

PROJECT FIRESMOKE

A JOINT USFA / NIOSH
STUDY OF FIREFIGHTERS



Sampling Protocols and NIOSH Human Subjects Research Participation Document

U.S. Department of Health and Human Services

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Center for Disease Control

National Institute for Occupational Safety and Health

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Preface

This document is a comprehensive protocol for the "Project Firesmoke" study conducted jointly by the National Institute for Occupational Safety and Health and the United States Fire Administration. It presents the criteria which will be followed by the Injury Prevention Research Branch of the Division of Safety Research and the Environmental Investigations Branch of the Division of Respiratory Disease Studies.

This outline is presented to inform interested parties of the purpose, methods, and materials to be used for conducting field studies for this project. However, any changes or deviations from these guidelines will be made as professional judgement deems necessary.

Disclaimer

Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

1. TITLE AND DESCRIPTION

Title: Project Firesmoke

General Description: The purpose of this project is to develop recommendations for improving the safety and health of firefighters regarding the selection and use of respiratory equipment during firefighting and overhaul activities.

2. INVESTIGATORS/COLLABORATORS

- a. Gary P. Noonan, Project Officer
- b. John T. Jankovic, Principal Investigator
- c. Judith A. Stevens, Investigator

3. METHODS

For a complete description of the methods to be used in this project refer to the appropriate "methods" section of this document.

4. PARTICIPANTS

The study participants will be trained, experienced firefighters who are performing in their normal capacity. Nothing additional will be requested from the participants except monitoring of their exposures, a pre- and post-exposure exhaled breath carbon monoxide sample, and a quantitative fit test.

5. INFORMED CONSENT PROCEDURES

Each potential study participant will be asked to read a copy of the NIOSH human subjects research participant document which was prepared for this study. A copy of the consent form is contained in Section C. A NIOSH representative will be available to answer any questions that are asked regarding the tests and procedures of this research study. Two copies of the consent form will be signed and dated by both the test subject and the NIOSH representative. One copy is for a test participant's records and the other copy will be maintained by NIOSH. Participants will be informed that they may voluntarily terminate their participation in the study without any prejudice to themselves.

6. RECORDS MANAGEMENT

No sensitive data will be collected and no identifying information, including the names of test subjects, will be used. Participants will be identified simply as subject A, B, C, etc. Signed NIOSH human subjects research participant documents will be maintained for at least ten years after the completion of the study in a locked file cabinet in the office of the Chief, Field Investigations Section, IPRB, DSR, NIOSH.

7. ASSURANCE OF CONFIDENTIALITY

A formal assurance of confidentiality is not necessary for this study.

8. EMERGENCY PLAN

In case of an emergency the fire department at the site will utilize their emergency action plan.

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I. Introduction

1.0 Purpose of Study

The purpose of the agreement between the Federal Emergency Management Agency/United States Fire Administration (FEMA/USFA) and the National Institute for Occupational Safety and Health (NIOSH) is to support both organizations' need to confirm the adequacy of SCBA to protect firefighters engaged in structural firefighting. This project will be a logical and necessary adjunct to two previous fireground studies which identified fireground contaminants and indicated a need for additional research in this area. In addition, this project will help to:

- a. Reinforce firefighter awareness of the need to wear SCBA during fire suppression and overhaul stages of fires.
- b. Identify fireground contaminants.
- c. Contribute to the data base needed by the Fire Service in order to better understand the relationship between fireground exposures and acute/chronic health effects.
- d. Develop recommendations for improving the safety and health of firefighters regarding the selection and use of respiratory equipment during firefighting and overhaul activities.

2.0 Background

Two previous studies, "Investigation of Combustion Atmospheres in Real Buildings"⁽¹⁾ (USFA Grant Number 80027) and "Air Contaminants in Structural Firefighting"⁽²⁾ (National Fire Prevention and Control Administration Grant Number (7X008) provided the fire service with evidence that indicated that self-contained breathing apparatus should be used during structural firefighting. The former study took place in Boston and the later in San Antonio.

The Boston study was jointly funded by the Department of Commerce/NFPCA and the Society of the Plastics Industry (SPI). The study was performed by the Harvard School of Environmental Health in cooperation with the Boston Fire Department. The San Antonio study was jointly funded by the Federal Emergency Management Agency/United States Fire Administration (FEMA/USFA) and the work was performed by Southwest Research Institute in cooperation with the San Antonio Fire Department.

In both studies, airborne concentrations of certain toxic gases, vapors and particulates were obtained by firefighters while fighting structural fires. The results of the studies were generally consistent. As a result of the Boston study, a mandatory mask rule was enacted in the Boston Fire Department (Appendix I). This rule enabled the Boston Fire Department to significantly reduce the number of smoke inhalation injuries occurring in the

department and the rule served as a model for other fire departments.

The San Antonio study, basically affirming the findings of the Boston study, indicated the need for increasing the data base that has been generated by these two studies. However, areas of information which still remain deficient are SCBA performance in actual firefighting situations and the characterization of organic combustion products and respirable particulates. For the same fire, collection and analysis of contaminants during the fire suppression and overhaul stages has also been identified as a research need.

The Division of Safety Research (DSR) and the Division of Respiratory Disease Studies (DRDS) of the National Institute for Occupational Safety and Health have been contracted to perform a two-phase study involving a performance evaluation of SCBA's and a characterization of the contaminants of exposure during firefighting activity.

Laboratory investigations have shown that air pressure inside the mask of the positive pressure SCBA can go negative at work rates that are similar to those experienced during firefighting activities. However, a field study has yet to be conducted during actual firefighting conditions to investigate the pressure variations and/or in-mask leakage within the facepiece of a

positive pressure SCBA. This project will be located within DSR and the Division will provide respirator research expertise. Industrial hygiene expertise will be coordinated with DRDS.

3.0 Study Design

This project will be conducted in two phases. Phase I (Control Phase) will involve preparation necessary for the field studies to be accomplished during Phase II (Fireground Phase). The feasibility and practicality of a personal monitor for recording in-facepiece pressure fluctuations and of conducting a workplace protection factor study of SCBA's will be determined. Methods of collecting and analyzing personal and general area samples will be evaluated at a site selected by the USFA. The International Association of Firefighters will be solicited for its input during the project.

Field studies will be conducted at four sites. Participants will be briefed and updated during the project. Based upon analysis of field work, recommendations for improving the safety and health of firefighters regarding the selection and use of respiratory protection during firefighting and overhaul activities will be made.

4.0 NIOSH Responsibilities

In accordance with this interagency agreement (#EMW-85-E-2131), NIOSH will:

Phase I

- a. Investigate the feasibility and practicality of a personal monitor for recording in-facepiece pressure fluctuations.
- b. Investigate the feasibility and practicality of conducting a workplace protection factor study of SCBAs. A workplace protection factor is defined as the estimated contaminant concentration to which a user would be exposed if not wearing a SCBA, divided by an estimate of the SCBA user's actual exposure.
- c. Review previous studies to evaluate methods of collecting and analyzing both personal and general area samples.
- d. Develop a protocol for the collection of personal and general area samples using the results of previous research studies conducted at fire sites.
- e. Conduct a preliminary field evaluation of the proposed sampling methods at a site selected by NIOSH and approved by the USFA.
- f. On a continuing basis, inform an IAFF contact person regarding the development and implementation of this project, and

solicit IAFF's input regarding the critical issues of the project.

- g. Finalize the study protocol and identify three study sites for Phase II. USFA must approve the study protocol before proceeding with Phase II of the study.

Phase II

- h. Conduct orientation of volunteer test subjects, their supervisors and union representatives concerning the study protocol. This will be done jointly by NIOSH and USFA.
- i. Conduct field research i.e., data collection and analysis of samples.
- j. Participate with USFA in briefings to provide fire departments and participants with updates of project activities.
- k. Prepare a final report to the Directors, NIOSH and USFA. This report should include a description of sampling methods, sampling data, and recommendations for improving the safety and health of firefighters during firefighting and overhaul activities.

1. Co-author at least one manuscript with USFA for submission to a fire service publication and author at least one manuscript for submission to a peer-reviewed technical journal.

Protocol to Evaluate the Performance of SCBA Used by
Firefighters During Actual Firefighting Situations

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II. Protocol to Evaluate the Performance of SCBA Used by Firefighters During Actual Firefighting Situations.

1.0 INTRODUCTION

Firefighters face many health hazards due to the dynamic occupational environment in which they must operate. During the past ten years, researchers have begun to characterize the hostile, life threatening environments which confront firefighters. Personal sampling data collected during actual firefighting episodes have demonstrated that there are possible exposures to many substances which may endanger life⁽¹⁻⁶⁾. Substances such as carbon monoxide, carbon dioxide, hydrogen cyanide, particulates, benzene, nitrogen dioxide, hydrogen chloride and acrolein, are but a few of many possible exposures. In most situations, however, the primary respiratory hazard is exposure to carbon monoxide and low oxygen levels. In fact, autopsies demonstrate that the cause of civilian fire deaths is usually carbon monoxide poisoning rather than burns⁽⁷⁾. Most reports to date contain exposure estimates for carbon monoxide which exceed the current ACGIH short term exposure limit (15 minutes) of 400 ppm⁽⁸⁾. Three of these reports^(1,4,6) contain exposure estimates which approach or exceed carbon monoxide's estimated short term lethal concentration (5 minutes) of 5000 ppm⁽⁹⁾. The NIOSH recommended exposure limit for carbon monoxide is 35 ppm (8-hr TWA) with a ceiling value of 200 ppm (no minimum time)⁽¹⁰⁾.

Attempts to reduce the extreme health risk associated with the inhalational hazards of firefighting require the conscientious use of the most protective respiratory protective equipment, the self-contained breathing apparatus (SCBA). While SCBA are certainly to be selected for firefighting over any other class of respirator, there have been those who have questioned the extent of the protective capabilities of both demand⁽¹¹⁻¹⁷⁾ and pressure-demand SCBA⁽¹⁸⁻²³⁾.

The danger from exposures to high carbon monoxide levels and other substances is clear but it is difficult to estimate the risk of exposure to the firefighter since no systematic attempt has been made to evaluate the performance and protectiveness of the SCBA to the firefighter under actual work conditions. This study will help define what respiratory protection is provided by the SCBA under actual conditions of use and further define hazardous contaminants at fire scenes.

2.0 BACKGROUND

Two types of SCBA use compressed air: demand and pressure-demand. Some units can be operated in either mode. In the "demand" mode, a slight negative pressure opens the supply air valve; in "pressure-demand" mode a slight positive pressure is maintained in the facepiece. If leakage occurs because of poor fit in the pressure-demand mode, the air supply is exhausted much more rapidly than if all the air was used for breathing⁽²⁴⁾.

OSHA Standard 1910.156⁽²⁵⁾ requires the use of only pressure-demand SCBA by fire brigade members while performing interior structural fire fighting. This requirement is based on the belief that the slight increase in pressure inside a SCBA wearer's facepiece relative to ambient pressure will prevent the inward leakage of contaminants. However, the results of laboratory experiments^(18-23,26,27) have suggested that the in-mask pressure of pressure-demand SCBA might go negative at work rates experienced by working firefighters, and thus permit the inward leakage of contaminants.

A study designed to evaluate carboxyhemoglobin levels (CoHb) in the blood of firefighters concluded that demand SCBA were protective, but that the difference in mean CoHb levels (pre- and post-exposure to carbon monoxide) between firefighters who used SCBAs and those who did not was minimally significant⁽¹¹⁾. In addition, a study designed to evaluate CoHb levels in the blood of firefighters during controlled situations also concluded that demand SCBA provided protection from the inhalation of carbon monoxide, providing they were worn when work was done in a burning or recently burned structure⁽¹³⁾. The increased risk of overexposure created presumably by intermittent SCBA usage has also been suggested by other researchers^(12,14-17). An important finding of a study which was published in three versions^(12,15,17) was that while the continued use of a demand SCBA offered protection from the inhalation of carbon monoxide, its intermittent use provided as little protection from exposure as did nonuse. This conclusion was based on the results of CoHb sampling. Coincidentally, measurements of

serum thiocyanate made during the same study⁽¹⁴⁾ to evaluate exposures to hydrogen cyanide did not result in the observation of the protective effect of demand SCBA noted previously with carbon monoxide^(12,15,17).

Finally, the authors of a study⁽¹⁵⁾ designed to measure acute changes in the ventilatory capacity of firefighters observed large decreases in FEV_{1.0} (forced expiratory value in 1 second) associated with the use of demand SCBA. A mean $\pm$ FEV_{1.0} of 0.21 liter was reported for five occasions when SCBA were used. The reason for this decrement was postulated to be due to (1) donning of the SCBA after significant exposure to irritant smoke, (2) facepiece penetration, or (3) removal of the SCBA before it was safe to do so.

The purpose of this portion of the project is to investigate the protective capabilities of pressure-demand SCBA during actual firefighting episodes. This will be accomplished by collecting in-mask pressure measurements real-time and by collecting air samples both inside and outside the facepiece of a firefighters' SCBA. Additionally, a pre-shift and post-exposure expired carbon monoxide breath sample will be collected from each firefighter.

3.0 PROTOCOL

This section contains a detailed description of 1) the sampling strategy; 2) laboratory testing of SCBA; 3) sampling methods; and 4) field activities.

The project will be conducted in the following order;

1. SCBA units received from manufacturers.
2. SCBA units modified with pressure sampling and air sampling facepiece probes by FIS/IPRB/DSR/NIOSH.
3. Laboratory testing of SCBA units by Certification Branch, DSR, NIOSH.
4. Field Study
 - a. Project described to firefighters
 - b. Signing of consent document
 - c. Quantitative fit testing
 - d. Pre-shift exhaled breath sample collection and questionnaire
 - e. Measurement of CO in SCBA breathing air
 - f. Fire episode - pressure measurement, air sampling
 - g. Post fire episode exhaled breath sample collection
 - h. Post fire episode questionnaire

3.1. SAMPLING STRATEGY

3.1.1 Field Study Site Selection/Sample Size

Field studies will be conducted in five major cities which have large fire departments. These cities are Pittsburgh, New York City, Phoenix, San Antonio, and Boston. One of the considerations

in selecting these cities is that in the two-week period of the study there should be enough firefighting activity to gather a required number of samples. In order to have statistically significant data, a minimum of 275 samples of each of the different types of data (environmental data, facepiece pressure data, temperature data, etc.) will be collected. The sample size is based on a 95% confidence interval of the assigned protection factor value of a pressure-demand SCBA, 10,000. After the collection of 30 sample sets the protection factors and standard deviation will be calculated. If these values differ greatly from the estimated values used to compute the sample size a recalculation of sample size will be performed using these revised estimates. The sample size equation derivations and calculations are contained in Appendix II.

NIOSH will stay at a survey site until 30 samples are collected. A lower limit will be set at 0 samples in three days and an upper limit of 100 samples in ten to twelve days.

3.1.2 SCBA Selection

Participants will wear SCBA that has been modified by DSR/NIOSH to accommodate the sampling devices. The SCBA will be identical to that the firefighter normally wears except for the modifications. Using SCBA the firefighter is already familiar with and has confidence in will minimize training needs.

3.1.3 Firefighter Selection

All firefighters on the unit to which NIOSH is assigned (who have granted consent) and who wear SCBA while performing their job will be sampled. In New York City (NYC), for example, there are four people including the driver on a ladder truck, and there are three people including the driver on the pumper truck. We would expect to sample three to four SCBA-wearing firefighters at each fire episode in the above example. In other cities this may differ. The maximum number of personal samples to be collected at one time at a fire episode will be five. This number is based on the number of firefighters who will typically be wearing SCBA, the complexity of taking this type of sample at a fireground, the number of industrial hygienists available to monitor the firefighter and the availability/cost of the equipment and analysis.

3.1.4 Shift Sampling

An attempt will be made to optimize the number of people that NIOSH has working on a shift by working at a time when a fire is more likely to occur. For example, in NYC most fires occur between the hours of 4:00 p.m. and 2:00 a.m. Therefore, we will try to work those hours. These times may differ at the other study sites.

3.2 Laboratory Testing of SCBA

Prior to field testing all SCBA that will be used by firefighters will be inspected by personnel from the Certification Branch of the Division of Safety Research, NIOSH. Laboratory performance testing will be performed as specified in 30 CFR Part 11. Only SCBA units which pass these tests will be used in the field study. Records of the laboratory testing will be maintained by the DSR Project Officer.

3.3 Sampling Methods

3.3.1 Sampling Apparatus Requirements and Design

Firefighters have indicated that the sampling apparatus should be lightweight, of minimum bulk and self-contained. The sampler must also be rugged and insensitive to the extreme environmental conditions to which it may be exposed. Sampling apparatus location was also an important consideration. The most appropriate location was determined to be the SCBA harness or backframe. The sampling apparatus would need to be mounted in such a way as to be of minimum hindrance to the firefighter when he was (1) putting on the SCBA and (2) changing SCBA bottles. An operating time for the sampling device of 45 minutes was required. This is based on an over-estimation of the time a 30-minute SCBA could be continuously used and on the estimated duration of most fires.

3.3.2 Respirator In-facepiece Pressure Monitoring

To measure and collect SCBA in-facepiece respirator pressures, a dynamic pressure sensor and portable data logging unit were devised. The pressure sensor will be located in a lightweight metal case mounted to the harness. The sensor measures pressures in the range of ± 5 inches of water. One pressure port is left open to ambient atmosphere while the other port is connected by silicone tubing to the inside of the respirator facepiece. The pressure sensor connected in this manner measures a differential pressure or the pressure inside the respirator facepiece. The case containing the pressure sensor will be insulated to insure that the temperatures inside the case do not exceed the operating range of the sensor. Pressure data will be collected real-time by a portable data logging unit which was constructed for this specific application. The unit is a self-contained unit which is powered by a 12 volt battery supply. Negative pressure excursions inside the SCBA facepiece have been measured, in the laboratory, to last as short as 50 milliseconds⁽²⁷⁾. Therefore, the data logging unit was designed to record pressure samples every 50 milliseconds. The accuracy of the pressure sensor is $\pm .02$ inches of water.

The data from the data logging unit is transferred to an IBM PC compatible lap top computer. The lap top computer is uniquely suited for field applications since it is extremely mobile.

Software specifically designed for the project converts the binary data transferred from the logger via a 15 pin serial connection into readable form. The software allows the data to be stored on a 3-1/2" disk in file format for later analysis and also to be sent to a printer so that a hard copy of the data can be obtained. The data is output in line format which presents a pressure measurement every 50 milliseconds and also in a graph which presents pressure inside the respirator facepiece versus time.

3.3.3 Temperature Monitoring

Temperature exposure data will also be measured during each firefighting episode. This data will be collected by a Type J thermocouple assembly and recorded by the data logger once every 30 seconds. The thermocouple probe, which has a measurement range of +32 to 1382°F, will be mounted on the outside of the case containing the pressure sensor.

3.3.4 Air Sampling for WPF Determination

To measure the firefighter's exposures, two 3-liter "bag" samples will be collected from each SCBA wearer on the firefighting team. One sample will be an in-facepiece sample. This sample will be collected through a probe in the SCBA facepiece. Where practical,

the sampling probe location will be based on latest NIOSH research to minimize the amount of sampling bias⁽²⁸⁾. The tubing will be connected to the inlet port of a low flow air sampling pump which will draw air at a rate of 100 cc/min. Another piece of tubing attached to the exhaust port of the pump will be connected to an 3-liter tedlar air sample bag.

The lapel or outside facepiece sample will be collected in the same way except that the tubing attached to the inlet port of the air sampling pump will be in the breathing zone of the firefighter. A particulate filter will be attached to the open end of the tubing to ensure that particulates do not interfere with sample collection.

Bag samples will be analyzed utilizing a series of analytical devices including a real-time carbon monoxide analyzer, direct reading length-of-stain color indicating tubes and a Fourier Transform Infrared Spectrophotometer (FT-IR). Sampled gases will be systematically quantitated utilizing a combination of the above methods. Additional components of the air samples may be qualitatively identified.

By collecting air samples inside the facepiece and in the breathing zone of the firefighter a "workplace protection factor"⁽²⁹⁾ for the SCBA used during the study can be calculated.

3.3.5 Sampler Assembly and Operation

The pressure data logging unit and both low flow pumps will be contained in a metal case mounted to the backframe of the SCBA. The case with sampling apparatus inside weighs less than five pounds and will minimally interfere with the firefighters activities but also protect the sampling equipment. The two pumps and pressure data logging unit will be connected to one switch which will be mounted on the exterior of the case. This explosion proof switch will be mounted to allow the firefighter to activate the entire package himself with minimal effort.

The two sampling bags will be attached to the SCBA backframe harness. The bags will be placed inside a heat reflective fire resistant bag to ensure sample bag survivability in the harsh firefighting environment.

3.4 Firefighter Instruction

Each subject will receive a full explanation of the study protocol, including purpose, expected duration of subject involvement, procedures to be followed, reasonably foreseeable risks or discomforts and benefits to the subjects and others, confidentiality of records, voluntary nature of the study and whom to contact concerning questions related to the research.

Following this, an opportunity will be made available for both group and individual question and answer periods with the investigator. Finally, the participant and project officer will sign the informed consent form. The project officer will retain the signature page and the subject will retain the information portion of the form. The consent document is contained in this report as Appendix III.

3.5 Measurement of Carbon Monoxide Concentration in SCBA Breathing Air

Prior to the field survey a sample of air will be collected from each SCBA air tank on which respirator sampling will be performed. This will be done to quantitate the carbon monoxide concentration in the breathing air tank. A two-liter "bag" sample will be collected from the tank. Analysis for carbon monoxide concentration will be performed by a variety of methods including an Ecolyzer 2000 CO analyzer.

3.6 Quantitative Facepiece Fit Testing

Preshift fit factors will be measured using standard quantitative fit testing equipment and methodology. This will be done to document the "quantitative" respirator fit the SCBA wearer had on the day of field testing.

The test device will be a Dynatech Frontier model 2000 Respirator Fit Test Instrument. The test device will generate a polydispersed aerosol from reagent grade corn oil. The size distribution of aerosol will be approximately $.6\mu\text{m}$ with a geometric standard deviation of 2.0 - 2.2. Quantitative facepiece fit test procedures are given in Appendix IV.

3.7 Exhaled Air Samples

An exhaled carbon monoxide (ECO) sample will also be collected from each firefighter who has granted consent. This will be done both pre- and post-fire episode and will require the fire fighter to provide information concerning his smoking habits. The sampling procedure involves the firefighter taking a full inspiration, holding his breath for 20 seconds at total lung capacity, exhaling the initial 500 cubic centimeters (dead space and early aveolar air) into a discard bag and then exhaling expired aveolar air into a 2-liter, 5-layer polyvinyl collection bag. This procedure is given in detail in Appendix V. The sample will be analyzed using Fourier transform infrared (FT-IR) spectroscopy (Appendix VII). The carbon monoxide level in the expired air will be measured in ppm. The data will be used to estimate carboxyhemoglobin levels from known regression equations⁽³¹⁾.

3.8 Firefighter Monitoring

Each firefighter sampled will be monitored by an assigned industrial hygienist. The firefighter will activate his own sampling apparatus after donning his SCBA. The industrial hygienist will activate the apparatus if a request is made by the firefighter and if time permits. The industrial hygienist will stay in close proximity of the firefighter when possible and thus be able to document any noticed equipment malfunction. When the firefighter is changing air tanks the industrial hygienist, if possible, would be able to de-activate the sampling apparatus. If the sampling apparatus is not de-activated and the firefighter works longer than anticipated the sampling apparatus will simply "shut-off" and the information can be retrieved later.

3.9 Data Recording

At the initial training period an ID number will be assigned to each participating firefighter. The same ID number will be marked on all sampling performed on that firefighter. For pressure data files, the ID number plus a 1-digit number corresponding to the fire episode (starting with 1) will be entered into the computer system. For example a firefighter with ID number 0001 first pressure measurements on the first firefighting episode, the data file tag would be 00011. Air sample bags will be marked similarly. An "I" will designate an inside facepiece sample, with an "A" designating an ambient sample.

For example, an in-facepiece air sample taken on a firefighter with ID number 0001 on the first firefighting episode would be labeled 0001-I-1. The sample ID will be recorded on the "Respirator Air Sample Data Form" which is presented in Appendix VI. Quantitative fit test results and ECO results will also be recorded by firefighter ID number on the data sheet presented in Appendix VI.

4.0 Data Analysis

Each in-facepiece sample of carbon monoxide which exceeds the individuals baseline measurement of CO (pre-shift ECO) will be considered indicative of facepiece leakage. Samples that are greater than the baseline measurement will be indicative that inward leakage occurred. In addition, a workplace protection factor⁽²⁹⁾ will be calculated for each of the sample sets. This factor will be determined by dividing each ambient time-weighted average concentration of carbon monoxide by its corresponding in-facepiece time-weighted average concentration. A log-normal probability plot will be prepared using the workplace protection factors. The fifth percentile value will be determined by the method of Natrella described previously by Lenhart and Campbell⁽²⁹⁾. This value will represent the assigned protection factor for the pressure-demand SCBA used during this research study.

Pressure data will be analyzed to determine the percentage of time that the pressure in the facepiece remains positive. Any negative pressure excursions will be quantified and an attempt will be made to correlate

those events to physical phenomenon such as breaking facepiece seal
(i.e., to talk), high work rate, etc.

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Environmental Sampling Protocol

by

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1.0 Analysis of Combustion Atmospheres

Since the first wood fires were lit, thermal degradation of polymeric materials has produced toxic products capable of exerting a variety of physiological effects. Modern civilization recognizes that fire causes a health hazard not only for accidental victims but also for firefighters. In most instances, exposure of firefighters is chronic - less intense but steadily repeated.⁽³⁾

In any fire situation with mixed fuel, toxic combustion products are a heterogeneous mixture of gases, liquid droplets and smoke particulates.⁽⁵⁾ Carbon monoxide is the chief toxin, but other substances such as acrolein, HCN, HCL, HF and CO₂, which may be present in the smoke can be very hazardous in certain cases and might exhibit synergistic effects.⁽⁴⁾

1.1 Carbon Monoxide

Carbon monoxide is a colorless gas produced by incomplete burning of carbon containing materials. On inhalation, it acts as an asphyxiant causing a decrease in the amount of oxygen delivered to the body tissue. Carbon monoxide combines with hemoglobin to form carboxyhemoglobin, which reduces the oxygen carrying capacity of the blood.⁽⁶⁾

In most fire situations, the primary respiratory hazard is exposure to carbon monoxide and low oxygen levels. Autopsies consistently demonstrate that the cause of civilian fire deaths is usually carbon monoxide poisoning.⁽⁷⁾ In deliberate burning of dwellings and other structures, combinations of high CO

concentrations and oxygen deficiency have been found that only a few breaths would be fatal.^(8,9)

The American Conference of Governmental Industrial Hygienists (ACGIH) recommended standard for carbon monoxide exposure is 50 ppm Time Weighted Average (TWA) for a normal 8-hour workday/40-hour work week and 400 ppm for a 15-minute Short Term Exposure Limit (STEL). The NIOSH recommended permissible exposure limit is 35 ppm TWA with a 200 ppm ceiling limit. One other set of useful industrial exposure guides are the concentrations at which substances pose an Immediate Danger to Life or Health (IDLH). The IDLH is defined as the concentration from which a worker might escape within 30 minutes without irreversible health effects or any physiological effects which would impede escape.⁽¹⁰⁾ The IDLH level for carbon monoxide is 1500 ppm.

