, you really want to sample from concentrations that are over the TLV.

Mr. McCammon: We look at five times the TLV concentrations and we usually put a volume limit on the sample. This could be, for example, 10 liters at a concentration five times the TLV, so that we will not exceed breakthrough at high concentrations. In field samples, that is not always possible.

Dr. Teass: In the material we have published we have broken that rule several times.

Mr. McCammon: Right. But before we talked only about breakthrough instead of capacity. It was only recently that we started thinking in terms of capacity.

Dr. Teass: The two are interrelated.

Mr. McCammon: Yes, but breakthrough is what we have really been interested in, on a practical basis.

Dr. Ballou: You are talking about breakthrough occurring at approximately five times the TLV?

Mr. McCammon: Right.

Dr. Ballou: Breakthrough is determined by bed geometry and flow rate, as well as capacity. In sampling, you wish to avoid breakthrough before the bed capacity has been used.

Mr. McCammon: We used to define breakthrough as 0.1 milligrams of the contaminant species found on the backup adsorbent tube. Now we define it as finding an amount on the backup tube equivalent to five percent of the main adsorbent tube capacity, or equivalent to adsorption of five percent of the influent concentration.

Dr. Teass: Using our experimental breakthrough curves, we now define breakthrough as that point where the concentration of the contaminant in the effluent from the bed is five percent of the influent concentration.

Dr. Lonnes: There are actually two different regimes in this type of sampling. One is similar to the conditions in gas chromatography. If a compound is injected it takes a characteristic time for the peak to come out of the chromatographic column. The time does not change with concentration in this range, as the coefficient of adsorption is independent of concentration.

At higher concentrations, the partition coefficent for adsorption becomes a function of concentration, and so there is a dependence of breakthrough time on concentration. In using an adsorbent to collect all the influent material, you should be in the lower concentration range, so that breakthrough time is independent of concentration of the contaminant species in the influent vapor.

Dr. Teass: We can still use the amount collected in the adsorption tube as an absolute sample, as long as we don't exceed the breakthrough volume.

Dr. Lonnes: Right, but one cannot make an absolute statement on the capacity of a sampler in terms of mass adsorbate, because it is always related to the influent concentration. So you can't say, "I can collect so many milligrams". You can say, "I can't exceed a certain balance". The limiting capacity has to be a function of vapor concentration.

Dr. D. Taylor: I think it's important that we have a list of what parameters we need in order to determine if the charcoal tube, or whatever type of sorbent we are using, is suitable for use for a particular adsorbate. We have talked about capacity and desorption. Are these the only things that need to be looked at in terms of evaluation, or are there other characteristics that are just as important?

We have looked at desorption efficiency initially, and now we are beginning to look at total tube capacity. What other characteristics are important in terms of evaluation?

Dr. Ballou: How about surface migration? With two sections in the tube, the adsorbed species can migrate from one section to the other on storage. Then, it cannot be determined whether it actually broke through the first section during sampling.

Dr. Teass: I was going to bring that up. The adsorbate often does appear to migrate upon storage.

Dr. Lonnes: Dr. Klier was asking a question which goes back to how you define capacity of these adsorbent sampling columns. In the lower concentration range where the partition coefficient of adsorption is independent of concentration, you may look at the amount of time of flow through the adsorbent. As in gas chromatography, an injected adsorbate sample will finally exit as a peak from the column, with a characteristic elution time. The elution time of the peak can be correlated with the breakthrough time, when exposed to a constant influent *concentration. Conversely, when breakthrough is complete, that time would be equivalent to the peak maximum retention time in gas chromatography. So, if you think of the adsorbent tube as a gas chromatographic column, the breakthrough is where the peak maximum is eluted.*

Dr. Klier: *I have a feeling the sorbent capacity is a different thing.*

Dr. Teass: *A lot of threshold limit values are higher than this concentration, which is in the realm of Henry's Law. The capacity which we are defining, the breakthrough volume so to speak, does not reflect the GC retention time at this temperature and under these conditions. Thus, the charcoal tube is apparently not a GC column under the required sampling conditions.*

Dr. Lonnes: *The experiments can be done with the GC experimental approach. If a certain concentration value is exceeded, there will be a reduction in the retention time. This is also seen in gas chromatography. The retention time changes when the concentration changes.*

Mr. Hughes: *At the point that the retention time changes, you have reached the capacity of the column. As long as you are below this concentration, you refer to removing compounds through a column with specific retention times. This can be done up to the point where you exceed the equilibrium capacity of the adsorbent tube. This is the situation referred to as volume capacity, but the volume of air has nothing to do with this capacity.*

Dr. Teass: *In the case of the sorbent tube functioning as a GC column the carrier gas (air) sweeps the analyte through the column, but a large amount is retained by the packing.*