In the Harvard Study⁽¹⁾, CO was found in virtually all the fire environments studied. Approximately 15% of the samples exceeded the STEL level. One fire approached the level at which lethality (5000 ppm) would be anticipated after a 10-minute exposure. The San Antonio study⁽²⁾ showed similar levels of carbon monoxide. CO concentrations ranged from 24 to 7450 ppm with the median concentration of 50 ppm. The results of both these studies are consistent in that CO was the most prevalent combustion product in fire environments.

1.2 Hydrogen Cyanide

Two commercial aircraft accidents in the United States during the 1960's contributed greatly to the initiation of the present concern over

hazards of toxic gases generated in fires, and cyanide specifically. Those accidents were of special significance because careful analysis indicated that few, if any of the occupants could have suffered significant physical injuries from the relatively mild impact, yet a total of sixty persons perished as a result of thermal and chemical injuries sustained in the ensuing fire.⁽¹¹⁾ Hydrogen cyanide vapor, a source of cyanide ion, is an asphyxiant due to an inhibitory action on metabolic enzyme systems and can be rapidly fatal. A few inhalations of high concentration of HCN may be followed by almost instantaneous collapse and cessation of respiration; 270 ppm HCN is immediately fatal to humans, 181 ppm is fatal after 10 minutes, and 110 ppm may be fatal in 1 hour.⁽¹²⁾

The ACGIH recommends that exposures to HCN should not exceed 10 ppm for any part of the working exposure (Ceiling Limit). The NIOSH recommended ceiling limit is 4.7 ppm and the IDLH level for HCN has been established at 50 ppm.

Hydrogen cyanide can be formed in the fire environment from natural products such as wool and silk, and a variety of nitrogen containing polymers, including nitriles, polyamides, nylons and polyurethanes in furniture upholstery and building materials.⁽¹⁾

In the Harvard study⁽¹⁾, hydrogen cyanide was detected in 27 of 253 samples with a maximum concentration of 3.6 ppm. The San Antonio study⁽²⁾ detected HCN in 32 of 36 samples with concentrations ranging

from less than 0.05 ppm to 8.9 ppm. The data from those two studies indicate that HCN may be a prevalent combustion product of fire environments, but concentrations measured were not sufficient to produce toxic effect. However, with the ever increasing use of polyurethanes in the furniture industry, the potential for this toxic gas to be present in fire environments in disabling or even lethal concentrations does exist.⁽²⁾

1.3 Hydrogen Chloride

In a fire situation, hydrogen chloride (HCl) is usually attributed to thermal decomposition from Polyvinyl Chloride (PVC) products.⁽⁵⁾ HCl gas irritates the eyes, mucous membranes, and skin. Exposure to the gas immediately causes severe irritation of the upper respiratory tract resulting in cough, burning of the throat, and a choking sensation, if inhaled deeply, pulmonary edema may occur.⁽¹²⁾ The ACGIH recommends that exposure to HCl not exceed 5 ppm for any part of the working exposure (Ceiling Limit). The IDLH level for HCl has been established at 100 ppm.⁽¹³⁾

The Harvard study⁽¹⁾ detected HCl in 36% of the 242 samples collected, with a maximum concentration of 280 ppm measured during one seven minute fire. Thirty percent of the samples exceeded the ACGIH-STEL and two percent the IDLH. In the San Antonio study⁽²⁾, HCl concentrations ranged from 3.7 ppm to 232 ppm, with a median concentration of 15.1 ppm. In both studies, HCl was frequently present in concentrations above the ACGIH ceiling limit.

1.4 Carbon Dioxide

Carbon dioxide (CO_2) results from complete combustion of organic materials. Carbon dioxide gas is an asphyxiant, a potent respiratory stimulant, and both a stimulant and depressant of the central nervous system. The ACGIH standard for CO_2 is 5000 ppm TWA and 15,000 ppm STEL. The NIOSH recommended level is 10,000 ppm TWA, with a 10 minute ceiling of 30,000 ppm. The IDLH for CO_2 is 50,000 ppm.⁽¹³⁾

The Harvard study⁽¹⁾ analyzed 89 samples for CO_2 , 3 samples exceeded the ACGIH-STEL and one exceeded the IDLH level. Concentrations reported from the San Antonio study⁽²⁾ ranged from 400 to 16,400 ppm. Except for two samples containing 7400 to 16,400 ppm, the samples had less than 3000 ppm. It was concluded that CO_2 , by itself, does not pose a toxic danger to unprotected firefighters.⁽²⁾

1.5 Nitrogen Dioxide

Nitrogen oxides (NO_x) are considered the most likely pulmonary irritant in fire situations.⁽⁵⁾ Nitrogen dioxide gas is a respiratory irritant, it causes pulmonary edema, which is serious in itself or as a contributing factor with other fire injuries. Nitrogen dioxide and other oxides of nitrogen are produced in small quantities from thermo-decomposition of fabrics and in larger quantities from nitrogenous materials (e.g. nitrocellulose), or the fixation of

atmospheric nitrogen.^(1,14) The current ACGIH standard for NO₂ is 3 ppm TWA and 6 ppm STEL. NIOSH has recommended that this level be reduced to a ceiling level of 1 ppm averaged over a 15 minute period. The IDLH for NO₂ is 50 ppm.

Only four of the 240 samples collected for NO₂ during the Harvard study exceeded the ACGIH-STEL limit. The highest concentration noted was 8.3 ppm. The Harvard study concluded that NO₂ concentrations observed in their study did not constitute a respiratory hazard to firefighters. Nitrogen dioxide was not sampled for in the later San Antonio study.

1.6 Aldehydes

Numerous aldehydes are produced in the process of combustion. Aldehydes produce four basic types of physiological effects. The first effect is the primary irritation of the skin, eyes, and respiratory tract. The second effect is the sensitization effect, primarily observed with liquid solutions. The third effect is the anesthetic effect and the fourth is the organic pathology.⁽¹¹⁾ The permissible exposure limits are as follows:

	ACGIH		NIOSH	IDLH
	TWA	STEL		
Acrolein	0.1 ppm	0.3 ppm	--	5 ppm
*Formaldehyde	1.0 ppm	2.0 ppm	.8 ppm /w 30 min. Ceiling	100 ppm
Acetaldehyde	100 ppm	150 ppm	--	10,000 ppm

* - Suspected Carcinogen

The formation of aldehydes at the fire scene can result from pyrolysis or combustion of cellulosic materials such as wood, cotton, and paper, plastic materials such as styrene and polyolefins, and oils and fats containing glycerol.⁽¹⁾ Acrolein is a more toxic aldehyde than formaldehyde and acetaldehyde. Because of this, the Harvard study⁽¹⁾ focussed on acrolein. It was detected above the STEL (0.3 ppm) in 56% of the fires. In one fire, the concentration of acrolein was at the upper end of the Short Term Lethal Concentration (STLC) of 30 to 100 ppm. This was the first time that acrolein had been identified in life-threatening concentrations. Acrolein was also measured during the San Antonio study. Of the 36 samples analyzed for acrolein, only two had detectable amounts, 3.9 and 0.86 ppm. Acrolein may be present in any fire environment and may be present in concentrations that will disable and incapacitate the unprotected firefighter.

Acetaldehyde was detected in 7 of 37 samples, with concentrations ranging from 0.02 to 7 ppm. This compound was not analyzed in the Harvard study.

1.7 Hydrocarbons

The source of hydrocarbons in structural fires are not precisely known, although likely sources include available petroleum products acting as fuel in the fire and the thermal degradation of certain plastics such as styrene.⁽¹⁾ Benzene has been identified in both the Harvard and San Antonio studies as being the most prevalent hydrocarbon measured at fire sites. The current ACGIH exposure limit for benzene is 10 ppm TWA and 30 ppm STEL. Since benzene is a suspected carcinogen, NIOSH recommends that exposures be kept below 1 ppm TWA and 5 ppm ceiling exposure. The IDLH for benzene is 2000 ppm.

Approximately 5% of the Harvard samples exceed the STEL and, in one sample, the concentration of benzene was 165 ppm. In the San Antonio study, benzene was found in all thirty six samples collected. Concentrations ranged from 0.07 ppm to 17.4 ppm, with the median concentration being 1.65 ppm. The analytical data from both studies indicate that insufficient benzene is produced in fires to produce narcotic and other acute toxic effects.⁽²⁾

1.8 Particulates

In fires using mixed fuels or natural polymers, smoke particulate is a tacky, oil aggregate of carbon particles with absorbed combustion products that are usually irritants. Massive exposures may cause direct mechanical plugging of the respiratory passages; but, more commonly,

smoke particulate is irritating to at least a minimal degree. The nature of the smoke particles generated may vary with the temperature of the fire. Smoke particles inhaled deeply into the lungs may convey absorbed irritants or transfer heat to any portion of the respiratory tract that they contact. Smoke may also cause obstruction of vision that can result in a life hazard if exists cannot be located.⁽³⁾

Particulates reached very high levels in the Boston study (up to 18 g/m³), much higher than in the San Antonio study (max. of 0.9 g/m³). This is consistent with the much higher ventilation in most of the San Antonio fires.⁽²⁾ The majority of the fire atmospheres in both studies contained particulates in quantities that would produce only minor irritation to the respiratory tract. As for possible toxic effects of particulates, the chemical composition, size distribution and concentration of the particulate are the determining parameters. In both studies, the particulate concentrations were measured but chemical composition and size distribution were not. Without this information, it is not possible to make any meaningful toxicological assessment of the hazards of exposure to particulates in the fire environment.⁽²⁾

2.0 Sampling and Analytical Methods

As previously outlined, the fire environment is a complex mixture of gases, particulates and droplets. Numerous contaminants have been identified in the smoke from structural fires. Turkington⁽¹⁵⁾ has identified over 100 different contaminants in his studies of fire environments. However, a major problem in designing a study of this magnitude is determining which

contaminates to sample and what methods are best suited for such a hostile environment. Even though over 100 contaminants may exist, it is important to keep focus on ones most commonly identified and pose the most danger to firefighters. Concentrating on contaminants which occur in only trace amounts would not provide much information but only tend to compound an already complex sampling strategy. Therefore, the major emphasis will entail sampling contaminants which have been reported to exist in amounts near or above known hazardous levels.

Contaminants will be collected using a variety of sampling techniques. The primary personal sampling method will consist of collecting a known volume of contaminant for subsequent qualitative and limited quantitative analysis using Fourier transform infrared (FT-IR) spectroscopy (Appendix VII). The area sampling methods consists of collecting contaminants using conventional sampling media (i.e. sorbent and detector tubes, and passive dosimeters). The following provides a more complete description of each sampling strategy that will be used in determining exposures for this study.

2.1 Personal Method

NIOSH has purchased from Nicolet Analytical Instruments an FT-IR for on-site gas analysis. The FT-IR system has several advantages which lends perfect for Project Firesmoke. The FT-IR system does not suffer from inherent problems of temperature and relative humidity extremes like sorbent and detector tubes. A known volume of gas is collected in a Tedlar bag, the bag contents are then introduced into the FT-IR for

analysis. Sampling results are near-immediate, since the gas bags are analyzed on site. Sampling problems can be identified and corrected on-site rather than waiting weeks/months for laboratory reports.

One additional key feature of the FT-IR is the data acquisition, spectra analysis and storage system. Nicolet has developed a quantitative analysis software package for analysis of trace concentrations. The program, LSFIT, uses a multicomponent least-squares fitting algorithm to calculate concentration. LSFIT uses the spectra from pure compounds as references to perform a least squares fit of the sample spectrum to the reference spectra, while simultaneously fitting the linear baseline. The sample spectrum can then be labeled and stored for future analysis. For example, it would be possible to re-analyze any sample spectrum using different reference spectra for different compounds. Also, the capabilities exist to compare one sample spectra to another, subtracting out the difference and re-analyze the resultant spectra. This means that samples collected on individual firefighters can be compared to different jobs, locations, or incidents for identifying supplementary exposures. For example, the sample spectra collected during knock-down can be over-layed to that of the overhaul spectra, subtract the differences and analyze the resultant. Or, one firefighters sample spectra can be compared to that of a co-firefighter to identify any differences. Sample spectra can also be stored for each firefighter and cumulatively analyzed for the duration of the survey.

Included in the equipment purchase was the provision for Nicolet to train our personnel in the operation of the FT-IR and to provide on-site expertise for the first field survey.

The specific instrumentation will consist of a Nicolet 20 SXB FT-IR equipped with an InSb/HgCdTe liquid nitrogen cooled "sandwich" detector. Samples will be collected in 8-liter Tedlar bags. The Tedlar bags will be placed in a fireresistant bag along with a sampling pump and a small impactor to remove particulates. This bag will be small enough to fit on the back frame of the SCBA. The sampling pump will be activated on-site by either NIOSH or the firefighter. The pump will be calibrated to deliver a 250 cc/minute flow providing a 30-minute sampling duration.

After the sample has been collected, it will be transported back to the mobile laboratory for analysis. A vacuum system, a gas inlet, and a dual range MKS Baraton pressure/vacuum gauge will be used for sample introduction to the FT-IR system at a known pressure. This system has also been designed by Nicolet. The sample spectrum will be analyzed using the LSFIT software program on a Nicolet 1280 computer having a 100 megabyte storage module. Samples will be analyzed for carbon monoxide, carbon dioxide, hydrogen chloride, hydrogen cyanide, nitrogen dioxide, acrolein and formaldehyde. Additional analyses for other unknowns may be performed at a later time.

The FT-IR system will be calibrated on site using certified gas standards. The calibration will be accomplished daily using specific

compounds for which the unknowns are analyzed. Prior to re-using any of the Tedlar sampling bags, each will be purged and evacuated three times with pure nitrogen. This should eliminate any cross contamination. In addition, the FT-IR will also be purged and evacuated with pure nitrogen after each sample analysis.

Particulates - One area which remains deficient from previous fire studies is the characterization of the organic combustion products and respirable particulates. This study will attempt to qualitate and quantitate the particulate matter generated from fire combustion.

Inertial classification is a method used to remove particulate from a gas stream with the option of separating particulates into different-sized fractions. The size characteristics of particulates generated from fires will be measured by mass characterization using a cascade impactor. Qualitative assessment will be attempted for the collected particles. The impactors to be used include a multistage-multijet air sampler which classifies airborne particles according to their aerodynamic characteristics, which include the size, shape, and density of the particles. A range of particle sizes is collected on each impaction stage depending on the jet velocity of the stage and the cut-off velocity of the previous stage. Collection is affected by particles having sufficient velocity and inertia to depart from the curving airstream and impact on the collection plate. A single stage impactor will be used on all pumps to prevent clogging.

The Sierra Instruments Marple Personal Cascade Impactor Model 298, or its equivalent, will be used to measure the distribution of particulate mass versus aerodynamic diameter. Prior to sampling, the impactor collection substrates (34 mm grease coated Mylar film) specifically designed for the radial-slot impactor, will be preweighed and placed in the impactor. The collection media are placed in the recess on the top surface of each impactor stage so that the slots in the stage are exposed. Thus, particles accelerating through a slot in an impactor stage will impact on the solid surface of the collection substrate laying over the top of the adjacent downstream stage, if velocity imparted to a particle is sufficiently great so that its inertia will overcome the aerodynamic drag of the turning gas stream. The particles smaller than the cut-off size for a given stage remain in the gas stream and proceed to the next plate. A sampling pump draws air through the impactor at 2.0 liters per minute. With that flowrate, particles are separated into eight fractions, from an equivalent aerodynamic diameter of 0.5 micrometers to 21.0 micrometers and above.

1

After sampling, the substrates are reweighed and adjusted for blank controls. The net weight increase on each filter is the mass of particulates in the size range of the impactor stage. The total weight of the particles on all stages is added up and the percent particle mass in each size range is calculated. The data can be presented graphically as a cumulative size distribution showing the percent of particle mass less than a specific aerodynamic particle diameter.

In addition, specific efforts will be attempted to determine the physical and chemical character of the particulates. No standard analytical techniques are available.

2.2 Area Sampling Methods

Area samples will be collected using conventional sampling methods as well as FT-IR analysis from various areas at the fire scene. The same compounds will be analyzed as for the personal samples. A variety of standard methods will be employed including solid sorbent collecting devices for subsequent analysis as well as direct-reading length-of-stain detector tubes and passive dosimeters. Standard analytical methods are listed in Appendix VIII.

3.0 Sampling Locations/Occupations

During the actual firefighting and overhaul phases, all firefighting activities will be sampled. This includes firefighters entering the structure to the firefighters operating the pumper. Only occupation titles will be recorded on personal identifiers will be used to link exposures to any individual firefighter. Area sampling packages will be placed at the fire scene during the various phases as each situation permits.

4.0 Sampling, Monitoring and Recordkeeping

As in the previous two fire studies^(1,2), periodic meetings will be held with the participating firefighters to keep them informed on the progress

of the study. At the pre-survey meeting, the firefighters will be instructed in the operation of the personal and area sampling packages. NIOSH investigators will be on the site of each fire to record the sampling times and to take note of any malfunctions with the packages. Also, it will be important to the study that the NIOSH investigators be able to collect as much information concerning the cause of the fire, materials burned and injuries or fatalities resulting from the fire. To collect this information will require the NIOSH investigators enter the structure when determined safe. Debriefings will also be conducted with the firefighters after each fire to gain their input as to possible problems with the package or exposures resulting from the fire.

5.0 Analytical Support

Three analytical laboratories will be utilized for the characterization of samples collected during field surveys.

5.1 Technical Support Team (TST)

Environmental Investigations Branch (EIB), DRDS, NIOSH

Morgantown, West Virginia 26505

(304) 291-4205

Coordinator - Jerry Clere

Type of Sample

particulates

Analytical Support

gravimetric

Laboratory Investigations Branch (LIB), DRDS, NIOSH
Morgantown, West Virginia 26505
Coordinator - Jim Tucker

<u>Type of Sample</u>	<u>Analytical Support</u>
particulates	SEM w/EDAX

5.2 Measurement Research and Support Branch (MRSB)

Division of Physical Science and Engineering (DPSE), NIOSH
Cincinnati, Ohio
Coordinator - Don Dollberg

(Note: D. Dollberg will decide to provide in-house
support or to utilize the NIOSH service contract
laboratory: Utah Biomedical Test Laboratory (UBTL),
Salt Lake City, UT)

<u>Type of Sample</u>	<u>Analytical Support</u>
all gas samples	high performance liquid
(secondary)	chromatography
ion exchange	
chromatography	
gas chromatography-FID	
spectrophotometry	

Environmental sampling equipment will be prepared and supplied from the
Technical Support Team. Any equipment or media unavailable from TST

will be supplied from the Measurement Research and Support Branch and/or Utah Biomedical Test Laboratory.

5.3 Collection of "Blanks"

"Blank" sampling media will be submitted for analysis from each survey to serve as controls. At least five (5) blanks or 10% per sample type will be collected. The media for each type of sample will be treated exactly as collected samples except that no air will be drawn through it. If significant results are determined by analysis of these blanks, appropriate corrections may be applied to the collected samples.

5.4 Shipment of Samples

Samples will be packaged and shipped to the appropriate analytical laboratories. Specific handling and shipping instructions outlined by each respective laboratory should be followed. (For example: refrigeration of samples collected for formaldehyde may be recommended.) Prior arrangements should be made with the respective laboratories for samples requiring priority analysis.

6.0 Analytical Results, Reports, and Dissemination

Samples will be analyzed by methods outlined in Section 6.0. Detailed description of specific analytical techniques are found in Appendices II through VI. Results of sample analysis will be reported by each laboratory to the environmental project officer. Sample results will be checked to ensure

sample validity. All surveys, methods, and reporting/notification requirements shall be in conformance with 42 CFR 85(a) (Appendix VIII). For each survey, a summary report of the environmental measurements as taken by the NIOSH research investigators will be sent to the Fire Company within 180 days of the visit. If analytical or statistical analysis is not completed to allow the report to be written and sent within the specified period, the proper officials will be notified by letter and an estimated date for receipt of the report provided.

The findings of the complete study may be disseminated in NIOSH or USFA Technical Reports, topical symposiums, scientific journals, meetings, or other similar means. These types of presentations will not identify specific employees or any link that can be associated with a particular employee.

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APPENDIX I

Bostons Mandatory Mask Rule

S. O. 69

OCTOBER 17, 1977

From: The Fire Commissioner/Chief of Department
To: Deputy Fire Chiefs, All Divisions
Subject: RESPIRATORY PROTECTIVE EQUIPMENT

For the past several years the department has engaged in a series of studies with the Harvard School of Public Health in an attempt to learn more about the Boston Fire Fighter and the environment in which he works. Some of these studies are completed and some are on-going.

An interim lung study report published in 1974 produced the startling information that the loss in pulmonary function (forced vital capacity FVC) for Boston Fire Fighters was more than twice the expected rate (77 vs. 30 ml). The report went on to state that "these changes were significantly related to frequency of fire exposure and could not be explained by differences in age, smoking habits or ethnic background. This study strongly suggests that occupational exposures are contributing to chronic impairment of pulmonary function in Boston Fire Fighters". The expected annual loss in the general population for Forced Vital Capacity is 25 to 30 ml per year. The rate seen in fire fighters more nearly resembles that rate of 80 ml per year seen in patients with chronic obstructive lung disease. The five year lung study has been completed and we are awaiting the final results from the Harvard School of Public Health.

Other Harvard studies have shown that the Boston Fire Fighter is subjected to high concentrations of carbon monoxide and reduced oxygen, as well as high radiant heat loads at fires.

One conclusion reached in the studies is:

"The fire fighter cannot accurately determine when breathing apparatus should be worn. It is obvious that breathing apparatus should be worn at all times during active structural fire fighting, based on concentration of carbon monoxide noted in this test."

The most recent study we are engaged in is a joint effort between the Harvard School of Public Health, the National Fire Prevention and Control Administration, and the Society of Plastics Industries to study many hazardous gases we are encountering at fires. This study has only been going on for two months and already hazardous amounts of several gases have been encountered and measured.

2-1

The following results are listed as examples of what is being detected;

STEL is the maximum concentration of an air contaminant to which persons can be exposed for a period of up to fifteen minutes continuously without hazard.

PPM means parts per million.

<u>Incident No.</u>	<u>Gas Detected</u>	<u>Amount Detected</u>	<u>STEL</u>
19131	Acrolien	3.9 PPM	.3 PPM
21792	Carbon Monoxide	2300 PPM	400 PPM
20919	Hydrogen Chloride	10.7 PPM	5 PPM
22531	Hydrogen Chloride	7.5 PPM	5 PPM
23598	Total Suspended Particles (TSP)	18,000 PPM	20 PPM
28676	Acrolien	98 PPM	.3 PPM
28676	Formaldehyde	2100 PPM	4. PPM
30694	Carbon Monoxide	4800 PPM	400 PPM

These are just a few of the incidents where hazardous gases have been detected in dangerous amounts. We are also finding Nitrous Oxide, Acetaldehyde, Acetone, Benzene, Toluene, and even traces of Hydrocyanic Acid, as well as other gases.

While all fire fighters have been aware our job is hazardous, these Harvard studies are providing direct, legitimate evidence not only of hazards, but also of their physical effect on members. Some of the measurements listed above would have been easily fatal if the member was without respiratory protective equipment.

This department has also engaged in a respiratory protective equipment program with National Aeronautics and Space Administration (NASA) for the past several years because of our dissatisfaction with the types of masks that have been available for fire fighters. This program resulted in the development of the Scott 4.5 mask and Boston is the first department in the country, not only to try these units, but to equip the entire department with them. The department feels these masks are superior to any we have used in the past and are the best available for the fire service at this time.

With the adoption of these masks and the direct evidence of the hazards we are encountering, the department has concluded that the more widespread use of respiratory protective equipment is essential and a mandatory mask rule is being established. This rule has been developed by requiring each District Fire Chief to submit his recommendations and the final rule was approved by the Deputy Fire Chiefs. Since it represents a major change in our operational procedures, it is not going to be easy to accomplish, but the need for the rule is obvious. Each member of the department is to be issued a copy of this rule and company officers shall include this rule in company drills.

MANDATORY MASK RULES

1. All company members and chiefs' aides shall don respiratory protective equipment before entering a building for fire fighting operations or other incidents that require respiratory protection. Masks may be removed after the fire has been knocked down and the building has been thoroughly ventilated.
2. Members raising ladders, operating lines outside a fire building, performing exterior ventilation, (roofs, etc.) or other external activities are not mandated to use respiratory protective equipment. However, any member of the fire fighting force may wear respiratory protective equipment at any alarm to which he responds.
3. To reduce possible injury, members responding to alarms are not required to don respiratory protective equipment while enroute.
4. Chief officers shall don respiratory protective equipment when it is necessary to enter a fire building for extended periods. It will not be mandatory at the initial stage of a fire while directing operations and maintaining radio communications with the Fire Alarm Office.
5. At ship fires and subway fires chemox masks must be used because of their longer duration.
6. Members responding to working fires or multiple alarms shall have their masks strapped on when they report to the chief in charge.
7. When masks are removed, they shall not be dropped or left in a building or other area where they will be subjected to damage. One member will be assigned by the company officer to carry the masks outside and safely place them on the apparatus.

It is anticipated that the adoption of this mandatory rule will greatly reduce, if not eliminate, incidents of fire fighters suffering smoke inhalation injuries during fire fighting operations. It is understood that extenuating circumstances may prevail at specific incidents and these will be considered.

The Mandatory Mask Rule will become effective October 17, 1977, and shall be Standard Operating Procedure No. 32A.

Per Order:

George H. Paul

Fire Commissioner/Chief of Department

March 8, 1978

From: The Fire Commissioner/Chief of Department
To: Deputy Fire Chiefs, All Divisions
Subject: SMOKE INHALATION

The following is published for the information of the department.

YEAR	INCIDENTS OF SMOKE INHALATION	MEMBERS OVERCOME	REDUCTION
1975	499	73	
1976	488	68	- 2.2% - 6.9%
1977	232	42	-52.4% -39.7%

It will be noted that there has been a significant reduction in both categories since the adoption of the Scott 4.5 gas mask and the mandatory gas mask rule in the latter part of 1977.

In the month of December there were only 3 cases of smoke inhalation with no member being overcome.

Based on this experience the department looks forward to further reductions in these injuries to fire fighters in 1978 when we have had the benefit of a full year's experience with this improved safety equipment.

Per Order:

George H. Paul

Fire Commissioner/Chief of Department

S. O. 30

May 30, 1978

From: The Fire Commissioner/Chief of Department
To: Deputy Fire Chiefs, All Divisions
Subject: I. SMOKE INHALATION STATISTICS

A comparison of inhalation of smoke, toxic gas fumes and overcome injuries within this department for April of 1977 - 1978 is as follows:

<u>Inhalation of</u>	<u>% Reduction</u>	<u>Overcome</u>	<u>% Reduction</u>
1977 - 1978		1977 - 1978	
25 14	44%	7 3	57%

II. ADJUSTMENT-TEMPORARY-SERVICE-OUT-OF-RANK

The week ending May 31, 1978 will reflect adjustments on temporary service out of rank from January 1, 1977 thru December, 1977.

III. ADJUSTMENT - OVERTIME

Overtime checks payable the first week in June, 1978 will reflect adjustments on any overtime payed from January 1, 1977 thru December, 1977. (Regular monthly overtime will also be included.)

IV. DORCHESTER DAY PARADE

The Rifle Honor Guard will participate in the Dorchester Day Parade on Sunday, June 4, 1978.

Members will report to District Fire Chief Robert Laing at Fierce Square, Dorchester at 1230 hours.

Per Order:

George H. Paul

Fire Commissioner/Chief of Department

I-5

S. O. 56

OCTOBER 23, 1978

From: Acting Fire Commissioner Joseph M. Clasby
To: Deputy Fire Chiefs, All Divisions
Subject: SMOKE INHALATION STATISTICS

A comparison of inhalation of smoke and toxic gas injuries within the department for June, July, August and September 1977 - 1978 and for the one year period since the inception of the mandatory mask rule is as follows:

<u>MONTH</u>	<u>1977</u>	<u>1978</u>	<u>% REDUCTION</u>
June	21	3	86
July	16	6	62.5
August	20	7	65
September	15	5	66 2/3

In 1975 and 1976, there were 499 and 488 reported cases of smoke or toxic gas inhalation injuries; an average of 493.5 cases per year.

From October 1, 1977 to September 30, 1978, there were 103 cases of smoke or toxic gas inhalation injuries; a reduction of 79% for this type of injury. Of these 103 reported injuries, many cases occurred during overhauling operations.

Officers shall be aware of Mandatory Mask Rule #1 which states that masks may be removed after the fire has been knocked down and the building has been THOROUGHLY VENTILATED.

On all smoke or toxic gas inhalation injuries, a Form 5 shall be forwarded in addition to the Form 5D so that the details of any extenuating circumstances may be documented. This Form 5 shall be made out by the officer in charge of the company. In the case of an officer sustaining this type injury, a Form 5 from the District Chief in charge of the fire shall also be forwarded.

Per Order:

Joseph M. Clasby

Acting Fire Commissioner

APPENDIX II

Sample size derivations and calculations to assign protection factors to positive pressure SCBA used during Project Firesmoke.

Assigned Protection Factor Sample Size

If Y_i represents a protection factors (ratio of outside mask concentration to inside mask concentration) for a particular type of mask, then C is the assigned protection factor, where

$$P(Y_i < C) = 0.05.$$

Let $Y_i = \ln(Y_i)$ and $C = \ln(C)$.

The sample size determinations will be based on a confidence interval (95%) on the mean of C , μ_C .

$$0.05 = P(Y_i \leq C) = P\left(\frac{Y_i - \mu}{s} \leq \frac{C - \mu}{s}\right)$$

$$\text{and thus, } \frac{C - \mu}{s} = t_{.05, n-1}.$$

$$\text{Thus } C = (s)t_{.05, n-1} + \mu \quad (s)t_{.05, n-1} + \bar{Y},$$

$$\text{and } \mu_C = (\sigma)t_{.05, n-1} + \mu$$

$$\text{and } \sigma_C^2 = t_{.05, n-1}^2 (\text{Var}(s)) + \text{Var}(\bar{Y}).$$

$$\text{Var}(\bar{Y}) = \frac{\sigma^2}{n}, \text{ but Var}(s) \text{ will have to be approximated.}$$

$$\text{Using a linearized Taylor's series on } s = f(s^2) = (s^2)^{1/2},$$
$$s = (\sigma^2)^{1/2} + (1/2)(\sigma^2)^{-1/2} (s^2 - \sigma^2) = \sigma + \frac{1}{2\sigma} (s^2 - \sigma^2).$$

$$\text{Then } E(s) = \sigma \text{ and } \text{Var}(s) = E(s - \sigma)^2$$

$$E \frac{1}{2\sigma} (s^2 - \sigma^2)^2$$
$$= \frac{1}{4\sigma^2} \text{Var}(s^2) = \frac{1}{4\sigma^2} \frac{2\sigma^4}{n-1} = \frac{\sigma^2}{2(n-1)}$$
$$\sigma_C^2 = t_{.05, n-1}^2 \frac{\sigma^2}{2(n-1)} + \frac{\sigma^2}{n} = F_{.10, 1, n-1} \frac{\sigma^2}{2(n-1)} + \frac{\sigma^2}{n}$$
$$= \sigma^2 \frac{F_{.10, 1, n-1}}{2(n-1)} + \frac{1}{n}$$

The confidence interval about μ_C would be described by:

$$95\% \text{ CI } C \pm (t_{.025, n-1}) s \frac{F_{.10, 1, n-1}}{2(n-1)} + \frac{1}{n}^{1/2}$$

Let K be the desired half width, i.e. $C-K \leq \mu \leq C + K$.

$$\text{Then } K = t_{.025, n-1} \quad s \quad \frac{F_{.10, 1, n-1}}{2(n-1)} + \frac{1}{n}^{1/2}$$

$$\text{and } K^2 = F_{.05, 1, n-1} \quad s^2 \quad \frac{F_{.10, 1, n-1}}{2(n-1)} + \frac{1}{n}$$

$$\frac{K^2}{F_{.05, 1, n-1}(s^2)} = \frac{nF_{.10, 1, n-1} + 2(n-1)}{2n(n-1)}$$

$$2n(n-1)K^2 = nF_{.10, 1, n-1}F_{.05, 1, n-1}(s^2) + 2(n-1)F_{.05, 1, n-1}(s^2)$$

$$2n^2K^2 + [-2K^2 - F_{.10, 1, n-1}F_{.05, 1, n-1}(s^2) - 2F_{.05, 1, n-1}(s^2)]n + 2F_{.05, 1, n-1}(s^2) = 0$$

$$n = \frac{[2K^2 + F_{.10, 1, n-1}F_{.05, 1, n-1}(s^2) + 2F_{.05, 1, n-1}(s^2)] \pm [2K^2 + F_{.10, 1, n-1}F_{.05, 1, n-1}(s^2) + 2F_{.05, 1, n-1}(s^2)]^2 - 16K^2F_{.05, 1, n-1}(s^2)]^{1/2}}{4K^2}$$

Sample Size Calculations for APF Study

The standard deviation for various respirator studies averaged about 3. Thus the standard deviation in the log scale would be $\ln(3) = 1.1$.

The following table summarizes sample size calculations that were computed using an APF of 10,000 and different ranges of a 95% confidence interval.

95% Confidence Interval on APF

	<u>n</u>
9000 to 11000	1095
8000 to 12000	275
7000 to 13000	126
6000 to 14000	73
5000 to 15000	37
2500 to 175000	13

APPENDIX III

NIOSH Human Subjects Research Participant Document

NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH (NIOSH)
CENTERS FOR DISEASE CONTROL
U. S. PUBLIC HEALTH SERVICE
U. S. DEPARTMENT OF HEALTH AND HUMAN SERVICES

CONSENT TO PARTICIPATE IN A RESEARCH STUDY

You have been asked to participate in a
NIOSH Research study. We explain here the
nature of your participation, describe your
rights, and specify how NIOSH will treat
your records.

I. DESCRIPTION

1. Title: Project Firesmoke
2. Project Officers: Gary P. Noonan
3. Purpose and Benefit: The field research associated with Project Firesmoke is being conducted in order to fulfill the terms of an interagency agreement between NIOSH and the Federal Emergency Management Agency/United States Fire Administration. The project's primary purpose is to evaluate the performance of self-contained breathing apparatus (SCBA) during structural fires and during overhaul activities. Firefighters will benefit from this research study through the insight gained concerning the extent of protection provided by SCBA during actual use conditions. In addition, firefighters will benefit from recommendations regarding the selection and use of respiratory protective equipment during overhaul activities.

II. CONDITIONS OF THE STUDY

1. You will participate in a two-fold experiment in this study. One experiment (environmental sampling) will be to estimate the amount of contaminants to which you would be exposed to if an SCBA was not used during structural firefighting activities. Exposure estimates will also be made during overhaul activities regardless of whether SCBA are used or not. A small fire resistant bag containing the components of the air sampler will be worn outside each test subject's turnout coat. The entire sampling system weighs approximately one and one-half pounds and will be placed in such a manner as to be of minimum hindrance to its wearer.

The other experiment (respirator sampling) of this study will investigate the amount of protection provided by SCBA during structural firefighting activities. This will be accomplished by simultaneous measurements of air concentrations both inside and

outside the facepiece of a firefighter's SCBA. The components of this sampling system will be contained in a 6" X 9" X 3" box which will be mounted on the SCBA backframe. The total weight of this sampling system is approximately two pounds and will also be placed in such a manner as to be of minimum hindrance to its wearer. Air samples will be collected during actual firefighting activities using a fire resistant bag mounted on the SCBA back frame. Tygon tubing will be used to probe the respirator facepiece and also to collect the lapel sample.

Pressure sensing inside the SCBA facepiece will be accomplished by using a pressure transducer that will be located in the box attached to the back frame. Tygon tubing will probe the facepiece and be connected to the pressure transducer. The tubing will be mounted in such a manner that it will not interfere with the form, fit, or function of the facepiece.

If you participate in the respirator sampling portion of the study you will be asked to provide an exhaled breath sample for the measurement of carbon monoxide at the beginning and near completion of each work shift and after each fire fighting event. This involves taking a deep breath, holding your breath for twenty seconds, then exhaling that breath into a bag to collect the expired air. This test will be supervised by a technician and will take about one minute.

You will also be asked to participate in a quantitative fit test. You will wear a full facepiece respirator similar to that worn with your SCBA. The test will be conducted in a special test chamber in which a corn oil aerosol is generated. While wearing the respirator, you will be asked to perform head and facial movements simulating those made during normal work. The movements include normal and deep breathing, turning head from side to side and up and down, and reading a paragraph. Each movement will be performed for approximately one minute.

This study will require participation by a firefighter subject for approximately one-half hour at the beginning of the work shift.

2. The discomforts and risks associated with participation in this research study are considered to be minimal. There is some additional risk associated with the sampling device attached to your respirator facepiece. Should one of the sample lines become detached, there could be outward leakage of air, and during high work rate conditions it is possible that there could be inward contaminant leakage. We feel that the possibility of these events happening are remote, but there is that possibility. Emergency procedures, should equipment malfunction occur will be discussed with you. Minor discomfort may be experienced as a result of wearing the respirator testing equipment.

If you have any reaction to the tests/procedures, you should contact Gary Noonan, Project Officer, (304) 291-4362.

3. No alternative test procedures are currently available. However, if alternative procedures advantageous to you become available during the project, the procedure most advantageous for you will be indicated and used or an explanation will be given as to use of any other procedure.
4. Injury from this project is unlikely. But if it results, medical care is not provided, other than emergency treatment. If you are injured through negligence of a NIOSH employee or an agent of NIOSH, you may be able to obtain compensation under the Federal Tort Claims Act. If an injury should occur to you as the result of your participation, you should contact: Gary Noonan, Project Officer, (304) 291-4362. Further information on the Federal Tort Claims Act can be obtained from Director, DIVPHS Claims at 301/443-1904.
5. If you have questions about this research or your rights as a member of this study, contact: Gary Noonan, Project Officer, (304) 291-4362.
6. Your participation is voluntary and you may withdraw your consent and end your participation in this study at any time without penalty or loss of benefits to which you are otherwise entitled.

III. USE OF INFORMATION

1. NIOSH's authority for collecting information in this study is the Occupational Safety and Health Act of 1970.
2. You do not have to furnish any information. Nothing will happen to you if you don't answer our questions, except that we may not use you in the study.
3. NIOSH will provide you and your doctor (if you wish) with all findings from your medical tests (and any other examinations). We will do this when the study is finished, or sooner if appropriate.
4. The information you and other persons give us will be used by us to help answer research questions regarding the degree of protection that can be expected from self-contained breathing apparatus during conditions of actual usage.
5. The information you provide us is covered by the Privacy Act, a federal law. We will not reveal your information in identifiable form to anyone without your permission, unless it is permitted by the Privacy Act. If requested, the Privacy Act permits the release of information in identifiable form under several specific conditions. All 12 conditions possible are stated on the back side

of sheet number 3. These releases are infrequently used, in general. When these kinds of requests occur, each is reviewed by us to ensure that a person would not reasonably object. The two reasons most often used to seek records subject to the Privacy Act are:

- (1) When the records are needed to protect the health and safety of other persons.
 - (2) When a researcher (for example, at a university) asks for information and it will be used for statistical purposes.
6. Your records are also covered by the Freedom of Information Act, a federal law. This law permits persons to request information held in our files. All Freedom of Information requests are reviewed to insure that the release of this information would not be a clearly unwarranted invasion of personal privacy.

The Privacy Act, a federal law, prohibits the release of your records from this study without your written permission. However, there are 11 situations written into this law which do permit releasing your information in identifiable form, without your permission. Your records could be released if:

- (1) They are necessary for PROTECTING THE HEALTH AND SAFETY of other persons.
- (2) A RESEARCHER uses them only for STATISTICAL RESEARCH.
- (3) NIOSH OFFICIALS, or groups working with NIOSH, need the records for USES compatible with the purpose for which the information was collected.
- (4) They are needed by AGENCY PERSONNEL, who need the records in performance of their duties.
- (5) The release is REQUIRED BY LAW.
- (6) The BUREAU OF CENSUS needs them for census or survey work.
- (7) The NATIONAL ARCHIVES needs them for historical purposes.
- (8) Either House of CONGRESS requests your records.
- (9) The COMPTROLLER GENERAL needs them for the General Accounting Office.
- (10) A COURT ORDERS them; or
- (11) A CONSUMER REPORTING AGENCY needs them to assist the federal government in collecting a claim owed to the government; or
- (12) The records are requested under the terms and conditions of the Freedom of Information Act, and their release would not invade your privacy.

IV.

- A. Experiment I (Environmental Sampling) Consent
- B. Experiment II (Respirator Sampling) Consent
Participant will also be required to provide a exhaled breath
sample for measurement of carbon monoxide.

I have read this consent form and I agree to participate in this study.

PARTICIPANT _____ Age _____
(and Guardian, (signature)
(if required) Date _____

I, the NIOSH representative, have accurately described this study to the
participant.

REPRESENTATIVE _____ Date _____
(signature)

APPENDIX IV

Quantitative Fit Test Procedure

Standard Quantitative Respirator Fit Test (QNFT) Protocol

"Quantitative Fit Test" is defined as the measurement of effectiveness of a respirator seal in excluding the ambient atmosphere. The test is performed by dividing the measured concentration of a challenge agent in a test chamber (C_o) by the measured concentration of the challenge agent inside the respirator facepiece (C_i) when the normal air purifying element has been replaced by an essentially perfect purifying element. "Challenge Agent" refers to the air contaminant introduced into a test chamber so that its concentration inside and outside the respirator may be compared.

A Dynatech Model 2000 polydispersed aerosol test system will be used to perform the standard respirator quantitative fit test. A test aerosol, U.S.P. Grade corn oil will be generated by the instrument using atomizing technology, jets, and impactors. A mean mass aerodynamic particle diameter (MMAD) of between 0.5 and 0.7 μm is generated and mixed with clean filtered air to obtain aerosol concentrations over a range of 10 to 30 $\mu\text{g/liter}$. This range is defined at the time of testing.

The instrument will be started and calibrated according to the manufacturer's instructions. Before the subject enters the chamber the instrument will perform a self check to insure that the system is stable and that the aerosol concentration in the enclosure has reached equilibrium. The test will then be explained to the test subject, making sure that he fully understands its purpose, the procedures, and the actions expected of him.

The subject will donn the SCBA and then enter the test enclosure and connect the sampling hose. Time (2-3 min.) will be allowed at this point for the test enclosure concentration to stabilize. Then a recheck of the test system calibration will be performed.

Prior to entering the test chamber, the subject shall be given complete instructions as to his/her part in the test.

In response to verbal instructions, the subject will begin head and facial movements simulating those made during normal work. The test subject shall perform the following for one minute each;

- (1) Normal breathing with head motionless. This will be done in the normal standing position.
- (2) Deep breathing simulating that is done during hard work with head motionless. This exercise will not be prolonged due to the danger of hyperventilation.
- (3) Turning head slowly from side to side while breathing normally, pausing when fully turned for at least two breaths before changing direction.
- (4) Moving head slowly up and down while breathing normally, pausing when fully extended for at least two breaths before changing direction.
- (5) Reading from a prepared text (Rainbow Passage) slowly and clearly, and loudly enough to be heard and understood by the test operator.
- (6) Normal breathing with head motionless.

After the test, the subject leaves the test enclosure and removes the respirator.

APPENDIX V

Carbon Monoxide Breath Sample Procedure

Carbon Monoxide Breath Sample Procedure

Scope

All members of the firefighting unit will be asked to provide breath samples which will be analyzed to determine the firefighters exposure to carbon monoxide.

Pre-Shift

A member of the investigating team will ask preliminary questions to each of the firefighters individually. All information will be recorded on an ECO data form. If the subject is a smoker his estimate of time since he last smoked, the total number of cigarettes smoked that day, and how many cigarettes he usually smokes per day will be recorded.

Pre-Exposure

1. A member of the investigating team will accompany the fire fighters to the fire site. While enroute to the fire the investigator will collect an expired breath sample from each subject.
2. Subject inspires a full breath and holds it for 20 seconds.
3. Subject immediately exhales into 1 liter discard bag via a disposable mouthpiece. (This removes the dead space air; 500 cc is sufficient.)
4. Subject, without taking a breath, now fills 2 liter collection bag (1 liter is sufficient) and seals with a pinch clamp.
5. Investigator labels the sample collection bag and records the time that the sample was collected on the ECO data form.
6. The sample will be analyzed by FT-IR within eight hours after collection.
7. After all samples have been collected and analyzed the sample collection bags will be purged three times with clean air so that they may be used to collect other samples.
8. The plastic mouthpieces (hose connectors) will be removed from the sample bags and cleaned/disinfected with Cidex so that they can be reused.

Post-Exposure

Immediately after each firefighting episode an ECO sample will be collected by the method described for the pre-exposure sample collection.

APPENDIX VI

Carbon Monoxide Breath Sample Data Sheet

Field Data Sheet

CARBON MONOXIDE BREATH SAMPLE DATA

DATE:

SHIFT:

FIREFIGHTER ID #:

PRE FIRE TEST 1

TIME OF TEST:

TIME OF ANALYSIS OF SAMPLE:

RESULTS:

POST FIRE TEST 1

TIME OF TEST:

TIME OF ANALYSIS OF SAMPLE:

RESULTS:

PRE FIRE TEST 2

TIME OF TEST:

TIME OF ANALYSIS OF SAMPLE:

RESULTS:

POST FIRE TEST 2

TIME OF TEST:

TIME OF ANALYSIS OF SAMPLE:

RESULTS:

PRE FIRE TEST 3

TIME OF TEST:

TIME OF ANALYSIS OF SAMPLE:

RESULTS:

POST FIRE TEST 3

TIME OF TEST:

TIME OF ANALYSIS OF SAMPLE:

RESULTS:

FIELD DATA SHEETS
To be filled out by NIOSH

PROJECT FIRESMOKE

SCBA STUDY DATA

FIRE STATION INFORMATION

LOCATION:

UNIT IDENTIFICATION:

DESCRIPTION:

SAMPLING INFORMATION

SAMPLE PACKAGE ID#

DATE

FIREFIGHTER ID#

TIME SAMPLING PACKAGE ACTIVATED:

TIME:

TIME SCBA IS DONNED:

TIME SCBA IS REMOVED:

TIME DIFFERENCE:

COMMENTS/DESCRIPTION OF FIREFIGHTING ACTIVITY/RESPIRATOR USAGE/FIRE SCENE:

DATA

DISK: FILE: NAME/TAG: COMMENTS:

APPENDIX VII

Theory of FT-IR

Theory of FT-IR

DECEMBER 1985



William F. Herget, Ph.D.
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1.0 INTRODUCTION

This manual presents the basic concepts of Fourier transform infrared (FT-IR) spectroscopy. As an elementary treatise for new users of infrared (IR) spectroscopy, it also points out the inherent advantages of FT-IR over the older dispersive technology.

An understanding of the concepts discussed here will allow you to maximize the use of your Nicolet FT-IR spectrometer and help you understand how the spectrometer's software commands interact with the associated hardware. For a more extensive treatise on FT-IR spectroscopy and its applications, refer to the following texts:

1. Robert J. Bell, "Introductory Fourier Transform Spectroscopy," Academic Press, New York, 1972.
2. Peter R. Griffiths, "Chemical Infrared Fourier Transform Spectroscopy," Wiley-Interscience, New York, 1975.
3. "Fourier Transform Infrared Spectroscopy," J.R. Ferraro and L.J. Basile, editors, Academic Press, New York; Vol. 1 1978, Vol. 2 1979.
4. "Infrared Methods for Gaseous Measurements," J. Wormhoudt, editor, Marcel Dekker, New York, 1985.

The goal of IR spectroscopic applications is to determine the chemical functional groups contained in a particular material. Each functional group absorbs characteristic frequencies of infrared radiation uniquely. Thus, a plot of radiation intensity versus frequency (the infrared spectrum) fingerprints the identifiable chemical groups in the unknown.

No known infrared detector, however, can accurately monitor both frequency and intensity of infrared radiation with any practical resolution. In addition, the currently used infrared detectors, typically thermocouples, are integrating detectors; they average all frequencies striking the detector into a single intensity reading.

There are two practical approaches to circumvent this problem: the dispersive technique and the Fourier transform technique. We describe each method to compare them in order to point out the inherent advantages available in FT-IR spectroscopy.

VII-5

2.0 DISPERSIVE SPECTROMETERS

In the traditional dispersive infrared spectrometer, radiation from the source passes through the sample and is dispersed by some optical element, usually a grating. Then the beam passes to a slit mechanism. The slit width determines the degree to which the radiation reaching the detector at any given moment is monochromatic. The narrower the slit the better the instrument is able to distinguish more closely spaced frequencies of light, i.e., the higher the resolution. A simplified diagram of a dispersive instrument is shown in figure 2-1.

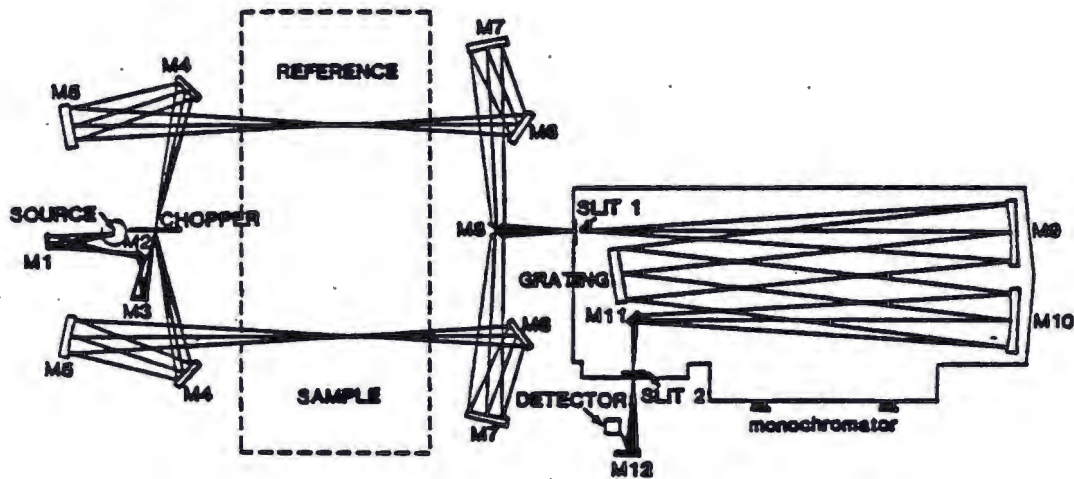


Figure 2-1 Typical Dispersive Spectrometer Design

Important features to note from figure 2-1 include the graybody source, mirrors M1 to M12, the optical chopper, the monochromator slits, the grating and the radiation detector.

As mentioned, an integrating infrared detector can be used in a dispersive spectrometer because the final radiation corresponds to only a narrow frequency band. Varying the frequency passed by the slit (typically by rotating the grating) produces a plot of intensity versus frequency. Further electromechanical and optical arrangements are necessary to filter unwanted radiation, to ratio the sample against the instrument background (thereby defining transmittance), etc.

Dispersive infrared spectrometers are well established and have been a workhorse in the analytical laboratory for over forty years. As research in infrared technology progressed, improvements were made (e.g., the replacement of prisms with ruled gratings for the dispersive element). These improvements provided more accurate and sensitive instruments.

Dispersive systems still work reasonably well. However, as current applications constantly push for greater speed, sensitivity, and accuracy a number of problems still persist. These include:

1. **Large number of moving parts.**

Even the simplest dispersive type system has a large number of moving parts:

- A chopping mechanism alternates the infrared beam between the sample and reference positions to produce an a.c. signal at the detector.
- A complex, precision grating drive turns the grating, which spacially disperses the beam into individual frequency components.
- For conventional (dual-beam) dispersive units, a reference beam attenuator is used to equalize the energy between the sample and reference beams.
- Slit controls are used to determine resolution. The slit width also changes across the spectrum in order to equalize the total energy through the slit.
- Filter changers eliminate unwanted energy.
- A mechanical analog (rather than digital) plotter drive records the spectrum in the older systems.

All of these are subject to mechanical wear and slippage. If any part is broken, the entire spectrometer is inoperable.

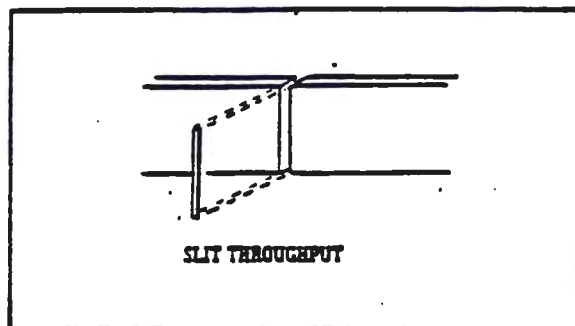
2. **Slow scanning speed.**

Only one resolution element is viewed at a time. This means the time required to obtain a spectrum is determined by how long the instrument takes to view each resolution element multiplied by the number of resolution elements in the spectrum. This can be a long time even for low resolution measurements.

The slow scanning speeds of dispersive type instruments make them impractical for monitoring the entire spectrum of a sample that is undergoing rapid chemical or physical changes. Thus, kinetic monitoring is generally limited to viewing a single absorption band, which limits the useful information obtained from these experiments.

3. **Decreased system sensitivity with slit effects.**

The slit mechanism (which determines resolution) blocks the majority of light from the source at any given time in the spectral measurement. This decreases the system's sensitivity, creating a problem for samples that exhibit low optical throughput or accessories that are not optically efficient. The problem is compounded at higher resolutions where the slits are narrowed, allowing even less light to reach the detector and decreasing the sensitivity proportionally.



4. **No internal reference.**

There is no internal reference for frequency accuracy. Each spectrum must be externally calibrated by running some material of known absorption frequencies, for example, polystyrene or indene, to determine the difference between the known frequency and what is plotted on the spectrum. In addition, calibration errors are not constant across the spectrum, which means the spectrum must be calibrated in several areas.

Adding a data system to a dispersive spectrometer allows you to store a calibration curve, which can be used to correct the measured spectrum. However, the calibration is affected by many factors, such as temperature, which means a calibration standard must be run often. This requires more of the operator's time and increases the cost of each analysis.

5. **Allows stray light.**

Because the chopper modulates the infrared beam as a constant frequency, contributions from stray light within the system are read by the detector and cause errors in intensity readings. For example, you may find the "appearance" of light in an area of the spectrum where the sample is truly totally absorbing. Such stray light is often difficult or impossible to eliminate.

The stray light makes dispersive IR instruments difficult to use in quantitative analyses where, according to Beer's Law, a linear relationship exists between the measured absorbance and the concentration of the sample. Dispersive systems are unreliable for quantitative analysis of samples that absorb beyond 1.0 absorbance unit (light levels below 10% transmittance). As a result, more time must be spent preparing a thinner or more dilute sample in order to keep the analytical bands in the useful range. Again, this adds to the cost of each sample analysis.