Dr. Hughes: *That is because a porous solid has a much higher capacity than most GLC columns, with liquid on solid supports.*

Dr. Zlatkis: *Will you tell me whether you are talking about total capacity or breakthrough capacity?*

Dr. Teass: *For our purposes, we monitor the effluent until the tube is saturated, and we measure time from the moment of contact of the influent sample with the sorbent bed. Total capacity is calculated from the area bounded by the detector signal output for the effluent concentration.*

Dr. Hughes: *I think capacity has nothing to do with the total amount of gas flows over the adsorber.*

Dr. Lonnes: *I think the best way to look at this problem is to look at capacity as a function of inlet concentration. If you plot this, you will find that the capacity will increase up to a hypercritical concentration. At this point the capacity begins to fall off with concentration.*

Dr. Klier: *It seems to me that, in the Henry's Law region, the capacity should inherently reflect the inlet concentration. Therefore the capacity does depend on the partial pressure of the contaminant in the inlet gas stream.*

Dr. Teass: *We find that when we go from 12 ppm to 190 ppm toluene in air the effective capacity of a 100 mg bed of charcoal increases from 19 mg to 28 mg of toluene, whereas the amount of air which can be sampled before breakthrough drops from 420 liters to 39 liters.*

Dr. Ballou: *I think most occupational contaminant vapor sampling situations are in the Henry's Law region. The isotherm regime at low vapor concentrations will depend also on the saturation vapor pressure of the species being adsorbed.*

Dr. Wood: *In the tube containing the adsorbent, there is a differential in vapor concentration. At the breakthrough point, or just before it, the vapor concentration is, essentially, zero.*

Dr. Hughes: *Let us consider the case of a charcoal that has 40 mg of toluene capacity and 40 mg of toluene is injected. If a flow of toluene in carrier gas is then started through the bed, do you immediately have the inlet concentration of toluene coming out the other end? The bed is saturated, but does it not still take a relatively long time before equilibration?*

Dr. Teass: *I can't answer that, but I think I will have the experiment run. We have not looked at bleedout.*

Dr. Tiernan: *We have't done any bleedouts either. That area has been neglected.*

Mr. McCammon: *What about flow rates? We are now recommending, in some cases, flow rates as low as 50 ml/minute instead of a liter/minute. What will this do to our capacity, and will we see a bleedout effect?*

Dr. Ballou: *The Henry's Law region is the linear part of the isotherm at low pressures. With increasing pressure, the isotherm generally deviates concave to the pressure axis.*

Dr. Klier: *There are five Brunauer types of isotherms. Some of them have curvatures the other way.*

Dr. Ballou: In most situations of trace contaminant vapor sampling, I believe type II isotherms would be applicable, and the partial vapor pressure of the contaminant species is low enough that the relation of the equilibrium volume adsorbed to the partial pressure would not be above the region of the isotherm concave to the pressure axis. However, in all isotherms, the volume adsorbed at a given temperature either remains constant or increases as pressure is increased in any part of the isotherm regime.

Dr. Klier: What is the desirable range of the heat of adsorption for collecting samples?

Dr. D. Taylor: I think two things should be kept in mind. One, the sorbent capacity has to be such that you can sample easily, say, one tenth to five times the threshold limit concentration or federal standard for a particular vapor species. That is the practical range desired for sampling. Regarding the heat of adsorption, it would be very nice to have it as relatively low as possible so that you don't require a high temperature difference in the heating cycle prior to desorption.

Dr. Lonnes: The heat of adsorption stays pretty much the same over quite a wide range of temperature. I haven't noticed any significant change in the heat of adsorption on a porous polymer from 25 to 150 degrees.

Mr. Crable: I think that is right, but there seems to be a range of heats of adsorption in Dr. Wood's examples. He has what he calls an irreversible portion of the isotherm and a reversible portion. It's been mentioned that occasionally you see two desorption peaks from the same adsorbate.

Dr. Hughes: This is very similar to our findings when SO_2 *is adsorbed on molecular sieve 5A. You can flow air across the sample for days and a certain amount desorbs, but a certain amount, called irreversible, remains adsorbed on active sites. Most of this latter amount can also be considered reversible under different conditions, as 85 percent is removed by heating.*

Dr. Lonnes: If you have a problem in desorbing a sample, you probably have much adsorbate on high energy sites.

Mr. Crable: I have a question. We have been trying to match various chemical species with suitable adsorbents. What is the possibility of modifying this procedure by preparing adsorbent samples with surfaces that meet our needs, as far as sampling given chemical species is concerned.

Dr. Klier: I think this is possible, but not at the moment. One, can for example, prepare a selective cobalt zeolite for NO_2 *adsorption.*

☆ U.S. GOVERNMENT PRINTING OFFICE: 1976—657-696/5582

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HEW Publication No. (NIOSH) 76 – 193