6. **Sample Heat-up.**

The sample is usually positioned close to the infrared source, which can cause the sample to heat up. This increases the potential for decomposition or other changes, particularly for solid samples.

7. **Sample emission.**

A heated sample (discussed above) can emit radiation. In some dual-beam system designs, the beam passes through the sample before it goes through the chopper. For this type of system, this means any radiation emitted by the sample will be read by the detector. Emission bands are "negative" compared to normal transmission bands, but when both appear simultaneously the spectral data can be difficult to interpret.

3.0 THE FOURIER TRANSFORM SPECTROMETER

The dispersive spectrometer's method of viewing one frequency element at a time is one solution to infrared detectors that are not frequency sensitive. The Fourier transform method presents a second solution that has found more extensive application.

Suppose we convert the information from infrared frequencies, where frequency-specific detectors are unavailable, to audio frequencies, where detectors and electronics are able to track both frequency and intensity. Based on this theory we can construct a more sensitive, accurate, and reliable spectrometer. This is the basis of Fourier Transform Infrared (FT-IR) spectroscopy.

3.1 THE FT-IR SYSTEM CONCEPT

The FT-IR spectrometer has three basic components:

- a source
- a Michelson Interferometer
- a detector

The Michelson Interferometer, which consists of a beamsplitter, a fixed mirror and a moving mirror, preserves both frequency and intensity information and replaces the conventional monochromator. Figure 3-1 shows a simplified diagram of the FT-IR spectrometer.

V22-10

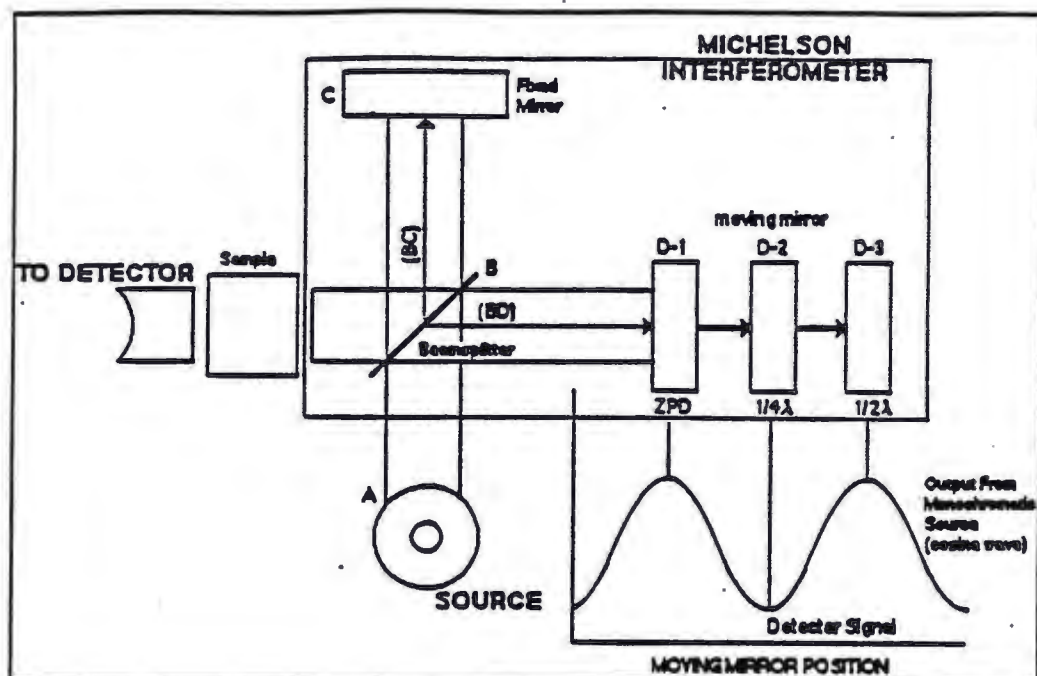


Figure 3-1 FT-IR System Concept

The following summarizes how the spectrometer works. Refer to figure 3-1 as you read through each step.

1. Collimated radiation from the broadband infrared source, A, is directed into the interferometer and impinges on the beamsplitter, B (basically a very thin film of germanium). As its name implies, the beamsplitter "splits" the incoming beam into two "arms" of about equal energy.
2. Approximately 50% of the light is transmitted through the film and is directed onto the fixed mirror, C. The remainder of light reflects off the beamsplitter and is directed onto the moving mirror, D.
3. The beams reflect off the surfaces of the two mirrors and recombine at the beamsplitter. Here constructive and destructive interference occurs, depending on the position of the moving mirror relative to the fixed mirror.
4. The resulting beam passes through the sample where selective absorption takes place, and then continues on to the detector.

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3.2 FT-IR DATA COLLECTION

The "scan" in FT-IR spectroscopy is the mechanical displacement of the moving mirror assembly; not a scan of individual frequencies as with a monochromator type system. We'll use a simple example to illustrate how FTIR data collection works.

Consider the detector response for a single frequency component from the infrared source. This simulates a monochromatic source, for example, a laser. The single frequency beam passes through the beamsplitter. The resulting two beams move through a sequence of constructive and destructive interference, depending on the position of the moving mirror relative to the fixed mirror. Refer to figure 3-1 as you read through the example.

Constructive Interference

$$2 (BD) = 2 (BC)$$

When the position of the moving mirror, D, is such that the distance between the beamsplitter and this mirror, BD, is exactly the same as the distance between the beamsplitter and the fixed mirror, BC, the two reflected beams pass through exactly the same path length and, consequently, are totally in phase with each other. As a result, the two beams interfere constructively and the detector observes a maximum signal intensity. This position of the moving mirror is called the point of 'Zero Path Difference', or ZPD.

Destructive Interference

$$2 (BD) - 2 (BC) = 1/2 \lambda$$

As the mirror moves away from the ZPD, the distance BD increases relative to the fixed distance BC. When the distance between the beamsplitter and the moving mirror, BD, is $1/4$ of the wavelength of light being observed longer than BC, the total optical path (beamsplitter-mirror-beamsplitter) difference between the two beams is $1/2$ wavelength. The two beams are now 180 degrees out of phase with each other and, at this point in the scan, interfere with each other destructively, causing a minimum in the detector response.

Constructive Interference

$$2 (BD) - 2 (BC) = 2 \times 1/2 \lambda$$

Continuing the scan, the mirror reaches a position where the distance BD is $1/2$ wavelength longer than BC. At this point the total path difference between the two beams is one full wavelength. The two beams are back in phase and constructive interference occurs again.

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Destructive/Constructive/Destructive

$$2(BD) - 2(BC) = n \times \frac{1}{2} \lambda$$

With each $1/4$ wavelength displacement, this pattern of constructive and destructive interference repeats itself. Since data sampling occurs continuously, a cosine wave results, like the one shown in figure 3-1.

We have established that radiation of a single frequency results in an interference pattern that is a cosine wave by the interferometric technique. However, this is a modulated or modified cosine wave whose frequency is determined by the velocity of the moving mirror. The higher the velocity, the higher the frequency of the modulated cosine function. Mathematically, the Fourier transformation of a single frequency is a cosine wave. Therefore, the interferometer is actually taking the Fourier transform of the incoming signal.

This same process occurs for every frequency emitted from the broadband infrared source. Figure 3-2 shows the cosine waves of three component frequencies. When three frequencies are sampled at once, the resulting signal observed by the detector is the signed summation of the individual modulated cosine waves. This type of signal, shown in figure 3-3, is called an interferogram or time domain spectrum (intensity versus time within the mirror scan).

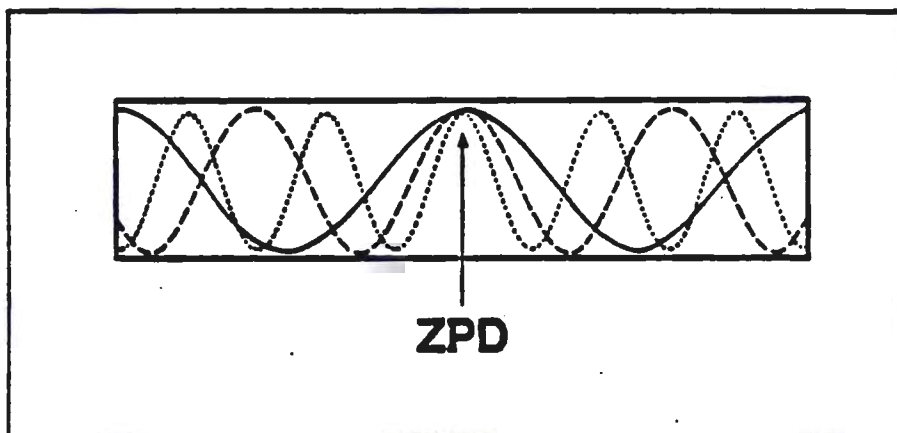


Figure 3-2 Three Modulated Cosine Waves as Produced by Three Monochromatic Light Beams Entering the Interferometer

V25-13

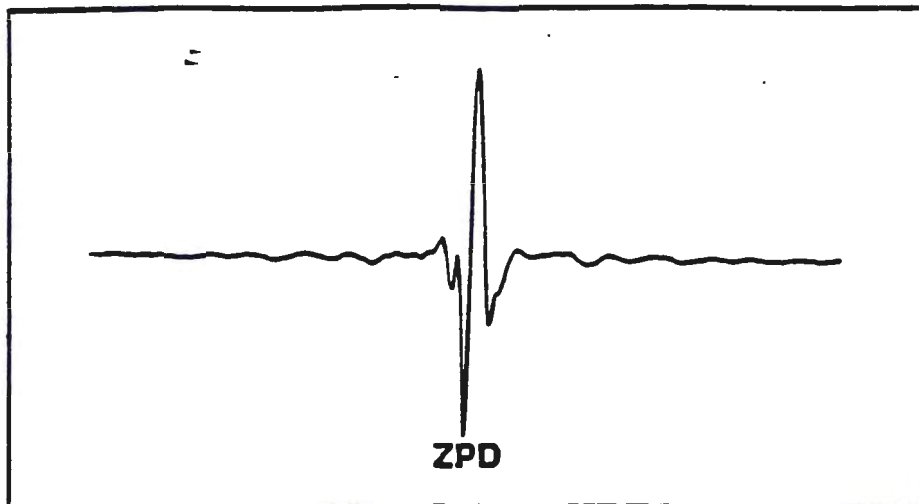


Figure 3-3 Typical Interferogram

Notice from figure 3-2 that all of the cosine waves have a maximum at the ZPD. This is the only position within the moving mirror scan where the optical paths are identical, so all of the frequencies are in phase simultaneously. This produces a large signal at the ZPD point in the interferogram with rapid cancellation on either side.

Resolution in an FT-IR system is defined by the length of mirror travel beyond the ZPD point. The further the mirror travels, the higher the resolving power of the instrument.

This phenomenon occurs because the Fourier transformation can only distinguish two different frequencies if there is a difference in their modulated cosine waves. If two frequencies are very similar, the resulting cosine waves will also be similar. Only a longer mirror travel can pick out the subtle differences.

In summary, the interferometer encodes the initial frequencies (by optically taking the Fourier transformation of the incoming signal) into a special form that the detector can observe in time. The inverse Fourier transformation is a mathematical means of resorting the individual frequencies for the final presentation of the infrared spectrum. In other words, a Fourier transformation simply converts from one domain into another; in this case, from the time domain (measured) to the frequency domain (desired). It is this final spectrum that interests the infrared spectroscopist.

It is important to remember that any data point of the interferogram represents the summation of components from each modulated frequency. Each data point contains information over the entire infrared region to which the detector is sensitive. In reality, the detector observes all frequencies simultaneously.

3.3 ADVANTAGES OF THE FT-IR SPECTROMETER

A number of features inherent to FT-IR spectrometers lead to distinct advantages over the earlier dispersive instruments. The advantages of FT-IR instruments are outlined here.

1. **Mechanical Simplicity (One moving part).**
There is only one continuously moving component in the FT-IR system: the moving mirror. This results in little system wear and high system reliability.
2. **Increased speed and sensitivity (Felgett Advantage).**
The interferogram signal is termed "multiplexed" because the detector observes all frequencies simultaneously. As a result, even at the slowest mirror velocities a standard resolution scan of the moving mirror takes only about one second. This single scan collected on a Nicolet FT-IR spectrometer yields a measurement of equal sensitivity (as defined by the signal-to-noise ratio, S/N) to that of a dispersive spectrometer. However, the FT-IR scan takes about one second compared to 10 to 15 minutes for the dispersive unit.

The Felgett advantage is, therefore, a speed advantage in that normal throughput experiments can be accomplished very rapidly and with good sensitivity. This is beneficial in two ways.

- First, you can measure more samples per unit time.
- Second, you can monitor a kinetic process, i.e., chemical reactions or curing processes can be measured in real time.

In addition, measuring a kinetic process on an FT-IR instrument produces a complete infrared spectrum of the product, whereas, dispersive instruments can only monitor a single band.

The Felgett advantage is also a sensitivity advantage. Since the time required to collect each scan is short, measurements can be repeated and coadded to take advantage of a signal-averaging process. The sensitivity of a measurement is determined by the signal to noise (or S/N) ratio. To define S/N for a measurement, take the ratio of the sample signal size to the magnitude of the noise. Sensitivity, therefore, is the ability to distinguish the smallest peak from the measurement noise.

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For a given amount of material analyzed, the signal (S) is a constant size. The noise (N) of the measurement, however, is random. By coadding several scans, the random noise averages out (the noise decreases while the signal remains constant and the ratio of signal to noise, S/N, increases.) In this way, tiny signals may be "pulled out" by decreasing the noise to a satisfactory level.

The S/N ratio is proportional to the square root of the total number of scans. Thus, 4 scan measurements are twice (square root of 4) as sensitive (S/N) as a single scan measurement; 16 scans give twice the sensitivity as 4 scans, etc. This means an FT-IR instrument can obtain far greater sensitivity than a dispersive instrument if the FT-IR spectrometer is allowed to signal-average for the same length of time that the dispersive spectrometer requires for a single measurement, usually 10 to 15 minutes. This sensitivity advantage allows FT-IR instruments to measure nanogram quantities while dispersive instruments are usually limited to microgram quantities.

The Fellgett (or multiplex) advantage can, therefore, be viewed in two ways.

- First, a speed advantage, i.e., a S/N ratio equivalent to that of a dispersive instrument can be obtained in a single scan.
- Second, greater sensitivity can be obtained by co-adding many scans, given the same measurement time of a typical dispersive unit.

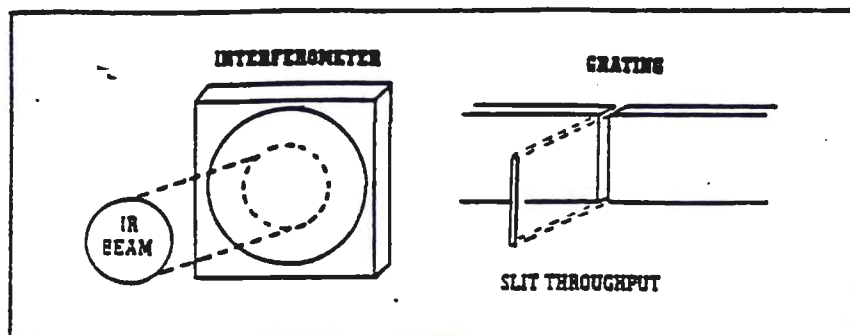
3. Greater optical throughput (Jacquinot Advantage).

There are no slits in the interferometer (as in the dispersive unit) to define resolution or to limit the amount of energy reaching the detector. FT-IR systems do not require slits. Instead, the FT-IR spectrometer uses an optical aperture; the proper aperture diameter must be used to achieve the desired resolution.

The beam area of an FT-IR system is 75 to 100 times larger than the slit width of a typical dispersive system. For example, for a corresponding resolution, the aperture on an FT-IR instrument (greater than 1 inch in diameter) is larger than the slit of a dispersive system (usually a few tenths of a millimeter). Thus, more energy is allowed to flow through the FT-IR system, resulting in greater sensitivity.

For data collections at spectral resolutions of 0.5 cm^{-1} or lower, the optical throughput of an FT-IR system is only limited by the size of the mirrors and interferometer itself.

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The Jaquinot advantage is important if the sample and/or sample accessory limits the optical throughput. Thick samples, such as paper, are severely energy limiting. ATR (Attenuated Total Reflectance) accessories are also energy limiting. They typically allow a maximum of 25% of the total energy through the system. With more energy initially in the system, the detector response on an FT-IR spectrometer is higher, resulting in greater sensitivity. Thus, the Jaquinot advantage is another sensitivity advantage of FT-IR spectroscopy.

4. Internal laser reference (Connes Advantage).

All Nicolet FT-IR spectrometers use an internal HeNe laser to monitor the position of the moving mirror within the scan. (This is discussed in detail in the section on interferogram sampling.) Since the wavelength of the HeNe laser is accurately known, this laser also provides an internal wavelength calibration standard.

Any measured data point is automatically calibrated by the system to be both precise and accurate to within 0.01 cm^{-1} . This accuracy level can be extremely important, for example, in digitally comparing two spectra for spectral subtraction or library searching. The accuracy of the FT-IR system guarantees that any differences found between two spectra are real differences, and not due to a calibration problem.

We need to emphasize that only the individual data points are guaranteed to this accuracy. If you are measuring sharp bands at a low resolution, you may not have enough data points to represent each band — there may not be a data point exactly on the peak of the band. If this happens, the computer's interpolation between data points, normally a straight line, can cause a minor error in the peak maximum. For the most accurate interpretation of your spectral data, be sure to choose a sufficient resolution to show the detail you require in the sample spectrum.

In summary, the FT-IR spectrometer provides a highly accurate internal laser reference system, which eliminates any need for external calibration.

5. Eliminates stray light.

In an FT-IR system, the interferometer modulates each infrared frequency uniquely. Thus, there is no equivalent to stray light. As a result, the quantitative linear relationship between the measured absorbance values and the sample concentration is accurate even for strongly absorbing bands (beyond 3 absorbance units or 0.1%T). This advantage eliminates a significant amount of sample preparation or reparation for quantitative analysis.

6. Less sample heat-up.

In FT-IR systems the sample is well removed from the source, making sample heat-up less of a problem. In addition, the interferometer is only approximately 50% efficient (part of the beam returns to the source).

7. No sample emission contributions.

In an FT-IR system, the detector responds to audio frequencies (the interferogram), which result from infrared frequencies that are modulated as they pass through the interferometer. The sample is typically placed after the interferometer and before the detector. Thus, radiation of infrared frequencies that might be emitted by the sample is not modulated and, consequently, is not detected. As a result, no emission bands appear in the spectrum to complicate spectral interpretation.

4.0 CONSIDERATIONS IN FT-IR SPECTROSCOPY

4.1 INTERFEROGRAM SAMPLING

The position of each data point in the interferogram must be accurately known. In addition, in order for the signal averaging process to work precisely, a specific data point must occur at exactly the same mirror position for every coadded scan.

In Nicolet FT-IR spectrometers, data sampling is timed using a separate interferogram from the internal HeNe reference laser. The reference laser is monochromatic, which means its resulting interferogram is a cosine wave. Each zero crossing of the interferogram signals the computer to collect data points. This system allows the spectrometer to monitor the exact position of the mirror.

If the velocity of the mirror varies during a scan, the laser cosine wave elongates and the data system "waits" until the mirror gets to the correct position for the next data point. This process also activates a servo mechanism that corrects for the velocity change. Thus, the data points line up from scan to scan and the signal averaging process operates correctly. The laser also guarantees that each data point is accurate and precise to within 0.01 cm^{-1} .

If the interferometer is to be used for signal averaging data, each scan must begin at exactly the same mirror position. This is accomplished by optoelectronically triggering on the moving mirror system. The exact mechanism for detecting the start-of-scan and end-of-scan varies for different instruments. All Nicolet instruments, however, monitor the optical scan timing using the HeNe reference laser.

The bandwidth (wavelength range) sampled depends on the number of laser crossings skipped between each collected data point. For most measurements, the system collects a data point at every other laser crossing, which gives a sampling range of 0 to 7399 cm^{-1} . In many systems, the measured wavelength range can be increased or decreased by altering the sample spacing. Altering the range, however, usually requires optical filters, which prevent "spectral aliasing" (the folding of signals from one frequency range into the spectral range of interest).

4.2 RESOLUTION

In FT-IR spectroscopy the measurement is made in the time domain with the final spectral presentation in the frequency domain. To determine resolution, you must consider the parameters for the time domain measurement and those for the transformation into the frequency domain. Both are discussed here.

Time Domain

For the measurement itself, resolution is determined by the length of the mirror scan away from the ZPD, i.e., the number of data points collected. Longer mirror travel is required to distinguish small differences between the modulated cosine waves of two very similar frequencies. It is the "interference" of these two signals that distinguish them through the Fourier transformation.

Under most conditions, the resolution is equal to the inverse of the maximum optical path difference (twice the physical mirror travel away from the ZPD). Thus, if the path difference is 0.25 cm, the resolution for the measurement will be 4.0 cm^{-1} . This path difference, or retardation, is adequate to achieve a resolution in the spectrum as measured by the FWHM (Full Width, Half Maximum) of a peak that is 4 cm^{-1} wide. The exact final resolution is determined by the apodization function, discussed later.

Frequency Domain

For resolution in the frequency domain (after the Fourier transformation), consider the Nyquist or Sampling Theorem. This theorem states that to accurately reproduce a given frequency by discrete sampling, a data point must be collected at least twice every wavelength. In other words, there must be at least two data points per resolution element. In the example above, the FWHM cannot be met if only one data point occurs every 4 cm^{-1} .

In the mathematical Fourier transformation, half of the points are real and half become imaginary and are thrown away. Therefore, the total number of transform points must be twice the number of data points you wish to end up with in the final frequency spectrum.

For most measurements, the spectral range sampled is between 0 and 7899 cm^{-1} (half the laser frequency). To simplify discussion, we round this range to $0\text{--}8000 \text{ cm}^{-1}$. If you want 4 cm^{-1} resolution in the final frequency spectrum, you must collect 4000 data points (one every 2 cm^{-1}) on the longest "side" of the interferogram away from the ZPD. In addition, since only half of the final transform points

For most applications, the Happ Genzel apodization function results in excellent attenuation of the sidebands with minimal reduction of instrument resolution. This is the standard apodization function on all Nicolet spectrometers. You may change the apodization function used by changing a single software parameter.

4.4 PHASE CORRECTION

In ideal instrument operation the system noise level is limited by the infrared detector noise. To minimize detector noise, components of noise outside the spectral region of interest are electronically filtered out. However, the filters introduce some signal phase shift that is not constant with frequency.

To correct the phase shift, a magnitude calculation could be used, i.e., calculate the square root of the sum of the squares of each real and imaginary point pair. However, this method makes all the noise positive and distorts the line shapes.

Instead, we use the following technique. Only a few data points (about 256) around the ZPD are used to calculate a transformation. Due to the high signal intensity in this region, the S/N ratio is also high. Using the 256 data points around the ZPD, the system calculates a phase array, θ , where:

$$\theta = \arctan (Im_i/Re_i)$$

and,

i denotes the point in the array,

Im is an imaginary number, and

Re is a real number resulting from the transformation.

The calculated phase array is essentially noise free and assumed to be the true phase array for the spectrum.

Now the system calculates a magnitude spectrum using the full data array. At this point, all the noise is positive. To make the noise randomly positive or negative, the magnitude spectrum is multiplied by:

$$\cos(\phi - \theta)$$

where:

ϕ is the phase array calculated from the full transformation, and

θ is the phase array calculated from the 256 point transformation.

If for a given point $\phi = \theta$ (no phase noise), then $\cos(\phi - \theta) = 1$ and there is no diminution of the point.

If for a given point there is no signal at all, $(\phi - \theta)$ will be randomly positive or negative, and $\cos(\phi - \theta)$ will be a random variable bounded by +1 and -1.

The phase multiplication introduces random noise of random sign where there was only positive noise in the magnitude calculation. In practice, the magnitude calculation, instrumental phase correction and mathematical correction for the ZPD point shift are combined into one quick calculation.

In some cases, the signal intensity of the interferogram is so low that the abbreviated phase array cannot be considered noise-free. If this is true, we recommend that you calculate the abbreviated phase array, θ , from a different spectrum than that used for the array, ϕ , (for example, the background spectrum). The FT-IR software allows you to do this by selecting the "Stored Phase" algorithm for the phase correction routine.

4.5 DATA PROCESSING

After the phase correction, the data are in the form of a single-beam spectrum. To get a transmittance spectrum, you must take the ratio of the single-beam spectrum against a background spectrum (a single-beam spectrum collected with no sample in the sample holder).

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True transmittance is defined as:

$$T = \left(\frac{I_s}{I_0} \right)_{\nu}$$

where:

I_s is the instrument response function (single-beam spectrum) with the sample, and

I_0 is the instrument response function without the sample.

ν is frequency

If the instrument response is identical with and without the sample, the transmittance value will be one. If the sample absorbs light, less energy reaches the detector and the transmittance value is less than one. If the sample is totally absorbing, no energy passes to the detector and the transmittance value is zero. Most systems multiply the transmittance value by 100, defining percent transmittance.

In taking the ratio of two spectra it is important that the velocity, filter settings, aperture and apodization functions be the same for both. The gain values and number of scans collected may be different.

The system uses the following formula to convert a percent transmittance spectrum to absorbance:

$$A = -\log_{10}(T/100)$$

where:

T is percent transmittance, and

A is absorbance.

The absorbance scale is useful for quantitative analysis where Beer's law states that a linear relationship exists between the measured absorbance and the concentration of a sample.

Additional data processing capabilities include interactive spectral subtraction, interactive baseline correction, integration, library searching, peak picking and smoothing.

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4.6 SIGNAL-TO-NOISE RATIO

There are a few trade-offs between system sensitivity (S/N ratio) and time or resolution. In signal averaging data, S/N improves with the square root of the measurement time. This fundamental statistical result is derived from the fact that the signal adds coherently while noise adds stochastically. Therefore, to double the S/N, the measurement time (or number of scans) must be quadrupled.

In absorbance spectroscopy, S/N is approximately proportional to the square root of resolution. Thus, for a particular sample, a 4 cm^{-1} spectrum is approximately half as noisy as a 2 cm^{-1} spectrum with the same number of scans. The 2 cm^{-1} spectrum also needs a longer stroke length and transformation time, so the system takes longer to collect and process the data.

The mirror velocity also effects the S/N ratio. Most Nicolet spectrometers can operate at different mirror velocities. By altering the velocity, you can optimize the modulation frequencies for the spectral response of the specific detector you are using. This allows you to use each detector most efficiently to obtain the greatest sensitivity.

The two most common detectors used for FT-IR spectroscopy are triglycine sulfate (TGS) and mercury-cadmium-telluride (HgCdTe or MCT). TGS detectors operate at room temperature while MCT detectors must be cooled to liquid nitrogen temperatures. Each detector has an associated parameter called D^* . D^* measures the S/N associated with the detector and is a function of the audio frequency being detected. Figure 4-1 shows a graph of D^* values as a function of frequency for TGS and MCT detectors.

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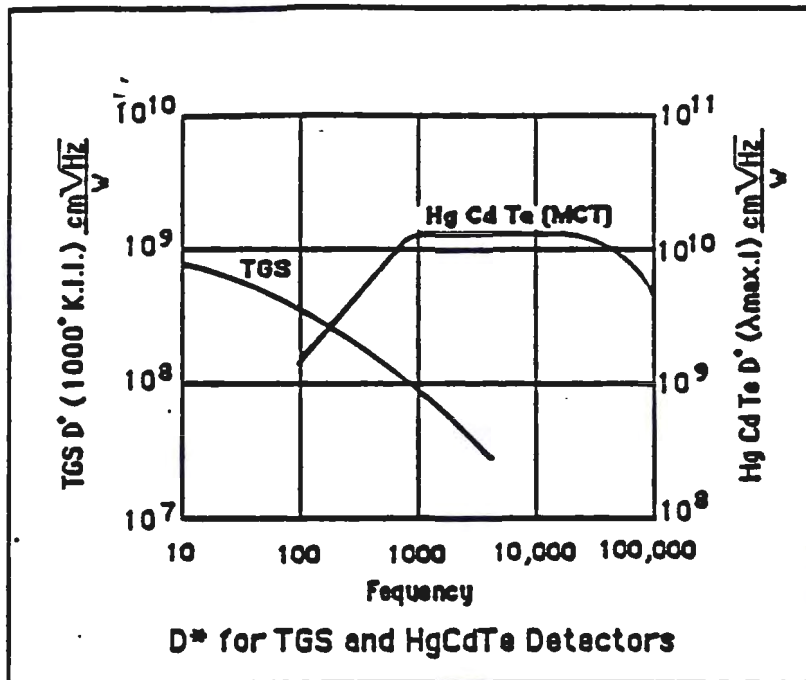


FIGURE 4-1 Detector D* Values as a Function of Frequency

Two features are apparent from this graph. First, the D* curve for the TGS detector decreases as the frequency increases. The D* curve for the MCT detector increases with increasing frequency at first and then levels off. Second, the frequency axis for the TGS detector is much lower than for the MCT detector. Note also, the different D* scales for the two detectors. In general, the MCT detector is more sensitive.

The faster the mirror velocity, the higher the audio frequency corresponding to each infrared frequency. Thus, TGS detectors are most efficient at slow mirror velocities (low frequency and high D* and S/N) and MCT detectors work best at high velocities (high frequency in the flat part of the curve).

There are, however, some further constraints. With a TGS detector the velocity should not be reduced below the point where the analog-to-digital converter (ADC) does not register at least one noise bit (for signal averaging to be effective). For MCT detectors, the velocity should be high, but not high enough to reach the high frequency end fall-off. With these detectors the retrace velocity (or the velocity on the return scan) eventually becomes the longest part of the total scan time.

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5.0 SUMMARY

The drawbacks of dispersive systems and the relative strengths of the interferometric instruments are tabulated below:

Dispersive

A large number of moving parts with associated mechanical tolerances, slippage, and wear.

Only a small frequency element is viewed at any one time, requiring 10 to 15 minutes for one scan of the entire spectrum.

Slow scan speed makes these instruments unsuitable for kinetic experiments.

To improve resolution, only a small amount of the IR beam may be allowed to pass through the slits.

There is no internal reference for frequency accuracy. Calibration against reference spectra is required.

Stray light within the instrument creates inaccurate absorbance readings.

The sample is close to the IR source and has a greater chance for thermal problems.

Any emission of infrared radiation by the sample is viewed by the detector and complicates the transmittance spectrum.

Interferometric

Essentially, only the mirror is in motion during an experiment.

All frequencies are viewed simultaneously (Felgett's advantage), producing a spectrum in as little as 1 second.

Rapid scan speeds allow an interferometer system to monitor kinetic experiments.

A large beam is used; there are no slits in the system to define resolution (Jaquinot advantage).

Use of a HeNe laser provides an internal calibration system with frequency accuracy to 0.01 cm^{-1} (Connes Advantage).

There is no equivalent to stray light because each frequency is modulated uniquely.

The sample is further removed from the source and has little problem with thermal effects.

Emitted radiation by the sample is not modulated and thus, is not viewed by the detector.

MEMORANDUM

DATE: November 25, 1986

TO: Those Concerned

FROM: Bill Herget

SUBJECT: C6H6, C7H8, C2HCl3 Analysis
Using Least Squares Fitting Procedures

Experimental Details

The purpose of these experiments was to show detection capabilities for three important solvents, benzene, toluene, and trichlorethylene, when they are present in air. The first step was to obtain a set of reference spectra of all concerned species. The data were collected on a Nicolet 20SXB (maximum resolution 0.5 cm⁻¹) FT-IR system utilizing a 10 meter fixed-path multiple-pass cell. The cell was connected to a vacuum pump and MKS Baratron pressure gauge with appropriate valves and tubing. The spectra shown are all at 2 cm⁻¹ resolution.

Figure 1 shows reference spectra for C6H6, C7H8, C2HCl3, and H2O. A laboratory air spectrum is shown in Figure 2. This spectrum showed the presence of Freon-113, which is usually present in our building air. It was observed that methanol was present in the air spectrum; this is a cell artifact caused by having had a formaldehyde/water/methanol sample in the cell several days prior to the current measurements. Thus reference spectra are included for Freon-113, CH3OH, as well as CO2 (Figure 2).

A mixture of C6H6, C7H8, and C2HCl3 was created in the cell. The spectrum of this mixture is seen as "SEM.312" in Figure 3. Air was added to this mixture to a total pressure of 736 torr ("SEM.313" in Fig.3). There after the cell contents were halved and air again added to a total pressure of 736 torr. This procedure was repeated to give four data sets approximately 1/2, 1/4, 1/8, and 1/16 the original concentrations of C6H6, C7H8, and C2HCl3. Two of these reduced concentration spectra are also shown in Figure 3.

For all of these spectra, the sample single-beam spectrum was ratioed to a background single-beam spectrum obtained with the cell evacuated to produce a transmittance spectrum, which was in turn converted to an absorbance spectrum. It is also possible to ratio an "air + mixture" spectrum to an "air spectrum" to produce an absorbance spectrum. Figure 4 shows plots of four samples processed in this manner.

Concentration Calculations

A special Nicolet program software utilizing a Least Squares Fitting (LSFIT) procedure is used to calculate concentrations. This program assumes Beer's Law and a linear baseline over the spectral range of interest, and does a least squares fit between a set of pure reference spectra and the sample spectrum while simultaneously fitting the linear baseline.

Memorandum

Subject: C6H6, C7H8, C2HCl3 Analysis

Using Least Squares Fitting procedures

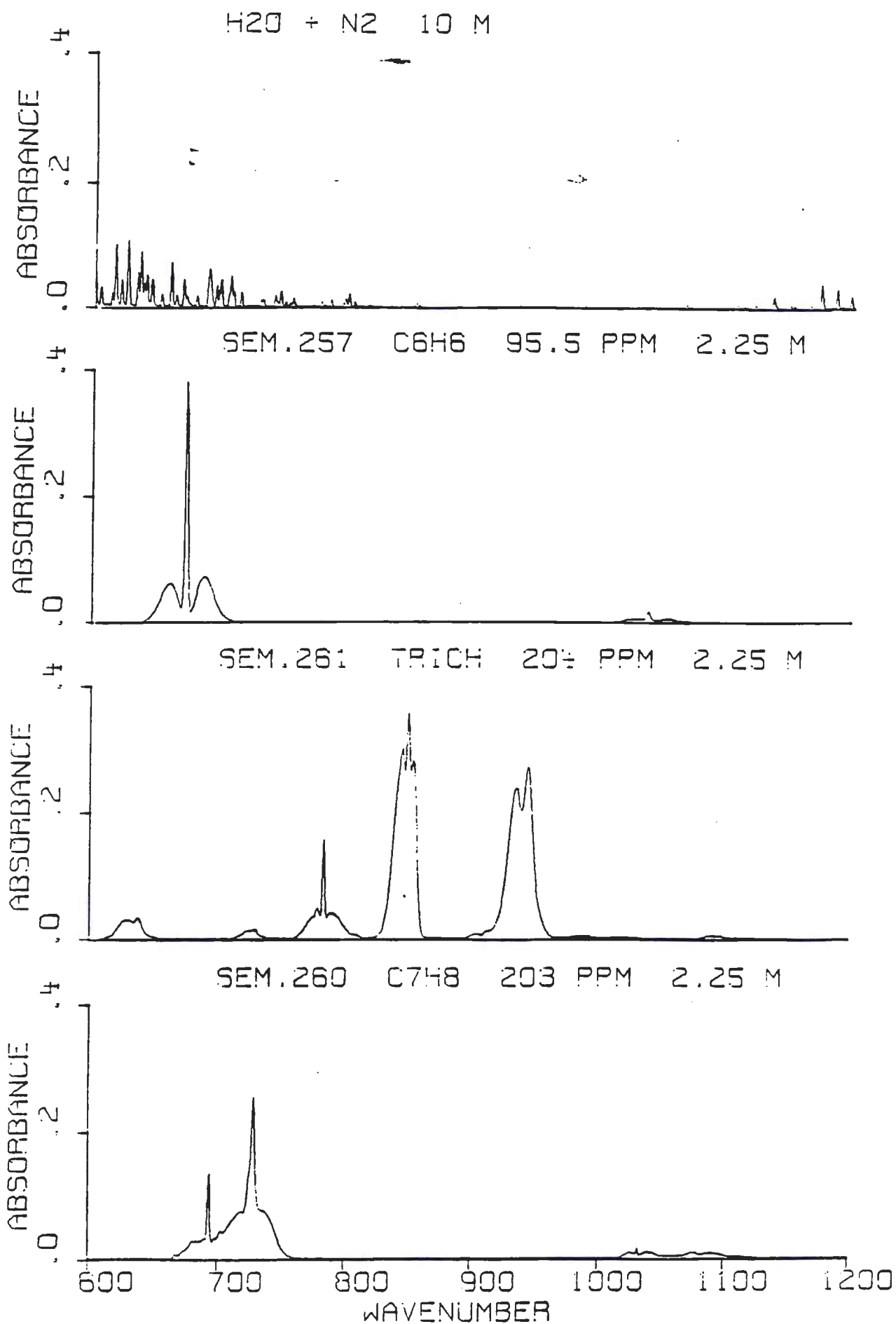
November 25, 1986

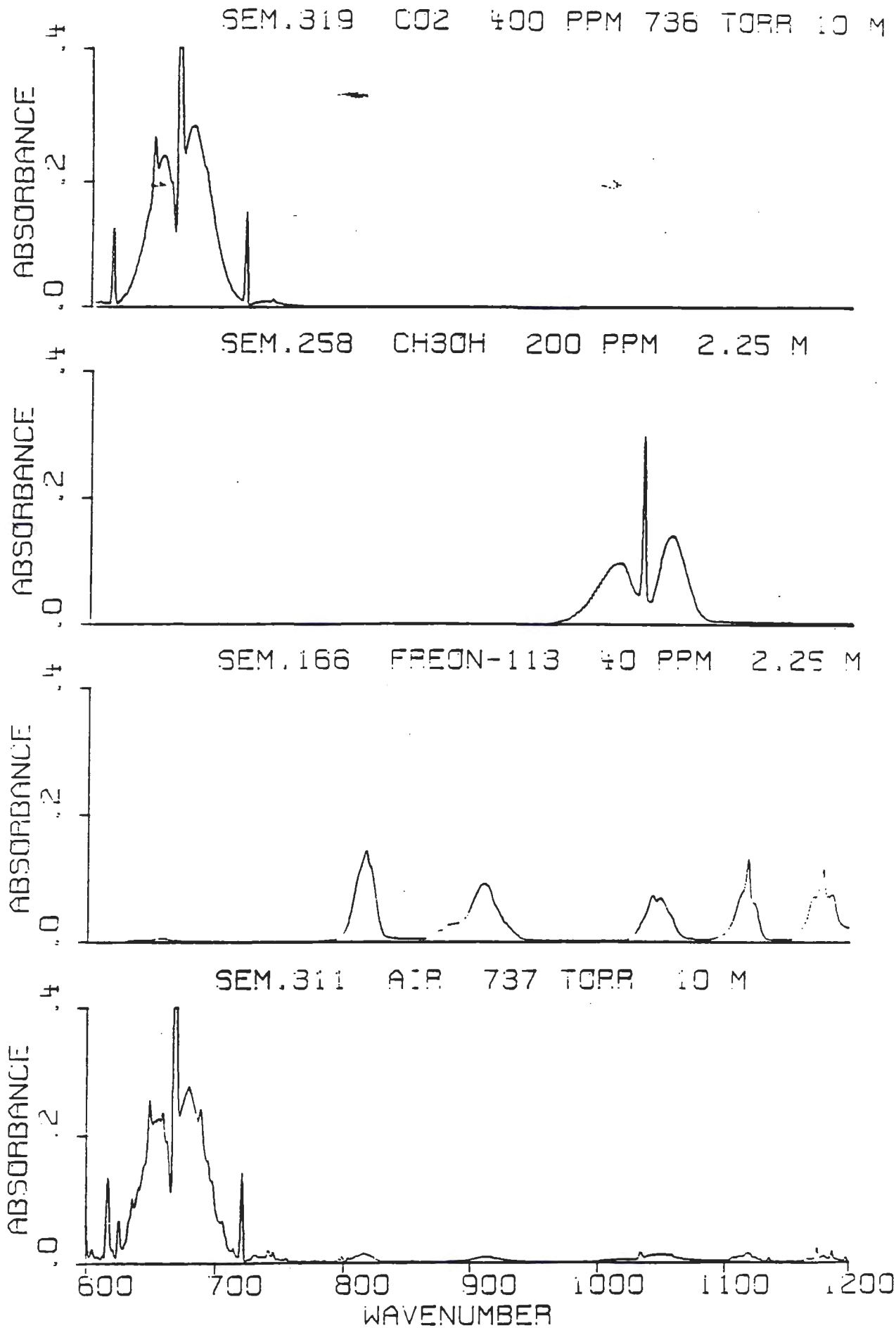
The LSFIT program is menu-driven. The data input to the program for this experiment are shown in Figure 5. Figure 6 shows the calculated concentrations for the C6H6 - C7H8 - C2HCl3 mixture before ("SEM.312") and after "SEM.313") air was added. The "+" values are indicative of the 95% confidence level. Note that the C6H6 concentration "increased" when the air was added. This is a result of the strong spectral overlap between C6H6 and CO2. As a result, the program seems to calculate a slightly higher C6H6 concentration than that actually present. Figures 7 and 8 show the results of the concentration calculations for the successively reduced concentration mixtures. Figure 9 and 10 show similar results for the sample spectra ratioed against air spectra.

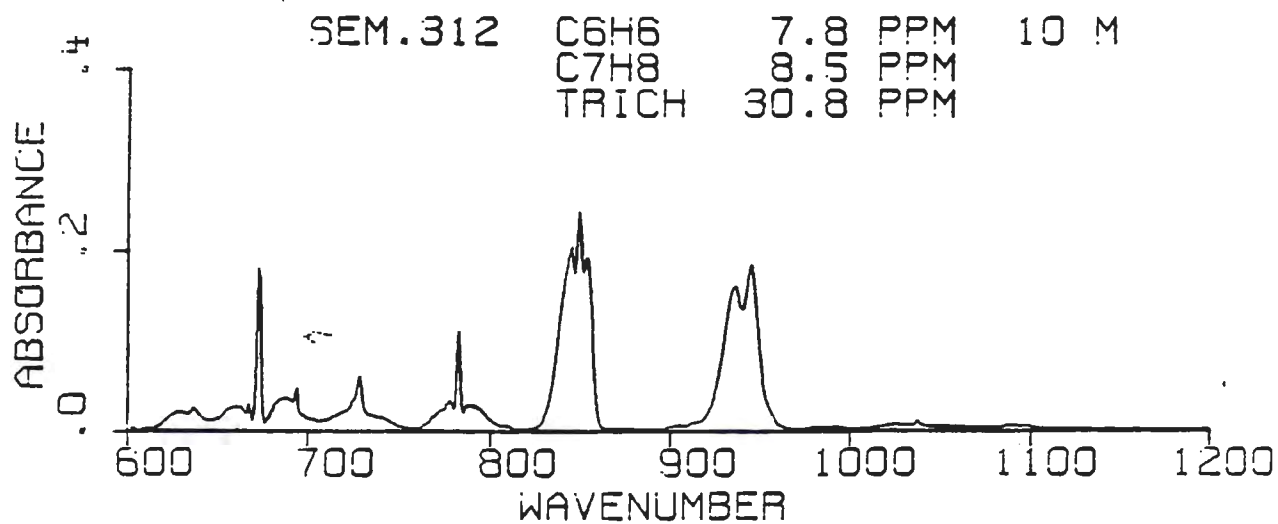
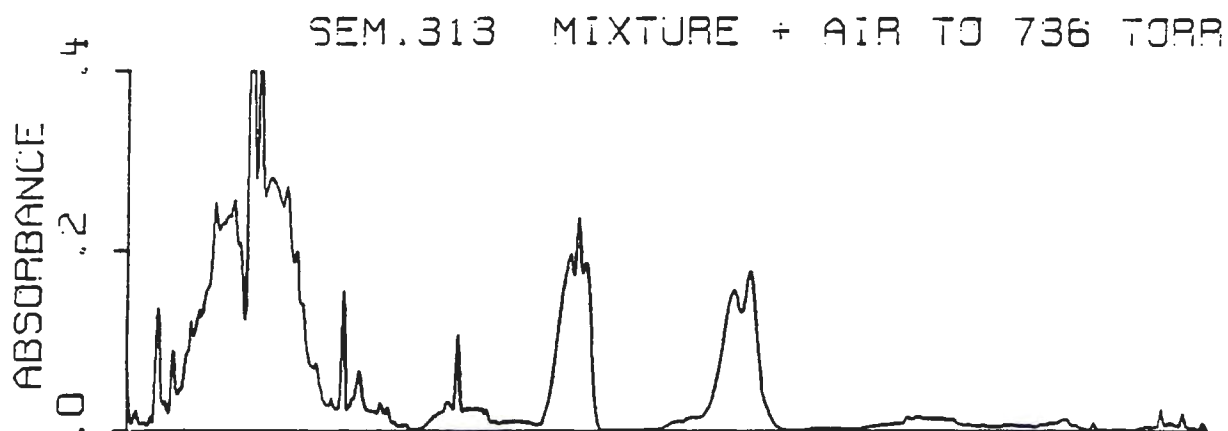
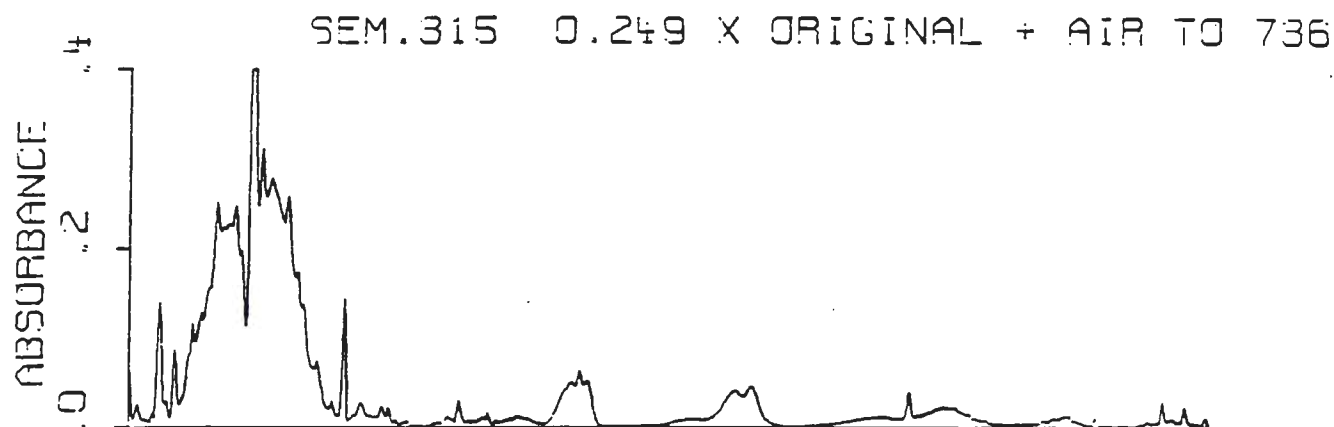
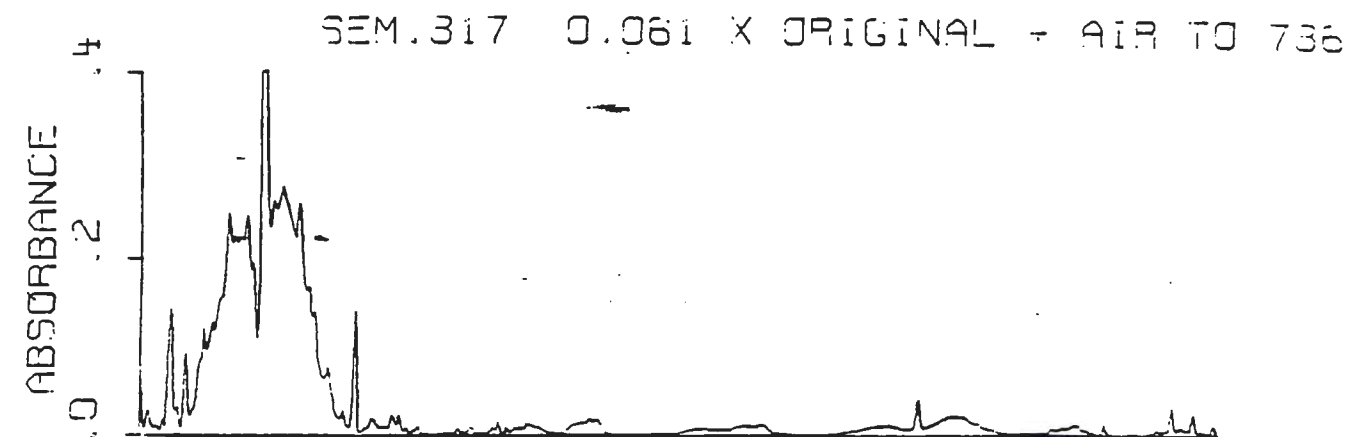
Discussion

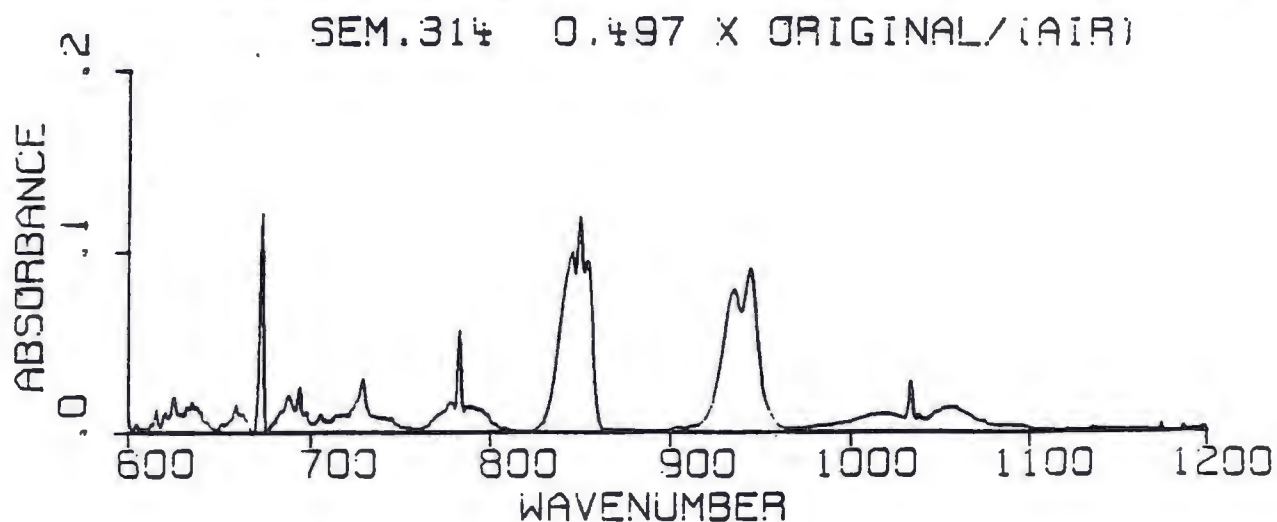
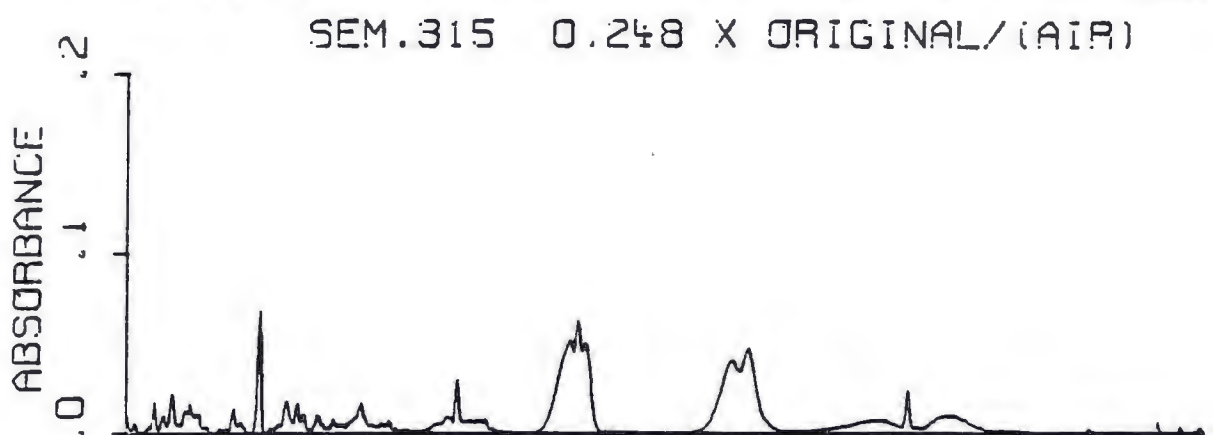
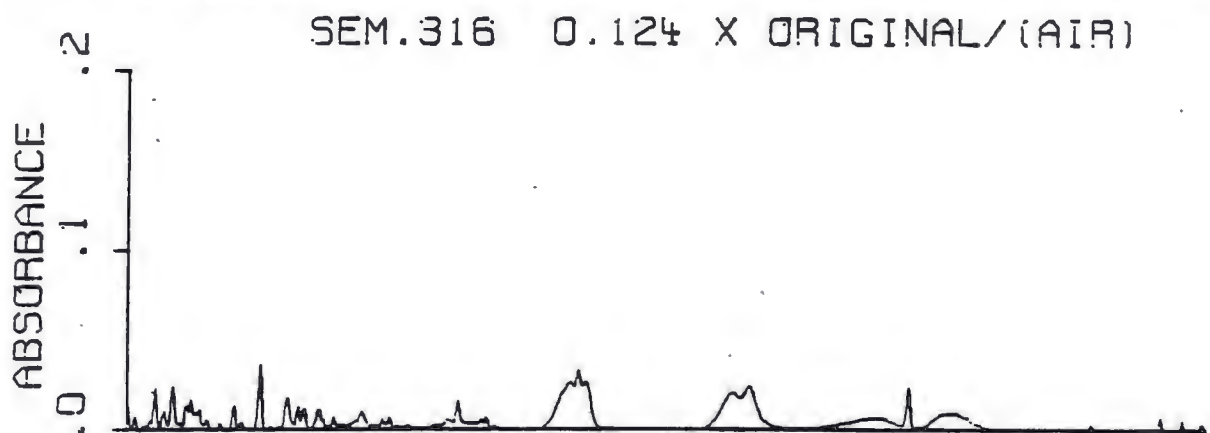
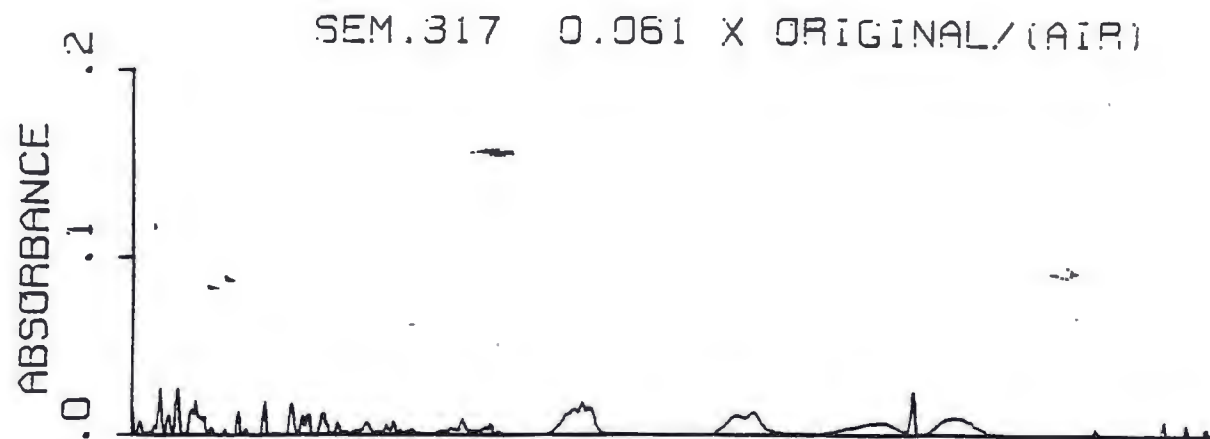
It is seen that analysis of benzene, Toluene, and Trichloroethylene can be made at sub-ppm levels in the presence of strong interference from CO2 in air. The accuracy of the calculations are estimated to be about $\pm 10\%$.

/ja









EXPERIMENT FILE NUMBER: 16

Experiment name: C6H6 C7H8 TRICH ANALYSIS
of pure references: 7 (8 max)

86/09/15 06:47

No.	File name	Ref. name	Conc.	Conc. units
1	C6H6_76.5X2	C6H6	.76500E+02	PPM
2	C7H8_203.X2	C7H8	.20300E+03	PPM
3	TRICH_204.X2	TRICH	.20400E+03	PPM
4	CH3OH_300.X2	CH3OH	.20000E+03	PPM
5	F113_40.X2	FREON-113	.40000E+02	PPM
6	CO2_400.X2	CO2	.40000E+03	PPM
7	H2O_10.X2	H2O	.10000E+04	PPM (RELATIVE)

No.	Start Freq. (cm-1)	End Freq. (cm-1)	Lower Thresh (abs.)	Upper Thresh (abs.)	Relative Pathlength
1	600.000	1100.000	-1.000	4.000	2.250
2	600.000	1100.000	-1.000	4.000	2.250
3	600.000	1100.000	-1.000	4.000	2.250
4	600.000	1100.000	-1.000	4.000	2.250
5	600.000	1100.000	-1.000	4.000	2.250
6	600.000	1100.000	-1.000	4.000	10.000
7	600.000	1100.000	-1.000	4.000	10.000

Total no. of data points: 520 (2000 max)
No. of peaks: 1 (20 max)

Peak No.	Start Freq. (cm-1)	End Freq. (cm-1)	No. of data pts. in peak
1	599.753	1100.190	520

Fig. 5.

ANALYSIS OF: SEM.312 C6H6 + C7H8 + TRICH
 DATE DATA ANALYZED: 86/09/15 06:47
 RELATIVE PATHLENGTH: 10.000

Calibrated peak file used in analysis: 16
 Title: C6H6 C7H8 TRICH ANALYSIS
 Date calibrated: 86/09/15 06:47

FIT #3 - FIT IF BASELINE LINEAR ACROSS EACH PEAK (WEIGHTED)

No. of peaks used in fit = 1

No. ---	Component -----	Concentration -----			Units -----
1	C6H6	7.79	+-	0.03	PPM
2	C7H8	8.52	+-	0.16	PPM
3	TRICH	30.76	+-	0.09	PPM
4	CH3OH	0.10	+-	0.1	PPM
5	FREON-113	0.016	+-	0.03	PPM
6	CO2	1.4	+-	0.4	PPM
7	H2O	0.0	+-	9.	PPM (RELATIVE)

ANALYSIS OF: SEM.313 MIXTURE + AIR TO 736 TORR
 DATE DATA ANALYZED: 86/09/15 06:54
 RELATIVE PATHLENGTH: 10.000

Calibrated peak file used in analysis: 16
 Title: C6H6 C7H8 TRICH ANALYSIS
 Date calibrated: 86/09/15 06:47

FIT #3 - FIT IF BASELINE LINEAR ACROSS EACH PEAK (WEIGHTED)

No. of peaks used in fit = 1

No. ---	Component -----	Concentration -----			Units -----
1	C6H6	3.49	+-	0.27	PPM
2	C7H8	3.25	+-	0.29	PPM
3	TRICH	30.02	+-	0.15	PPM
4	CH3OH	1.20	+-	0.24	PPM
5	FREON-113	0.83	+-	0.05	PPM
6	CO2	359.5	+-	2.1	PPM
7	H2O	674.	+-	19.	PPM (RELATIVE)

ANALYSIS OF: SEM.314 0.497 X ORIGINAL + AIR TO 732
 DATE DATA ANALYZED: 86/09/15 06:57
 RELATIVE PATHLENGTH: 10.000

Calibrated peak file used in analysis: 16
 Title: C6H6 C7H8 TRICH ANALYSIS
 Date calibrated: 86/09/15 06:47

FIT #3 - FIT IF BASELINE LINEAR ACROSS EACH PEAK (WEIGHTED)
 No. of peaks used in fit = 1

No.	Component	Concentration			Units
---	-----	-----	-----	-----	-----
1	C6H6	4.29	+-	0.24	PPM
2	C7H8	4.27	+-	0.28	PPM
3	TRICH	15.17	+-	0.12	PPM
4	CH3OH	5.56	+-	0.24	PPM
5	FREON-113	0.84	+-	0.05	PPM
6	CO2	363.7	+-	2.0	PPM
7	H2O	728.	+-	18.	PPM (RELATIVE)

ANALYSIS OF: SEM.315 0.248 X ORIGINAL, AIR TO 736 TO
 DATE DATA ANALYZED: 86/09/15 06:58
 RELATIVE PATHLENGTH: 10.000

Calibrated peak file used in analysis: 16
 Title: C6H6 C7H8 TRICH ANALYSIS
 Date calibrated: 86/09/15 06:47

FIT #3 - FIT IF BASELINE LINEAR ACROSS EACH PEAK (WEIGHTED)
 No. of peaks used in fit = 1

No.	Component	Concentration			Units
---	-----	-----	-----	-----	-----
1	C6H6	2.78	+-	0.19	PPM
2	C7H8	2.26	+-	0.24	PPM
3	TRICH	7.92	+-	0.10	PPM
4	CH3OH	4.87	+-	0.20	PPM
5	FREON-113	0.82	+-	0.04	PPM
6	CO2	366.5	+-	1.7	PPM
7	H2O	794.	+-	16.	PPM (RELATIVE)

VZJ-35

Fig. 7.

ANALYSIS OF: SEM.316 0.124 X ORIGINAL + AIR TO 736
 DATE DATA ANALYZED: 86/09/15 07:03
 RELATIVE PATHLENGTH: 10.000

Calibrated peak file used in analysis: 16
 Title: C6H6 C7H8 TRICH ANALYSIS
 Date calibrated: 86/09/15 06:47

FIT #3 - FIT IF BASELINE LINEAR ACROSS EACH PEAK (WEIGHTED)

No. of peaks used in fit = 1

No. ---	Component -----	Concentration -----			Units -----
1	C6H6	1.54	+-	0.17	PPM
2	C7H8	1.25	+-	0.22	PPM
3	TRICH	4.21	+-	0.09	PPM
4	CH3OH	5.01	+-	0.19	PPM
5	FREON-113	0.80	+-	0.04	PPM
6	CO2	368.6	+-	1.6	PPM
7	H2O	351.	+-	15.	PPM (RELATIVE)

ANALYSIS OF: SEM.317 0.061 X ORIGINAL + AIR TO 736
 DATE DATA ANALYZED: 86/09/15 07:06
 RELATIVE PATHLENGTH: 10.000

Calibrated peak file used in analysis: 16
 Title: C6H6 C7H8 TRICH ANALYSIS
 Date calibrated: 86/09/15 06:47

FIT #3 - FIT IF BASELINE LINEAR ACROSS EACH PEAK (WEIGHTED)

No. of peaks used in fit = 1

No. ---	Component -----	Concentration -----			Units -----
1	C6H6	0.84	+-	0.17	PPM
2	C7H8	0.75	+-	0.22	PPM
3	TRICH	2.28	+-	0.09	PPM
4	CH3OH	5.15	+-	0.19	PPM
5	FREON-113	0.80	+-	0.04	PPM
6	CO2	368.6	+-	1.5	PPM
7	H2O	338.	+-	15.	PPM (RELATIVE)

ANALYSIS OF: SEM.314 0.497 X ORIGINAL/(AIR/
 DATE DATA ANALYZED: 86/09/15 07:13
 RELATIVE PATHLENGTH: 10.000

Calibrated peak file used in analysis: 16
 Title: C6H6 C7H8 TRICH ANALYSIS
 Date calibrated: 86/09/15 06:47

FIT #3 - FIT IF BASELINE LINEAR ACROSS EACH PEAK (WEIGHTED)
 No. of peaks used in fit = 1

No. ---	Component -----	Concentration -----			Units -----
1	C6H6	4.54	+-	0.13	PPM
2	C7H8	4.19	+-	0.29	PPM
3	TRICH	15.23	+-	0.13	PPM
4	CH3OH	3.76	+-	0.25	PPM
5	FREON-113	0.0	+-	0.05	PPM
6	CO2	0.0	+-	0.7	PPM
7	H2O	119.	+-	16.	PPM (RELATIVE)

ANALYSIS OF: SEM.315 0.248 X ORIGINAL/(AIR)
 DATE DATA ANALYZED: 86/09/15 07:16
 RELATIVE PATHLENGTH: 10.000

Calibrated peak file used in analysis: 16
 Title: C6H6 C7H8 TRICH ANALYSIS
 Date calibrated: 86/09/15 06:47

FIT #3 - FIT IF BASELINE LINEAR ACROSS EACH PEAK (WEIGHTED)
 No. of peaks used in fit = 1

No. ---	Component -----	Concentration -----			Units -----
1	C6H6	2.56	+-	0.08	PPM
2	C7H8	2.21	+-	0.19	PPM
3	TRICH	7.96	+-	0.09	PPM
4	CH3OH	3.07	+-	0.17	PPM
5	FREON-113	0.0	+-	0.03	PPM
6	CO2	0.0	+-	0.5	PPM
7	H2O	138.	+-	11.	PPM (RELATIVE)

ANALYSTS OF: SEM.316 0.124 X ORIGINAL/(AIR)
 DATE DATA ANALYZED: 86/09/15 07:29
 RELATIVE PATHLENGTH: 10.000

Calibrated peak file used in analysis: 16
 Title: C6H6 C7H8 TRICH ANALYSIS
 Date calibrated: 86/09/15 06:47

FIT #3 - FIT IF BASELINE LINEAR ACROSS EACH PEAK (WEIGHTED)
 No. of peaks used in fit = 1

No. ---	Component -----	Concentration -----			Units -----
1	C6H6	1.33	+-	0.06	PPM
2	C7H8	1.21	+-	0.15	PPM
3	TRICH	4.24	+-	0.06	PPM
4	CH3OH	3.20	+-	0.14	PPM
5	FREON-113	0.0	+-	0.03	PPM
6	CO2	0.0	+-	0.4	PPM
7	H2O	249.	+-	9.	PPM (RELATIVE)

ANALYSTS OF: SEM.317 0.061 X ORIGINAL/(AIR)
 DATE DATA ANALYZED: 86/09/15 07:30
 RELATIVE PATHLENGTH: 10.000

Calibrated peak file used in analysis: 16
 Title: C6H6 C7H8 TRICH ANALYSIS
 Date calibrated: 86/09/15 06:47

FIT #3 - FIT IF BASELINE LINEAR ACROSS EACH PEAK (WEIGHTED)
 No. of peaks used in fit = 1

No. ---	Component -----	Concentration -----			Units -----
1	C6H6	0.70	+-	0.05	PPM
2	C7H8	0.71	+-	0.13	PPM
3	TRICH	2.30	+-	0.05	PPM
4	CH3OH	3.36	+-	0.12	PPM
5	FREON-113	0.0	+-	0.02	PPM
6	CO2	0.0	+-	0.3	PPM
7	H2O	285.	+-	3.	PPM (RELATIVE)

APPENDIX VIII

Analytical Methods

Carbon Monoxide

Acids, Inorganic

Formaldehyde

Hydrocarbons

Hydrocarbons, Aromatic

Weighing Microporous Filters

Carbon monoxide

DRAGER Long-Term Tube Carbon Monoxide 10/a-L

67 28 741

OPERATING INSTRUCTIONS 234-337410 • 1st Edition • January 1968

1 General and Application

Determination of the mean CO concentration over a prolonged period of time (a maximum of 4 hours).

The Tubes are to be used in conjunction with the DRAGER long-term pump. For use, see Section 4 of these Operating Instructions.

2 Description

See illustration.

With the long-term tube connected at the input side, the rate of flow of the air should be 10 to 20 gpm.

3 Range of Measurement (20°C, 1013 mbar, corresponding to 20°C, 760 mm Hg)

in absolute units: 10 to 100 µl (micrograms) carbon monoxide

Range of measurement in ppm for maximum duration of use:

2.5 to 25 ppm (a volume of 4 litres at approximately 4 hours)

Range of measurement in ppm for shorter periods of use:

10 to 100 ppm (a volume of 1 litre at approximately 1 hour)

4 Test and Evaluation of the Result

4.1 Check the pump for leaks and rate of air sample flow.

4.2 Break off the tip of the DRAGER Tube.

4.3 Insert the DRAGER Tube tightly in the pump connector (arrow points towards the pump).

4.4 Switch on the pump. The maximum total measuring period is 4 hours, if the air sample contains carbon monoxide, the white measuring layer turns brown. The total length of the discoloration is a measure of the CO concentration.

Calculation:

$$\text{ppm CO} = \frac{\text{indication in µl CO}}{\text{volume sucked through in litres}}$$

5 Remarks

The DRAGER Tube cannot be used again even after a negative test result. The indication lasts for several days, if the Tube is sealed with rubber caps.

6 Influence of Ambient Conditions

6.1 Temperature

The DRAGER Tubes can be used in a temperature range of from 0 to 30°C.

6.2 Humidity

Below 20 mg H₂O per litre, humidity has no influence on the indication.

6.3 Atmospheric pressure

For pressure correction, multiply the Tube reading by the following correction factor:

$$\text{Correction factor} = \frac{1013}{\text{actual atmospheric pressure (in mbar)}}$$

7 Specificity (Cross-Sensitivity)

The CO indication is based on a color reaction with iodine pentoxide, selenium dioxide and fuming sulphuric acid.

In addition to carbon monoxide, carbon oxides and hydrocarbons are indicated. There are a few examples of the sensitivity of indication:

100 ppm carbon oxide gives an indication of 20 ppm.

100 ppm benzene gives an indication of 10 ppm.

Hydrogen sulphide does not interfere with the indication at concentrations up to 100 ppm.

8 Shelf Life

For every date and storage temperature, see data on package card.

9 Toxicity Data

TLV (MSHA 1970): 25 ppm

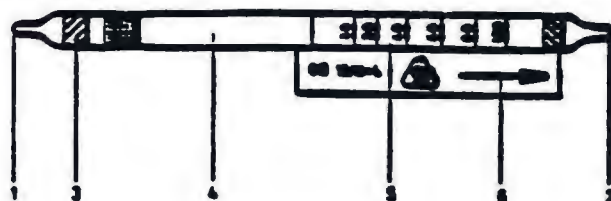
(See also the official guidelines on the effects of CO).

10 Information

At the request of the Tube user, we will supply the following information:

a) The methods used for calibration of the detector tubes.

b) The effects (including reactions) on the operation and accuracy of the gas detector tube used caused by specific environmental conditions described by the user, if the effects are known to us.



- 1 and 2 head cap
- 3 warning band
- 4 pressure warning
- 5 measuring layer (white) with color change (brown) value as µl CO (20°C, 1013 mbar)
- 6 arrow (must point towards pump during testing)

VIII-1

Carbon monoxide

DRAGER Long-Term Tube Carbon Monoxide 50/a-L

CH 21

OPERATING INSTRUCTIONS 234-337210 • 1st Edition • June

1 General and Application

Determination of the mean CO concentration over a long period of maximum of 4 hours.

The tubes are to be used in conjunction with the DRAGER long-term pump. (If any other pump is used, the calibration of the long-term tube be checked). For operation, see Section 4 of these Operating Instructions.

2 Description

See illustration.

With the long-term tube fitted on the intake side, the rate of air flow be 10 to 20 gpm.

3 Range of Measurement (20°C, 1013 mbar, corresponding to 20°C, 760 mm Hg)

in absolute units: 50 to 500 µl (micrograms) CO

Related to concentration: 5 to 50 ppm with a 10-litre air sample

10 to 100 ppm with a 5-litre air sample

50 to 500 ppm with a 1-litre air sample

4 Test and Evaluation of the Result

4.1 Check the pump for leaks and check rate of air flow.

4.2 Break off the tip of the DRAGER Tube.

4.3 Insert the DRAGER Tube tightly in the pump connector (arrow points towards pump).

4.4 Switch on the pump. The maximum total measuring time is 4 hours, if the air sample contains carbon monoxide, the white measuring layer turns brown. The total length of the discoloration is a measure of the CO concentration.

Calculation:

$$\text{ppm CO} = \frac{\text{indication in µl CO}}{\text{volume sucked-through in litres}}$$

5 Remarks

The DRAGER Tube cannot be used again even after a negative test result. The indication lasts for several days, provided that the tubes are sealed with caps.

6 Influence of Ambient Conditions

6.1 Temperature

The DRAGER Tubes can be used in a temperature range of from 0 to 30°C.

6.2 Humidity

Below 20 mg H₂O per litre, humidity has no influence on the indication.

6.3 Atmospheric pressure

For pressure correction, multiply the tube reading by the following correction factor:

$$\text{Correction factor} = \frac{1013}{\text{actual atmospheric pressure (in mbar)}}$$

7 Specificity (Cross-Sensitivity)

The CO indication is based on a color reaction with iodine pentoxide, selenium dioxide and fuming sulphuric acid.

In addition to carbon monoxide, carbon oxides and hydrocarbons are indicated. There are a few examples of the sensitivity of indication:

100 ppm carbon oxide gives an indication of 20 ppm.

100 ppm benzene gives an indication of 10 ppm.

Hydrogen sulphide does not interfere with the indication at concentrations up to 100 ppm.

8 Shelf Life

2 years with storage temperatures below 30°C. The lower the temperature, the longer the DRAGER Tubes are stored, the smaller the change in their properties.

9 Toxicity Data

Threshold limit value (MSHA 1970): 50 ppm

(See also official regulations for CO exposure).

10 Information

At the request of the tube user, we will supply the following information:

a) The methods used for calibration of the detector tubes.

b) The effects (including reactions) on the operation and accuracy of the gas detector tube used caused by specific environmental conditions described by the user, if the effects are known to us.



- 1 and 2 head cap
- 3 warning band
- 4 pressure warning
- 5 measuring layer (white) with color change (brown) value as µl CO (20°C, 1013 mbar)
- 6 arrow (must point towards pump during testing)

FORMULA: (1) HF (4) HBr
(2) HCl (5) HNO₃
(3) H₃PO₄ (6) H₂SO₄

ACIDS, INORGANIC

METHOD: 7903
ISSUED: 2/15/84

OSHA/NIOSH/ACGIH: Table 1

PROPERTIES: Table 1

SYNONYMS: (1) hydrofluoric acid; hydrogen fluoride; CAS #7664-39-3.
(2) hydrochloric acid; hydrogen chloride; CAS #7647-01-0.
(3) phosphoric acid; ortho-phosphoric acid; meta-phosphoric acid; CAS #7664-38-2.
(4) hydrobromic acid; hydrogen bromide; CAS #10035-10-6.
(5) nitric acid; aqua fortis; CAS #7697-37-2.
(6) sulfuric acid; oil of vitriol; CAS #7664-93-9.

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE (washed silica gel, 400 mg/200 mg with glass fiber filter plug)	! TECHNIQUE: ION CHROMATOGRAPHY ! ! ANALYTE: F ⁻ , Cl ⁻ , PO ₄ ³⁻ , Br ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ ! ! DESORPTION: 10 mL 3 mM NaHCO ₃ /2.4 mM Na ₂ CO ₃ ! ! INJECTION LOOP VOLUME: 100 µL ! ! ELUENT: 3 mM NaHCO ₃ /2.4 mM Na ₂ CO ₃ ; 3 mL/min ! ! COLUMNS: anion separator, fast run; anion precolumn, fast run; anion suppressor ! ! CONDUCTIVITY SETTING: 10 µS full scale ! ! RANGE: see EVALUATION OF METHOD ! ! ESTIMATED LOD: see EVALUATION OF METHOD ! ! PRECISION (s _p): see EVALUATION OF METHOD ! ! ! ! ! ! !
FLOW RATE: 0.2 to 0.5 L/min	
VOL-MIN: 3 -MAX: 100	
SHIPMENT: routine	
SAMPLE STABILITY: stable	
BLANKS: 2 to 10 field blanks per set	
ACCURACY	
RANGE STUDIED: see EVALUATION OF METHOD	
BIAS: not significant [2,3,6]	
OVERALL PRECISION (s _p): see EVALUATION OF METHOD	

APPLICABILITY: The working range is ca. 0.01 to 5 mg/m³ for a 50-L air sample (see EVALUATION OF METHOD). This method measures the total concentration of six airborne anions. The corresponding acids may be collected on a single sampler and determined simultaneously.

INTERFERENCES: Particulate salts of all the acids will give a positive interference. Chlorine or hypochlorite ion interfere with chloride determination and bromine interferes with bromide. Collection efficiency of Br₂ and Cl₂ on silica gel has not been investigated. Acetate, formate and propionate have elution times similar to F⁻ and Cl⁻. If these anions are present, use a weak eluent (e.g., 1.5 mM NaHCO₃) in the IC for greater resolution.

OTHER METHODS: This is P&CAM 339 in a revised format [1]. Alternate methods are 7902 for fluoride and P&CAM 268 for sulfate [5].

REAGENTS:

1. Silica gel, 20/40 mesh, grade 01, thoroughly washed with deionized water (see APPENDIX).
2. Distilled, deionized water, filtered through 0.45- μ m membrane filter.
3. Eluent: bicarbonate/carbonate buffer solution (3 mM NaHNO_3 /2.4 mM Na_2CO_3). Dissolve 1.008g NaHCO_3 and 1.018 g Na_2CO_3 in 4 L filtered deionized water.
4. Calibration stock solutions, 1 mg/mL (as the anion). Dissolve salt in filtered deionized water.
 - a. Fluoride: 0.2210 g NaF /100 mL.
 - b. Chloride: 0.2103 g KCl /100 mL.
 - c. Phosphate: 0.1433 g KH_2PO_4 /100 mL.
 - d. Bromide: 0.1288 g NaBr /100 mL.
 - e. Nitrate: 0.1371 g NaNO_3 /100 mL.
 - f. Sulfate: 0.1814 g K_2SO_4 /100 mL.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 11 cm x 7 mm OD, containing a 400-mg front section and 200-mg backup section of washed silica gel. Front section is retained with a glass fiber filter plug. Urethane plugs separate and retain the backup section. Tubes are commercially available (Supelco Orbo 53 or equivalent) or may be prepared according to APPENDIX.
2. Personal sampling pump, 0.2 to 0.5 L/min, with flexible connecting tubing.
3. Ion chromatograph, fast-run anion separator and precolumn, anion suppressor column, conductivity detector, integrator and strip chart recorder.
4. Waterbath: hotplate with beaker of boiling water.
5. Centrifuge tubes, 15-mL, graduated, plastic, with caps.*
6. Syringes, 10-mL, polyethylene with luer tip.
7. Filters, luer tip, with membrane filter, 13-mm, 0.8- μ m pore size.
8. Micropipettes, disposable tips.
9. Volumetric flasks, 50- and 100-mL.*
10. Laboratory timer.
11. Bottles, polyethylene, 100-mL.

*See Special Precautions.

SPECIAL PRECAUTIONS: Acids, particularly HF, are extremely corrosive to skin, eyes, and mucous membranes. HF will attack glass. Plastic labware is recommended.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.2 and 0.5 L/min for a total sample size of 3 to 100 L.

NOTE: Do not exceed 0.3 L/min when sampling for HF.

SAMPLE PREPARATION:

4. Score sampler with a file in front of primary sorbent section.
5. Break sampler at score line. Transfer glass fiber filter plug and primary sorbent section to a 15-mL graduated centrifuge tube.
6. Place backup sorbent section in separate centrifuge tube. Discard urethane plugs.
7. Add 6 to 8 mL eluent to each centrifuge tube. Heat in boiling waterbath for 10 min.

NOTE: Eluent used for desorption should be from same batch as the eluent used on the chromatograph to avoid carbonate/bicarbonate peaks near F^- and Cl^- .
8. Allow to cool, dilute to 10.0-mL volume with eluent.
9. Cap the centrifuge tube and shake vigorously.
10. Pour sample into 10-mL plastic syringe fitted with in-line filter.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least five working standards covering the range 0.001 to 0.3 mg of each anion per sample.
 - a. Add known aliquots of calibration stock solution to eluent in 50-mL volumetric flasks and dilute to the mark.
 - b. Store working standards in tightly-capped polyethylene bottles. Prepare fresh working standards weekly.
 - c. Analyze working standards together with samples and blanks (steps 12 through 14).
 - d. Prepare a calibration graph for each anion [peak height (mm or μ S) vs. mg].

MEASUREMENT:

12. Set ion chromatograph to conditions give on page 7903-1, according to manufacturer's instructions.
13. Inject 100- μ L sample aliquot. For manual operation, inject 2 to 3 mL of sample from filter/syringe to ensure complete rinse of sample loop.

NOTE: All samples, eluents and water flowing through the IC must be filtered to avoid plugging system valves or columns.

14. Measure peak height.

NOTE: If sample peak height exceeds linear calibration range, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

CALCULATIONS:

15. Determine the mass, mg, of anion found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
16. Calculate concentration, C, of acid in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3 \cdot F}{V}, \text{ mg/m}^3$$

where: F (conversion factor from anion to acid) = 1.053 for HF; 1.028 for HCl;
 1.032 for H_3PO_4 ; 1.012 for HBr;
 1.016 for HNO_3 ; and 1.021 for H_2SO_4 .

EVALUATION OF METHOD:

The method was evaluated for hydrochloric, hydrobromic, nitric, phosphoric and sulfuric acids by laboratory generation of mixed acids [2]. Data for the individual analytes are:

Acid	Range Studied		Measurement Precision (s_r)	Overall Precision (s_r)	Estimated LOD (μ g per sample)
	(mg/m ³)	(μ g/sample)			
HF [6]	0.35 - 6	0.5 - 200	0.053	0.116	1
HCl [3]	0.14 - 14	0.5 - 200	0.025	0.059	2
H_3PO_4 [2]	0.5 - 2	3 - 100	0.029	0.096	2
HBr [2]	2 - 20	3 - 960	0.056	0.074	1
HNO_3 [2]	1 - 10	3 - 500	0.018	0.085	1
H_2SO_4 [2]	0.5 - 2	3 - 100	0.028	0.087	4

The method was field-evaluated at two electroplating facilities using side-by-side silica gel tubes and bubblers. The method was evaluated for hydrofluoric acid in 1983 using the silica gel tubes and impingers [6]. Recovery based on impinger collection was 106% with s_r of 0.116. The capacity of the silica gel sampler for HF was 820 μg . This is equivalent to an 8-hr sample at two to three times the OSHA PEL. Samples were stable for at least 21 days at 25 °C.

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METHOD WRITTEN BY: Mary Ellen Cassinelli, NIOSH/DPSE.

APPENDIX:

SAMPLING TUBE PREPARATION

Silica gel cleaning procedure: Add 500 to 600 mL deionized water, slowly and with stirring, to ca. 200 mL volume of silica gel in 1-L beaker. When exothermal reaction has subsided, heat in boiling waterbath for ca. 30 min with occasional stirring. Decant and rinse four to five times with deionized water. Repeat cleaning procedure and dry overnight in 100 °C oven until free flowing. If blank of silica gel shows impurities, repeat cleaning procedure.

Silica gel tubes: Pack glass tubes, 7 mm OD, 4.8 mm ID, 11 cm long, with 400 mg of 20/40 mesh washed silica gel in front section and 200 mg backup section. Use urethane foam plugs between sorbent sections and at back end. Hold front section in place with 6-mm diameter, 1-mm thick glass fiber filter plug (Gelman 66088).

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Table 1. General information.

Acid and M.W.	EXPOSURE LIMITS (ppm)				PROPERTIES				
	OSHA	NIOSH	ACGIH	mg/m ³ = 1 ppm @ NTP	Physical State	MP (°C)	BP (°C)	Sp. Gr. (liq.)	VP @ 20 °C kPa (mm Hg)
HF (20.01)	3	3; 6/15 min	3; STEL 6	0.818	gas	-83.1	19.5	0.987	>101 (>760)
HCl (36.46)	C 5	—	C 5	1.491	gas	-114.8	-85.0	1.194	>101 (760)
H ₃ PO ₄ (97.99)	1 mg/m ³	—	1 mg/m ³ ; STEL 3 mg/m ³	4.01	liquid	21.0	260	1.7	0.0038 (0.03)
HBr (80.92)	3	—	3	3.31	gas	-88.5	-66.8	2.16	>101 (>760)
HNO ₃ (63.01)	2	2	2; STEL 4	2.58	liquid	-42.0	83	1.50	0.39 (2.9)
H ₂ SO ₄ (98.08)	1 mg/m ³	1 mg/m ³	1 mg/m ³	—	liquid	3.0	290	1.84	<0.0001 (<0.001)

7903-6

11222-7

FORMULA: $H_2C=O$; CH_2O

FORMALDEHYDE

M.W.: 30.03

METHOD: 2502

ISSUED: 2/15/84

OSHA: 3 ppm; C 5 ppm; peak 10 ppm
NIOSH: lowest feasible level (1)
ACGIH: 1 ppm; STEL 2 ppm
(1 ppm = 1.23 mg/m³ @ NTP)

PROPERTIES: gas; BP -19.5 °C;
vapor density 1.067 (air = 1);
explosive range 7 to 73% v/v in air

SYNONYMS: methanal; CAS #50-00-0; Formalin (aqueous 30 to 50% w/v HCHO).

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE (2-(benzylamino)ethanol on Chromosorb 102 or XAD-2, 120 mg/60 mg)	! TECHNIQUE: GAS CHROMATOGRAPHY, FID !
FLOW RATE: 0.01 to 0.05 L/min	! ANALYTE: 3-benzylloxazolidine !
VOL-MIN: 1 L @ 3 ppm -MAX: 15 L	! DESORPTION: 2 mL isooctane; ultrasonic bath 45 min or shake 4 hr !
SHIPMENT: routine	! INJECTION VOLUME: 1 µL, splitless; split vent time 30 sec !
SAMPLE STABILITY: 4 weeks @ 25 °C	! TEMPERATURE-INJECTION: 210 °C ! -DETECTOR: 220 °C ! -COLUMN: 70 °C for 1 min; 10 °C/min; hold @ 200 °C for 11.5 min !
BLANKS: 2 media blanks and 2 field blanks per set of 10; 6 unopened tubes for DE determination (same lot as samples)	! GASES-CARRIER: He, 100 kPa, ca 0.5 cm ³ /min; makeup flow, 29 cm ³ /min !
ACCURACY	! COLUMN: fused silica capillary, 25 m x 0.2 mm; Carbowax 20M !
RANGE STUDIED: 0.55 to 4.7 mg/m ³ [2]	! CALIBRATION: solutions of 3-benzylloxazolidine in isooctane !
BIAS: not significant [2]	! RANGE: 4 to 60 µg per sample !
OVERALL PRECISION (s _p): 0.061 [2]	! ESTIMATED LOD: 1 µg per sample [3] !
	! PRECISION (s _p): 0.055 [2] !

APPLICABILITY: The working range is 0.3 to 5 mg/m³ (0.25 to 4 ppm) for a 12-L air sample.

INTERFERENCES: Phenol has a retention time close to that of 3-benzylloxazolidine but is baseline-resolved. Acid mists may inactivate the sorbent leading to inefficient collection of formaldehyde.

OTHER METHODS: This method was formerly designated POCAN 354 [4]. It has improved sample stability and ease of personal sampling compared to Methods 3500 and 3501. Method 3500 (chromotropic acid) is the most sensitive.

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VIII-8

REAGENTS:

1. Water, distilled, deionized.
2. Eluent: Isooctane, chromatographic grade, containing 0.025% (v/v) hexadecane or other suitable internal standard.
3. Formalin solution, 37%.*
4. Sulfuric acid, 0.02 M.
5. Sodium hydroxide, 0.01 M.
6. Sodium sulfite, 1.13 M.
7. Toluene, distilled in glass.
8. 2-(benzylamino)ethanol, distilled, 100 to 130 °C at 130 Pa (1 mm Hg).
9. 3-Benzylloxazolidine (see Appendix).
10. Formaldehyde stock solution, 1 mg/mL (see Appendix). Stable at least 3 months.
11. Helium, purified.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 10 cm x 4 mm ID, containing a 120-mg front section and 60-mg backup section of 2-(benzylamino)ethanol on either Chromosorb 102 or XAD 2. Sorbent sections are retained and separated by small plugs of glass wool. Pressure drop ca. 0.2 kPa (0.8 inch water) at 50 cm³/min airflow. Tubes are commercially available or may be prepared according to the Appendix.
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, capillary column capability, FID, integrator (page 2502-1).
4. Vials, 4-mL, with plastic screw caps.
5. Ultrasonic bath or mechanical shaker.
6. Pipettes, volumetric, 1-, 5- and 10-mL, with pipet bulb.
7. Flasks, volumetric, 10-mL and 1-L.
8. Burettes, 50-mL.
9. pH meter.
10. Disposable pipettes, 2-mL.
11. Syringe, 10-μL, readable to 0.1 μL.

SPECIAL PRECAUTIONS: Formaldehyde is viewed as a potential occupational carcinogen by NIOSH [1].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 1 to 15 L.

NOTE 1: Sampling rate is limited by the speed of reaction of formaldehyde with the sorbent coating. At 0.10 L/min, appreciable formaldehyde (ca. 25%) is found on the backup section, possibly invalidating the sample. At higher flow rates, formaldehyde concentrations will be grossly underestimated.

NOTE 2: The presence of acid mists or gases may interfere indirectly by reacting with the 2-(benzylamino)ethanol to form amine salts which are not reactive with formaldehyde. If a sufficient amount of the 2-(benzylamino)ethanol is consumed by the acid, formaldehyde concentrations found with the method may be lower than the true concentrations.

4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Score each sampler with a file in back of the rear sorbent section.
6. Break sampler at score line. Remove and place glass wool plug and rear sorbent section in a vial.
7. Transfer front section with the remaining glass wool plugs to a vial.

8. Add 2.0 mL eluent to each vial. Screw cap tightly onto each vial.
9. Agitate vials in an ultrasonic bath for at least 45 min or in a shaker for 4 hr.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least five working standards.
 - a. Add known amounts of 3-benzylloxazolidine to eluent in 10-mL volumetric flasks and dilute to the mark.
NOTE: Prepare standard solutions for splitless injection in the range 1 to 50 µg/mL; for split injection, in the range 1 to 400 µg/mL.
 - b. Analyze together with samples and blanks (steps 13 and 14).
 - c. Prepare calibration graph (ratio of peak area or height of analyte to peak area or height of internal standard vs. µg 3-benzylloxazolidine) for the injection technique used.
11. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 10). Prepare three tubes at each of five levels plus three media blanks.
 - a. Remove and discard back sorbent section of a media blank sampler.
 - b. Inject a known amount of formaldehyde stock solution directly onto front sorbent section with a microliter syringe.
 - c. Cap the tube. Allow to stand overnight.
 - d. Desorb (steps 5 through 9) and analyze together with working standards (steps 13 and 14).
 - e. Prepare a graph of DE vs. µg 3-benzylloxazolidine recovered.
12. Analyze three quality control blind spiked and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

13. Set gas chromatograph to conditions given on page 2502-1. Set air and hydrogen flows on the flame ionization detector to manufacturer's specifications. Inject 1-µL sample aliquot via the splitless injection technique. $t_p = 11.5$ min for these conditions.
NOTE: If sample amount of 3-benzylloxazolidine overloads the column (> 50 ng/µL for 0.2 mm ID column), either dilute sample with eluent or inject via split injection technique, reanalyze, and apply appropriate volume correction factor in calculations. Column overloading is indicated by a plateau on the calibration graph at high concentrations. If split injection is required, the following conditions are typical:

Column temperature program:	150 °C for 7 min; 10 °C/min; hold at 200 °C
Split flow rate:	10 cm ³ /min He
Retention time:	5.9 min

14. Measure peak area or height. Divide the peak area or height of analyte by the peak area or height of internal standard on the same chromatogram.

CALCULATIONS

15. Determine the mass, µg (corrected for DE) of 3-benzylloxazolidine found in the sample front (M_f) and back (M_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.

NOTE 1: If $M_b > M_f/10$, report breakthrough and possible sample loss.

NOTE 2: A blank level of 1 to 7 µg HCHO is typical. Measure sufficient media blanks (at least 2 per 10 samples) to determine a representative mean value.

16. Multiply by the desorption volume (2 mL) and the conversion factor (0.184) from 3-benzylloxazolidine to formaldehyde to calculate concentration, C, of formaldehyde in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 2 \text{ mL} \cdot 0.184}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD

Side-by-side comparisons of this method using laboratory-prepared samplers with a 2,4-dinitrophenylhydrazine-coated silica gel tube method [5] were done in a formaldehyde production facility. Means of the two methods were not significantly different [6]. Lab testing with spiked samplers and atmospheres generated by syringe pump/air dilution [2]; verified by 2,4-dinitrophenylhydrazine-coated silica gel tubes [5]. Breakthrough volume of laboratory-prepared samplers (80% RH, 6 mg HCHO/m³, 0.05 L/min) was greater than 16 L; DE (10.5, 37.5, 76.0 µg per sample) = 99%; recovery after storage (0.85 µg per sample) = 94.3% after two weeks at 25 °C; precision and accuracy as given on page 2502-1 (24 samples). When acetaldehyde was present as a cocontaminant, 5% breakthrough volume was 16 L (80% RH, 10 mg HCHO/m³, 10 mg acetaldehyde/m³, 0.05 L/min). Sampling rate influences reaction of formaldehyde with the sorbent coating. Rates above 0.05 L/min give low results with laboratory-prepared samplers.

In a breakthrough study done using commercially-available tubes, the breakthrough volume was found to be greater than 73 L at 8.7 mg/m³ and greater than 58 L at 28 mg/m³ of formaldehyde. These atmospheres were sampled at 0.078 L/min.

An atmosphere of 0.36 mg/m³ formaldehyde, as determined by POCAN 125 [7], was sampled with sets of six tubes at ca. 0.08 L/min for 70 min, 286 min and 482 min. The average amount indicated by these tubes was 0.32 mg/m³ with the relative standard deviation less than 10% in all cases. The tube loadings for these sampling periods were 1.6, 6.3 and 10.8 µg. This information indicates that concentrations as low as 0.1 mg/m³ should be measurable with a sampling rate of 0.08 L/min and a sampling time of 8 hrs.

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METHOD WRITTEN BY: Eugene R. Kennedy, Ph.D., and Robert H. Hill, Jr., Ph.D., NIOSH/DPSE.

VJJD-11

APPENDIX:

SAMPLING TUBE PREPARATION

Extract Chromosorb 102 or XAD-2 with a 50/50 (v/v) mixture of acetone/methylene chloride in a soxhlet apparatus for 4 hrs using a 30-min cycle time. Vacuum dry [1 mm Hg (133 Pa)] the sorbent at ambient temperature overnight. To a slurry of the dried, extracted sorbent (10 g in 100 mL toluene), add 1 g distilled 2-(benzylamino)ethanol in 10 mL toluene. Allow to stand for 1 hr with occasional swirling. Remove the solvent by rotary evaporation and vacuum dry [1 mm Hg (133 Pa)] at ambient temperature overnight. For each batch of the coated sorbent, desorb several 100-mg portions with isooctane and analyze. If the background is greater than 7 µg 3-benzylloxazolidine/100 mg coated sorbent, discard the batch.

PREPARATION OF 3-BENZYLOXAZOLIDINE

Add a solution of 1.51 g (10 mmole) 2-(benzylamino)ethanol in 10 mL toluene dropwise to a solution of 1 mL 37% formalin (0.37 g formaldehyde, 12.3 mmole) in 25 mL toluene. Stir 1 hr. Remove the solvent at reduced pressure by rotary evaporation. The product is a yellow viscous oil. Vacuum distill at 58 to 62 °C at 1 mm Hg (133 Pa); yields 3-benzylloxazolidine as a clear, colorless oil, stable at room temperature for several months in a closed vial.

PREPARATION AND STANDARDIZATION OF FORMALDEHYDE STOCK SOLUTION (ca. 1 mg/mL)

Dilute 2.7 mL 37% formalin solution to 1 L with distilled, deionized water. This solution is stable at least three months. Standardize as follows:

Place 5.0 mL 1.13 M sodium sulfite solution in a beaker, stirred with a magnetic stirrer. Adjust pH to between 7 and 9 with base or acid. Record the pH. Add 10.0 mL stock formaldehyde solution. The pH should now be about 12. Titrate the solution back to its original pH with 0.02 M sulfuric acid (1 mL acid = 0.600 mg HCHO; about 17 mL acid needed). If the endpoint pH is overrun, back titrate to the endpoint with 0.01 M sodium hydroxide. Calculate the concentration, C_s (mg/mL), of the formaldehyde stock solution:

$$C_s = \frac{30.0 \cdot [(N_a \cdot V_a) - (N_b \cdot V_b)]}{V_s}$$

where: 30.0 = 30.0 g/equivalent of formaldehyde

N_a = normality of sulfuric acid

V_a = volume of sulfuric acid (mL) used for titration

N_b = normality of NaOH

V_b = volume of NaOH (mL) used for back titration

V_s = volume of HCHO stock solution (10.0 mL).

VJ27-12

FORMULA: Table 1

M.W.: Table 1

HYDROCARBONS, BP 36 - 126 °C

METHOD: 1500

ISSUED: 2/15/84

OSHA, NIOSH, ACGIH: Table 2

PROPERTIES: Table 1

COMPOUNDS: benzene
(Synonyms: cyclohexane
in Table 1) cyclohexane

n-heptane
n-hexane
methylcyclohexane

n-octane
n-pentane
toluene

SAMPLING

MEASUREMENT

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal,
100 mg/50 mg)

FLOW RATE, VOLUME: Table 3

SHIPMENT: no special precautions

SAMPLE STABILITY: at least 2 weeks

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: desirable, 1 to 10 mL; ship in
separate containers from samples

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTES: hydrocarbons listed above

DESCRIPTION: 1 mL CS₂; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 250 °C

-DETECTOR: 250 °C

-COLUMN: see step 11

CARRIER GAS: N₂ or He, 25 mL/min

COLUMN: glass, 3.0 m x 2 mm, 20% SP-2100 on
80/100 mesh Supelcoport

ACCURACY

RANGE STUDIED,

BIAS and OVERALL PRECISION (s_p): Table 3

CALIBRATION: analytes in CS₂

RANGE AND PRECISION (s_p): Table 4

ESTIMATED LOD: 0.001 to 0.01 mg per sample
with capillary column [1]

APPLICABILITY: This method is intended for determining the OSHA-regulated hydrocarbons included within the boiling point range of n-pentane through n-octane. It may be used for simultaneous measurements; however, interactions between analytes may reduce breakthrough volumes and change desorption efficiencies.

INTERFERENCES: At high humidity, breakthrough volumes may be reduced by as much as 50%. Other volatile organic solvents, e.g., alcohols, ketones, ethers, and halogenated hydrocarbons, are likely interferences. If interference is suspected, use a more polar column or change column temperature.

OTHER METHODS: This method is based on and supercedes Methods PCAR 127, benzene and toluene [2]; S28, cyclohexane [3]; S82, cyclohexane [3]; S89, heptane [3]; S90, hexane [3]; S94, methylcyclohexane [3]; S311, benzene [4]; S343, toluene [4]; S378, octane [4]; and S379, pentane [4]. For benzene or toluene in complex mixture of alkanes (C₁₀), Method 1501 (aromatic hydrocarbons) is more selective.

REAGENTS:

1. Eluent: Carbon disulfide*, chromatographic quality with (optional) suitable internal standard.
2. Analytes, reagent grade.*
3. Nitrogen or helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg, back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section, and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1500-1).
4. Vials, glass, 1-mL, with PTFE-lined caps.
5. Pipet, 1-mL, with pipet bulb.
6. Syringes, 5-, 10-, 25- and 100- μ L.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and extremely flammable (flash point = -30 °C); benzene is a suspect carcinogen. Prepare samples and standards in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min (0.01 to 0.05 L/min for n-pentane) for a total sample size as shown in Table 3.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial immediately.
7. Allow to stand at least 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the appropriate range (ca. 0.01 to 10 mg analyte per sample; see Table 4).
 - a. Add known amounts of analyte to eluent in 10-mL volumetric flasks and dilute to the mark.
 - b. Analyze together with samples and blanks (steps 11, 12 and 13).
 - c. Prepare calibration graph (peak area of analyte vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
 - a. Remove and discard back sorbent section of a media blank sampler.
 - b. Inject a known amount of analyte directly onto front sorbent section with a microliter syringe.

Table 2. Permissible exposure limits, ppm [7-11].

Substance	OSHA			NIOSH		ACGIH		mg/m ³ per ppm @ NTP
	TLV	C	Peak	TLV	C	TLV	STEL	
benzene ^a	10	25	50 ^b	1		10	25	3.19
cyclohexane	300					300	375	3.44
cyclohexene	300					300		3.36
n-heptane	500			85	440	400	500	4.10
n-hexane ^a	500			100	510	50		3.52
methylcyclohexane	500					400	500	4.01
n-octane	500			75	385	300	375	4.67
n-pentane	1000			120	610	600	750	2.95
toluene	200	300	500 ^b	100	200 ^c	100	150 (skin)	3.77

^aThe ACGIH recommendation for other hexane isomers is: TLV 500, STEL 1000.^bMaximum duration 10 min in 8 hr.^c10-min sample.^{*}ACGIH: suspect carcinogenTable 3. Sampling flowrate^a, volume, capacity, range, overall bias and precision [2-4, 12].

Substance	Sampling			Breakthrough		Range at VOL-NOM (mg/m ³)	Overall	
	Flowrate (L/min)	Volume (L) VOL-NOM	VOL-MAX ^b	Volume at Concentration (L)	(mg/m ³)		Bias (%)	Precision (%)
benzene	50.20	2 ^c	30	>45	149.1	41.5 - 165	0.8	0.059
cyclohexane	50.20	2.5	5	7.6	1650	510 - 2010	5.4	0.060 ^d
cyclohexene	50.20	5	7	10.4	2002	510 - 2030	9.0	0.073
n-heptane	50.20	4	4	6.1	4060	968 - 4060	-6.5	0.056
n-hexane	50.20	4	4	5.9	3679	877 - 3679	-3.8	0.062
methylcyclohexane	50.20	4	4	6.1	3941	940 - 3941	5.5	0.052
n-octane	50.20	4	4	6.5	4612	1050 - 4403	-5.2	0.060
n-pentane	50.05	2	2	3.1	5640	1476 - 6190	-9.7	0.055
toluene	50.20	2 ^c	8	11.9	2294	548 - 2190	3.8	0.052

^aMinimum recommended flow is 0.01 L/min.^bApproximately two-thirds the breakthrough volume.^c10-min sample.^dCorrected value, calculated from data in [12].

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EVALUATION OF METHOD:

Precisions and biases (Table 3) were determined by analyzing generated atmospheres containing one-half, one, and two times the OSHA standard. Generated concentrations were independently verified. Breakthrough capacities were determined in dry air. Storage stability was not assessed. Measurement precisions (Table 4) were determined by spiking sampling media with amounts corresponding to one-half, one, and two times the OSHA standard for nominal air volumes. Desorption efficiencies for spiked samplers containing only one compound exceeded 75%. Reference [12] provides more specific information.

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METHOD REVISED BY: R. Alan Lunsford, Ph.D., and Julie R. Okenfuss; based on results of NIOSH Contract CDC-99-74-45.

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Table 4. Measurement range, precision, and chromatographic conditions [2-4,12].

Substance	Measurement ^a		Carrier		Column Parameters ^b			
	Range	Precision	Gas	Flow	t	Length	Dia-	Packing ^c
	(mg)	(s _r)		(mL/min)	(°C)	(m)	meter (mm)	
benzene	0.09-0.35	0.036	N ₂	50	115	0.9	3.2	A
cyclohexane	1.3 - 5.3 ^d	0.024	N ₂	50	210	1.2	6.4	B
cyclohexane	2.4 - 9.7 ^d	0.021	N ₂	50	205	1.2	6.4	B
n-heptane	4.08-16.3	0.016	He	30	80	3.0	3.2	C
n-hexane	3.56-14.5	0.014	He	30	52	6.1	3.2	D
methylcyclohexane	3.98-16.1	0.012	He	30	55	6.1	3.2	D
n-octane	4.75-18.9	0.009	He	30	52	6.1	3.2	D
n-pentane	2.98-11.8	0.014	He	30	52	6.1	3.2	D
toluene	1.13-4.51	0.011	N ₂	50	155	0.9	3.2	B

^aInjection volume, 5.0 µL; desorption volume, 1.0 mL, except cyclohexane and cyclohexane, 0.5 mL.

^bAll columns stainless steel. Diameter is outside dimension.

CA, 50/80 mesh Porapak P; B, 50/80 mesh Porapak Q; C, 10% OV-101 on 100/120 mesh Supelcoport; D, 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS.

^cCorrected value, calculated from data in [12].

FORMULA: Table 1

M.W.: Table 1

HYDROCARBONS, AROMATIC

METHOD: 1501

ISSUED: 2/15/84

OSHA, NIOSH, ACGIH: Table 2

PROPERTIES: Table 1

COMPOUNDS:	benzene	cunene	α -methylstyrene	styrene	vinyltoluene
(Synonyms in Table 1)	p-tert-butyltoluene	ethylbenzene	naphthalene	toluene	xylene

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)	! TECHNIQUE: GAS CHROMATOGRAPHY, FID
FLOW RATE, VOLUME: Table 3	! ANALYTES: hydrocarbons listed above
SHIPMENT: no special precautions	! DESCRIPTION: 1 mL CS ₂ ; stand 30 min
SAMPLE STABILITY: not determined	! INJECTION VOLUME: 5 μ L
BLANKS: 2 to 10 field blanks per set	! TEMPERATURE-INJECTION: 225 $^{\circ}$ C
BULK SAMPLE: desirable, 1 to 10 mL; ship in separate containers from samples	! -DETECTOR: 225 $^{\circ}$ C
	! -COLUMN: see step 11
	! CARRIER GAS: N ₂ or He, 25 mL/min
	! COLUMN: glass, 3.0 m x 2 mm, 10% OV-275 on 100/120 mesh Chromosorb W-AW or equivalent
	! CALIBRATION: analytes in CS ₂
	! RANGE AND PRECISION (s _p): Table 4
	! ESTIMATED LOD: 0.001 to 0.01 mg per sample with capillary column [1]

APPLICABILITY: This method is for peak, ceiling and TWA determinations of aromatic hydrocarbons. It may be used for simultaneous measurements, though there is the possibility that interactions between analytes may reduce the breakthrough volumes and change desorption efficiencies.

INTERFERENCES: One of the recommended column will prevent interference by alkanes (C₁₀). Under conditions of high humidity, the breakthrough volumes may be reduced by as much as 50%. Other volatile organic solvents, e.g., alcohols, ketones, ethers and halogenated hydrocarbons, are possible interferences. If interference is suspected, use a less polar column or change column temperature.

OTHER METHODS: This method is based on and supercedes Methods P&CAM 127, benzene, styrene, toluene and xylene [2]; S311, benzene [4]; S22, p-tert-butyltoluene [3]; S23, cunene [3]; S29, ethylbenzene [3]; S26, α -methylstyrene [3]; S292, naphthalene [4]; S30, styrene [3]; S343, toluene [4]; S25, vinyltoluene [3]; S318, xylene [4].

REAGENTS:

1. Eluent: Carbon disulfide*, chromatographic quality containing (optional) suitable internal standard.
2. Analytes, reagent grade*
3. Nitrogen or helium, purified
4. Hydrogen, prepurified.
5. Air, filtered.
6. Naphthalene calibration stock solution, 0.40 g/mL in CS₂.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg, back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pumps, 0.01 to 1 L/min (Table 3), with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and column (page 1501-1).
4. Vials, glass, 1-mL, with PTFE-lined caps.
5. Pipet, 1-mL, and pipet bulb.
6. Syringes, 5-, 10-, 25- and 100- μ L.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and extremely flammable (flash point = -30 °C); benzene is a suspect carcinogen. Prepare samples and standards in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min (to 1 L/min for naphthalene or styrene) for a total sample size as shown in Table 3.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial immediately.
7. Allow to stand at least 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the appropriate range (ca. 0.01 to 10 mg analyte per sample; see Table 4).
 - a. Add known amounts of analyte (calibration stock solution for naphthalene) to eluent in 10-mL volumetric flasks and dilute to the mark.
 - b. Analyze together with samples and blanks (steps 11, 12 and 13).
 - c. Prepare calibration graph (peak area of analyte vs. mg analyte).

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9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
 - a. Remove and discard back sorbent section of a media blank sampler.
 - b. Inject a known amount of analyte (calibration stock solution for naphthalene) directly onto front sorbent section with a microliter syringe.
 - c. Cap the tube. Allow to stand overnight.
 - d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11, 12 and 13).
 - e. Prepare a graph of DE vs. mg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1501-1. Select appropriate column temperature:

Substance ^a	Approximate Retention Time (min), at Indicated Column Temperature			
	50 °C	100 °C	150 °C	Programmed ^b
benzene	2.5			2.5
toluene	4.3	1.1		4.2
xylene (para)	7.0	1.4		5.2
ethylbenzene	7.0	1.4		5.5
xylene (meta)	7.2	1.5		5.6
cumene	8.3	1.6		6.0
xylene (ortho)	10	1.9		6.5
styrene	16	2.6		7.6
α -methylstyrene		3.2	1.0	8.1
vinyltoluene (meta)		3.8	1.2	8.5
naphthalene		25	4.3	12

^aData not available for *p*-tert-butyltoluene and *p*-vinyltoluene.

^bTemperature program: 50 °C for 3 min, then 15 °C/min to 200 °C.

NOTE: Alternatively, column and temperature may be taken from Table 4.

12. Inject sample aliquot manually using solvent flush technique or with autosampler.

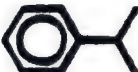
NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
13. Measure peak area.

CALCULATIONS:

14. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.

NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.

Table 1. Synonyms^a, formula, molecular weight, properties [5].

Name/Synonyms	Structure	Empirical Formula	Molecular Weight	Boiling Point (°C)	Vapor Pressure @ 25 °C		Density @ 20 °C (g/ml)
					(mm Hg)	(kPa)	
benzene CAS #71-43-2		C ₆ H ₆	78.11	80.1	95.2	12.7	0.879
p-tert-butyltoluene CAS #98-51-1 1-tert-butyl-4-methylbenzene		C ₁₁ H ₁₆	148.25	192.8	0.7	0.09	0.861
cumene CAS #98-82-8 isopropylbenzene		C ₉ H ₁₂	120.20	152.4	4.7	0.62	0.862
ethylbenzene CAS #100-41-4		C ₈ H ₁₀	106.17	136.2	9.6	1.28	0.867
α-methylstyrene CAS #98-83-9 isopropenylbenzene (1-methylethenyl)-benzene		C ₉ H ₁₀	118.18	165.4	2.5	0.33	0.911
naphthalene CAS #91-20-3		C ₁₀ H ₈	128.18	80.2 ^a	0.2	0.03	1.025
styrene CAS #100-42-5 vinylbenzene		C ₈ H ₈	104.15	145.2	6.1	0.81	0.906
toluene CAS #108-88-3 methylbenzene		C ₇ H ₈	92.14	110.6	28.4	3.79	0.867
vinyltoluene ^b CAS #25013-15-4 methylstyrene methylvinylbenzene		C ₉ H ₁₀	118.18	167.7	1.6	0.22	0.898
	(p-vinyltoluene)	(meta)		171.6	1.9	0.26	0.911
		(para)		172.8	1.8	0.24	0.911
		(ortho)		169.8	1.8	0.24	0.904
xylene ^c CAS #1330-20-7 dimethylbenzene		C ₈ H ₁₀	106.17	144.4	6.7	0.89	0.880
	(p-xylene)	(meta)		139.1	8.4	1.12	0.864
		(para)		138.4	8.8	1.18	0.861

^aMelting point.^bCommercial mixture of meta and para isomers.^cMixture of isomers.

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15. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^6}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Precisions and biases listed in Table 3 were determined by analyzing generated atmospheres containing one-half, one, and two times the OSHA standard. Generated concentrations were independently verified. Breakthrough capacities were determined in dry air. Storage stability was not assessed. Measurement precisions given in Table 4 were determined by spiking sampling media with amounts corresponding to one-half, one, and two times the OSHA standard for nominal air volumes. Desorption efficiencies for spiked samplers containing only one compound exceeded 75%. Reference [12] provides more specific information.

REFERENCES:

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- [2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, POCAM 127, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
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METHOD REVISED BY: R. Alan Lunsford, Ph.D., and Julie R. Okenfuss; based on results of NIOSH Contract CDC-99-74-45.

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Table 4. Measurement range, precision and conditions^a [3,4,12].

Substance	Description Volume (mL)	Measurement		Carrier Flow (mL/min)	Column Parameters ^b		
		Range (mg)	Precision (%)		t (°C)	Length (m)	Packing ^c
benzene	1.0	0.09- 0.35	0.038	50	115	0.9	A
p-tert-butyltoluene	0.5	0.27- 1.09	0.021 ^d	50	115	3.0	B
cumene	0.5	0.86- 3.46	0.010	50	99	3.0	B
ethylbenzene	0.5	2.17- 8.67	0.010	50	85	3.0	B
m-methylstyrene	0.5	0.69- 3.57	0.011	50	115	3.0	B
naphthalene	1.0	4.96-19.7	0.019	30	125	3.0	C
styrene	0.5	2.17- 8.49	0.013 ^d	50	109	3.0	B
toluene	1.0	1.13- 4.51	0.011	50	155	0.9	D
vinyltoluene	0.5	2.41- 9.64	0.008	50	120	3.0	B
xylene	1.0	2.60-10.4	0.010	50	180	0.9	D

^aInjection volume, 5.0 µL; nitrogen carrier gas.^bAll columns stainless steel, 3.2 mm outside diameter.^cA, 50/80 mesh Porapak P; B, 10% FFAP on 80/100 mesh Chromosorb W AG-ONCS;

C, 10% OV-101 on 100/120 mesh Supelcoport; D, 50/80 mesh Porapak Q.

^dCorrected value, calculated from data in [12].

Table 2. Permissible exposure limits, ppm [6-11].

Substance	OSHA			NIOSH		ACGIH		mg/m ³ per ppm
	TWA	C	Peak	TWA	C	TLV	STEL	
benzene	10	25	50 ^a	1		10 ^{**}	25 ^{**}	3.19
p-tert-butyltoluene	10					10	20	6.06
cumene	50 (skin)					50	75 (skin)	4.91
ethylbenzene	100					100	125	4.34
α-methylstyrene		100				50	100	4.83
naphthalene	10					10	15	5.24
styrene	100	200	600 ^b	50	100	50	100	4.26
toluene	200	300	500 ^a	100	200 [*]	100	150 (skin)	3.77
vinyltoluene	100					50	100	4.83
xylene	100			100	200 [*]	100	150	4.34

^aMaximum duration 10 min in 8 hr.^{**}ACGIH: suspect carcinogen [10].^bMaximum duration 5 min in any 3 hr.^{*} 10-min sample.Table 3. Sampling flowrate^a, volume, capacity, range, overall bias and precision [3,4,12].

Substance	Sampling			Breakthrough		Range	Overall	
	Flowrate	Volume (L)		Volume @		at	Bias	Precision
	(L/min)	VOL-NOM	VOL-MAX ^b	Concentration	(L)	(mg/m ³)		
				(L)		(mg/m ³)	(%)	(s _p)
benzene	≤0.20	2 ^c	30	>45	149	42- 165	0.8	0.059
p-tert-butyltoluene	≤0.20	10	29	44	112	29- 119	-10.4	0.071 ^d
cumene	≤0.20	10	30	>45	480	120- 480	4.6	0.059
ethylbenzene	≤0.20	10	24	35	917	222- 884	-8.1	0.089 ^d
α-methylstyrene	≤0.20	3 ^f	30	>45	940	236- 943	-10.8	0.061 ^d
naphthalene ^g	≤1.0	200	200	>240	81	19- 83	-0.5	0.055
styrene	≤1.0	58	14	21	1710	426-1710	-10.7	0.058 ^d
toluene	≤0.20	2 ^c	8	12	2294	548-2190	3.8	0.052
vinyltoluene	≤0.20	10	24	36	952	256- 970	-9.5	0.061 ^d
xylene	≤0.20	12	23	35	870	218- 870	-2.1	0.060

^aMinimum recommended flow is 0.01 L/min.^bApproximately two-thirds the breakthrough volume, except for naphthalene.^c10-min sample.^dCorrected value, calculated from data in Reference 12.^eNaphthalene shows poor desorption efficiency at low loading; 100-L minimum volume is recommended.^f15-min sample.^g95-min sample.

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INSTRUCTION NUMBER: AI-1

TASK: Weighing Microporous Filters

DATE PREPARED: June 10, 1981

PAGE NUMBER 1

TOTAL PAGES 5

PURPOSE: This instruction is intended to present a logical process for tare weighing microporous filters, post weighing microporous filters, and reporting results from these weighings.

FORMS REQUIRED: Filter weight worksheet

STORED IN: Room 143, 1st drawer, file cabinet. **SECTION I. Tare Weighing**

FUNCTION	IMPORTANT STEP
1. Check conditions in the environmental chamber to insure conditions of $70^{\circ}\text{F} \pm 0.5^{\circ}\text{F}$ and $50\% \pm 5\%$ relative humidity. If not, adjust controls and re-check until conditions are met.	Use the recording hydrothermograph to get these data. Do not rely on panel gauges. Periodically check the hydrothermograph with a psychrometer.
2. Check vacuum chamber to insure that the seal between top and bottom is evenly greased and that the external desiccant cartridge is not expended.	Expended cartridge will show a pink color. A good cartridge will be blue or mostly blue with a small layer of pink. Desiccant can be regenerated by heating at 200°C in the oven.
3. Place a maximum of 30 filters and backup pads in the vacuum chamber, seal, and using the vacuum pump provided, pull a vacuum on the chamber. Close stopcock, remove pump and attach the external desiccant cartridge.	Allow vacuum to remain for a minimum of 15 minutes.
4. Using stopcock, slowly release vacuum and remove vacuum chamber cover. Allow filters to equilibrate to environmental chamber conditions for a minimum of one hour.	
5. Lay out enough cassette bottom sections to accommodate the filters to be weighed. Number the backup pads with appropriate filter sequence numbers and place in cassette bottom sections with the numbered side toward the bottom.	Number the backup pads with a ballpoint pen or <u>finer</u> <u>point</u> fiber pen. The numbers must be legible enough to be read through the ribbed bottom of the cassette.
6. Using the form "Filter Weight Work Sheet", number the form to correspond with the numbers on the backup pads.	Be sure to fill in all information requested along the top margin of the form.
7. <u>STOP</u> : - <u>STOP</u> : - <u>STOP</u> : If you are not familiar with the proper set up and calibration of the balance you are using, do not proceed to next step until you have read instruction <u>AI-2</u> .	

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INSTRUCTION NUMBER: AN-1		TASK: Weighing Microporous Filters	
DATE PREPARED: June 10, 1981		PAGE NUMBER 2	TOTAL PAGES 5
FUNCTION		IMPORTANT STEP	
9. Zero and calibrate balance.			
9. Using forceps, remove the filters, one at a time, from the dessicator chamber. Pass each filter over the Polonium 210 anti-static bar and place filter on balance weighing pan. Close the balance window and allow time for the balance display to stabilize. This may take as little as 5 seconds to more than a minute, depending on the type filter used and the range weighed on. The first few filters weighed in the sequence should allow you to adjust this settling time accordingly.		If filters do not want to release from the forceps or seem to "draw" the pan they still contain static and must be passed over the anti-static bar again. This static, if not eliminated, will cause the balance to display erroneous weights.	
10. After each filter is weighed, record the weight on the Filter Weight Work Sheet beside the corresponding filter sequence number in the column "1st weight" and place the filter in the appropriately numbered cassette bottom section.		Sometimes the weight of a filter will fall into a mid-range where the last digit displayed will not settle but will bounce back and forth between two numbers. In these instances record the even number.	
11. Allow weighed filters to remain in open cassettes for an additional equilibration period (over night). <u>NOTE: In the case of an "OVER-CHARGE" request, isolate this and the next two steps.</u>			
12. After this second equilibration, re-weigh the filters using the same procedures as before except that filters will be handled directly from the cassettes and not re-encased. Record the weights by the corresponding filter number on the Filter Weight Work Sheet.		Do not try to "dig" the filter from the cassette. Placed by the balance is a wooden block with a spike protruding from it. Insert this spike through the outlet hole of the cassette section and lift the backup pad and filter far enough above the cassette lip that the filter can be grasped with forceps.	
13. Compare the first and second filter weights for each filter. If they vary more than ± 0.01 milligram the filter will not be used. Discard and condition/reweigh replacement filters.			

INSTRUCTION NUMBER:		TASK: Weighing Microporous Filters	
DATE PREPARED: June 10, 1961		PAGE NUMBER 1 TOTAL PAGES 5	
FUNCTION		IMPORTANT STEP	
1b. After it is determined that all filter weights are valid, assemble the cassette and close by using the rim tool. Place a plug in each opening of the cassette. Place a shrink-band on each cassette and allow to dry. After drying, the band is to be marked with indelible pen with the filter number that appears on the weighing pad. Place the filters in a bin or container and label the outside of the container with the following information: a. Type of filter b. Number of filters in the container c. Sequence numbers of filters in the container d. Project number and name of project officer.		Do not mix filters-of different types or that are for different sampling purposes in the same container. Separate them into individual marked containers. These containers may then be placed in a larger overpack for ease of shipment. The overpack should be marked to reflect the contents.	
1g. Mark project sequence book to reflect that each weighing of this sequence has been completed.		File the completed Filter Weight Mark Sheet in a folder marked with the same information from step 1b. These folders are kept in a file in Room 1b3 until post-weights are made.	
SECTION IX: Post Weighing			
FORMS REQUIRED: "Filter Weight Mark Sheet" STORED IN: Project Sequence File, Room 1b3 "Report of Filter Weighing" STORED IN: File Cabinet, top drawer, Room 1b3.			
1i. When filters are returned for post weighing by weighing until you are sure that you know (1) which project the filters are from, (2) which filters are designated as blank controls and (3) the final disposition of the filters.		This information can be gotten from the project sequence file or the project officer.	

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INSTRUCTION NUMBER:	TASK: Weighing Microscopic Filters
DATE PREPARED: June 10, 1961	PAGE NUMBER 6 TOTAL PAGES 9

FUNCTION	IMPORTANT STEP
2. Condition filters as in steps 1 through 4, Section I of this instruction. Before desiccating filters remove the top and bottom plugs of the cassette.	
3. After filters are equilibrated, remove the cassette head, pry open the cassette. Using the wooden block/spike provided, place the spike through the bottom hole of the cassette and gently lift the filter until you can grasp it with fingers. Handle the cassette and filters very gently to avoid loss of dust.	(1) Handle the filter by the outermost edge only. (2) If the filter sticks to the underside of the cassette top <u>very</u> gently lift away by using the <u>full</u> side of a scalped blade. This must be done carefully or the filter will tear.
4. Weigh each filter in turn using the procedures outlined in section I of this instruction. Record this post weight on the Filter Weight Work Sheet beside its correction factor weight.	If there is anything remarkable about a filter (overloaded, leakage, wet, torn, etc.) record this information in the Remarks column of the Filter Weight Work Sheet. <u>Be sure</u> to designate control blanks on this sheet.
5. Do the correction for control blanks: a. Subtract the tare weight from each blank. b. Determine the average (mean) weight gain or loss for the blanks. c. Determine the standard deviation and 2 times the standard deviation for the blanks. d. If the average weight change of the blanks was a (+) value then subtract this value from the post weight of each filter used for sampling. If the average weight change was a (-) value then <u>add</u> this to all post weights.	Use the IP 97 calculator located in Room 243 to determine these values.

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INSTRUCTION NUMBER: AE-1

TASK: Weighing Microporous Filters

DATE PREPARED: June 10, 1961

PAGE NUMBER 5

TOTAL PAGES 5

FUNCTION	IMPORTANT STEP
6. After all weights have been corrected, prepare a report for the Project Officer on "Report of Filter Weighing". Complete all sections of the report form except "Sampling dates and shifts". Forward this report to the Project Officer concerned.	
7. According to disposition instructions, either discard or reuse the filters. Do not discard the cassettes.	
8. If there are more filters to be weighed in the sequence, file the folder containing the filter weight work sheet back in the filter sequence file. If the sequence is completed, turn the folder in to the Lab Supervisor for final disposition.	Completed sequences will be held for one year from the date of completion and then forwarded to the Project Officer.

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APPENDIX IX

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SUBCHAPTER G—OCCUPATIONAL SAFETY AND HEALTH RESEARCH AND RELATED ACTIVITIES

PART 80—ADMINISTRATIVE FUNCTIONS, PRACTICES, AND PROCEDURES

Subparts A-C [Reserved]

Subpart D—Tuition Fees for Direct Training

Sec.

80.41 Applicability.

80.42 Definitions.

80.43 Tuition fees.

80.44 Schedule of fees.

80.45 Procedure for payment.

80.46 Refunds.

AUTHORITY: Sec. 501, 65 Stat. 290; 31 U.S.C. 483a.

SOURCE: 38 FR 16645, June 25, 1973, unless otherwise noted.

Subparts A-C [Reserved]

Subpart D—Tuition Fees for Direct Training

§ 80.41 Applicability.

The provisions of this subpart set forth the policies of the National Institute for Occupational Safety and Health with respect to its charging fees for direct training in occupational safety or health.

§ 80.42 Definitions.

Any term not defined herein shall have the same meaning as given it in the act. As used in this subpart:

(a) "Act" means the Occupational Safety and Health Act of 1970 (29 U.S.C. 651 et seq.).

(b) "Direct training" means all technical training courses conducted directly by NIOSH for personnel of State and local governmental agencies, other Federal agencies, private industries, universities, and other non-NIOSH agencies and organizations.

(c) "NIOSH" or "Institute" means the National Institute for Occupational Safety and Health.

(d) "Registration Office" means the Direct Training Registration Office, NIOSH, 1014 Broadway, Cincinnati, Ohio 45202.

§ 80.43 Tuition fees.

In accordance with the provisions of the subpart, the National Institute for Occupational Safety and Health will charge fees for all students attending NIOSH direct training courses which commence on or after July 1, 1973.

§ 80.44 Schedule of fees.

(a) Tuition fees will be computed on the basis of the cost to the Government for the Institute's participation in the course, as determined by the Director of the Institute.

(b) Total tuition charges for each course will be set forth in the course announcement.

§ 80.45 Procedure for payment.

(a) Applications for direct training courses shall be completed and submitted to the registration office in accordance with the instructions issued by that office.

(b) Federal agency personnel shall, upon notification of their acceptance, submit a letter identifying the agency and office to be billed, the agency order number, and any code numbers or other information necessary for billing purposes.

(c) All other applicants shall, upon notification of their acceptance by NIOSH, submit a check payable to the National Institute for Occupational Safety and Health in the amount indicated by the course announcement prior to the commencement of the training course.

§ 80.46 Refunds.

An applicant may withdraw his application and receive full reimbursement of the fee provided that written notification to the registration office is mailed no later than 10 days before the commencement of the course for which registration has been submitted.

PART 85—REQUESTS FOR HEALTH HAZARD EVALUATIONS

Sec.

- 85.1 Applicability.
- 85.2 Definitions.
- 85.3 Procedures for requesting health hazard evaluations.
- 85.3-1 Contents of a request for health hazard evaluations.
- 85.4 Acting on requests.
- 85.5 Authority for investigations.
- 85.6 Advance notice of visits.
- 85.7 Conduct of investigations.
- 85.8 Provision of suitable space for employee interviews and examinations; identification of employees.
- 85.9 Representatives of employers and employees; employee requests.
- 85.10 Imminent dangers.
- 85.11 Notification of determination to employers, affected employees, and Department of Labor.
- 85.12 Subsequent requests for health hazard evaluations.

AUTHORITY: Sec. 8(g), 84 Stat. 1600; 29 U.S.C. 657(g) and sec. 508, 83 Stat. 803; 30 U.S.C. 957.

SOURCE: 37 FR 23640, Nov. 7, 1972, unless otherwise noted.

§ 85.1 Applicability.

This Part 85 applies to health hazard evaluations requested by any employer or authorized representative of employees under section 20(a)(6) of the Occupational Safety and Health Act of 1970 or section 501(a)(11) of the Federal Mine Safety and Health Act of 1977. This part is not intended to preclude the use of other channels of communication with the National Institute for Occupational Safety and Health to obtain information and technical assistance concerning toxic substances or physical agents.

[45 FR 2652, Jan. 14, 1980]

§ 85.2 Definitions.

Any term defined in the Occupational Safety and Health Act of 1970 or the Federal Mine Safety and Health Act of 1977 and not defined below shall have the meaning given it in the respective Acts. As used in this part:

"OSH Act" means the Occupational Safety and Health Act of 1970 (29 U.S.C. 651, et seq.).

"FMSH Act" means the Federal Mine Safety and Health Act of 1977 (30 U.S.C. 801, et seq.).

"Authorized representative of employees" means any person or organization meeting the conditions specified in § 85.3-1(e) (1), (2), or (3).

"Employee" has the same meaning as stated in the OSH Act and for the purposes of this part includes "miner" as defined in the FMSH Act.

"Employer" has the same meaning as stated in the OSH Act and for the purposes of this part includes "Operator" as defined in the FMSH Act.

"Health hazard evaluation" means the investigation and the determination of potentially toxic or hazardous effects of: (a) any substance normally used or found in any place of employment to which the OSH Act is applicable, or (b) any substance or physical agent normally used or found in any place of employment to which the FMSH Act is applicable.

"Investigation" means a physical inspection of the place of employment under section 8 of the OSH Act or section 103 of the FMSH Act and includes inspection, sampling, observations, review of pertinent records, and other measurements reasonably necessary to determine whether any substance or physical agent found in the place of employment has potentially toxic or hazardous effects in the concentrations or levels used or found.

"NIOSH" means the National Institute for Occupational Safety and Health, Center for Disease Control, Public Health Service, Department of Health and Human Services.

"NIOSH officer" means a NIOSH employee who has been authorized by the Director, NIOSH, to conduct investigations according to this part.

"Physical agent" means any condition produced by the environment and/or work processes that can result in hazardous effects as defined in this section. Examples of physical agents are noise, temperature, illumination, vibration, radiation, and pressure.

"Place of employment" means any coal or other mine, factory, plant, establishment, construction site, or other area, workplace, or environment where work is performed by any employee of an employer.

"Substance" means any chemical or biological agent or dust which has the potential to produce toxic effects.

"Toxic effects" or "hazardous effects" are those effects which result in short- or long-term disease, bodily injury, affect health adversely, or endanger human life.

[45 FR 2652, Jan. 14, 1980]

§ 85.3 Procedures for requesting health hazard evaluations.

(a) Requests for health hazard evaluations should be addressed to the National Institute for Occupational Safety and Health as follows:

(1) *Requests from general industry.* Hazard Evaluations and Technical Assistance Branch, Division of Surveillance, Hazard Evaluations, and Field Studies, NIOSH, 4676 Columbia Parkway, Cincinnati, OH 45226.

(2) *Requests from mining industry.* Environmental Investigations Branch, Division of Respiratory Disease Studies, NIOSH, 944 Chestnut Ridge Road, Morgantown, WV 26505.

(b) Requests for health hazard evaluations shall be submitted in writing and signed by either: (1) The employer in whose place of employment the substance or physical agent is normally found, or (2) an authorized representative of employees (see § 85.3-1(e)) in the place of employment where the substance or physical agent is normally found.

[45 FR 2653, Jan. 14, 1980]

§ 85.3-1 Contents of a request for health hazard evaluation.

Each request for health hazard evaluation shall contain:

(a) The requester's name, address, and telephone number, if any.

(b) The name and address of the place of employment where the substance or physical agent is normally found.

(c) The specific process or type of work which is the source of the substance or physical agent, or in which the substance or physical agent is used.

(d) Details of the conditions or circumstances which prompted the request.

(e) A statement, if the requester is not the employer, that the requester is:

(1) An authorized representative or an officer of the organization representing the employees for purposes of collective bargaining; or

(2) An employee of the employer and is authorized by two or more employees employed in the same place of employment to represent them for purposes of these Acts (each such authorization shall be in writing and a copy submitted with the request for health hazard evaluation); or

(3) One of three or less employees employed in the place of employment where the substance or physical agent is normally found.

(f) A statement indicating whether or not the name(s) of the requester or those persons who have authorized the requester to represent them may be revealed to the employer by NIOSH.

(g) The following supplementary information if known to the requester:

(1) Identity of each substance or physical agent involved;

(2) The trade name, chemical name, and manufacturer of each substance involved;

(3) Whether the substance or its container or the source of the physical agent has a warning label; and

(4) The physical form of the substance or physical agent, number of people exposed, length of exposure (hours per day), and occupations of exposed employees.

NOTE: NIOSH has developed two forms entitled "Request for Health Hazard Evaluation" and "Request for Mining Health Hazard Evaluation" to assist persons in requesting evaluations. The forms are available upon request from the offices listed in § 85.3(a) (1) and (2) or from the Regional Consultant for Occupational Safety and Health in any Regional Office of the Department of Health and Human Services.

[45 FR 2653, Jan. 14, 1980]

§ 85.4 Acting on requests.

(a) Upon receipt of a request for health hazard evaluation submitted under this part, NIOSH will determine whether or not there is reasonable cause to justify conducting an investigation.

(b) If NIOSH determines that an investigation is justified, a NIOSH officer will inspect the place of employment, collect samples where appropriate, and perform tests necessary to the conduct of a health hazard evaluation, including medical examinations of employees.

(c) If NIOSH determines that an investigation is not justified, the requester will be notified in writing of the decision.

[45 FR 2653, Jan. 14, 1980]

§ 85.5 Authority for investigations.

(a) NIOSH officers who have been issued official NIOSH credentials (Form No. CDC/NIOSH 2.93) are authorized by the Director, NIOSH, under sections 20(a) (6) and 8 of the OSH Act and sections 501(a)(11) and 103 of the FMSH Act: To enter without delay any place of employment for the purpose of conducting investigations of all pertinent processes, conditions, structures, machines, apparatus, devices, equipment, records, and materials within the place of employment; and to conduct medical examinations, anthropometric measurements, and functional tests of employees within the place of employment as may be directly related to the specific health hazard evaluation being conducted. Investigations will be conducted in a reasonable manner, during regular working hours or at other reasonable times and within reasonable limits. In connection with any investigation, the NIOSH officers may question privately any employer, owner, operator, agent, or employee from the place of employment; and review, abstract, and duplicate records required by the Acts and regulations and any other related records.

(b) Areas under investigation which contain information classified by any agency of the United States Government in the interest of national security will be investigated only by NIOSH officers who have obtained the proper security clearance and authorization.

[45 FR 2653, Jan. 14, 1980]

§ 85.6 Advance notice of visits.

(a) Advance notice of visits to the place of employment may be given to

expedite a thorough and effective investigation. Advance notice will not be given when, in the judgment of the NIOSH officer, giving such notice would adversely affect the validity and effectiveness of the investigation.

(b) Where a request in accordance with this part has been made by an authorized representative of employees, advance notice in accordance with paragraph (a) of this section will be given by NIOSH to the requester, the representative of the employees for purposes of collective bargaining if such representative is other than the requester, and to the employer.

(c) Where a request in accordance with this part has been made by any employer, advance notice will be given by NIOSH to the employer. Upon the request of the employer, NIOSH will inform the authorized representative of employees of the visit: *Provided*, The employer furnishes NIOSH in writing with the identity of such representative and with such information as is necessary to enable NIOSH promptly to inform such representative of the visit.

§ 85.7 Conduct of investigations.

(a) Prior to beginning an investigation, NIOSH officers shall present their credentials to the owner, operator, or agent in charge at the place of employment, explain the nature, purpose, and scope of the investigation and the records specified in § 85.5 which they wish to review. Where the investigation is the result of a request submitted by an authorized representative of employees, a copy of the request shall be provided to the employer, except where the requester or any person authorizing the requester pursuant to § 85.3-1(e)(2) has indicated that NIOSH not reveal his name to the employer, in which case a summary of the basis for the request shall be provided to the employer.

(b) At the commencement of an investigation, the employer should precisely identify information which can be obtained in the workplace or workplaces to be inspected as trade secrets. If the NIOSH officer has no clear reason to question such identification, such information shall not be dis-

closed except in accordance with the provisions of section 20(a)(6) and section 15 of the OSH Act or section 501(a)(11) of the FMSH Act. However, if NIOSH at any time questions such identification by an employer, not less than 15 days' notice to an employer shall be given of the intention to remove the trade secret designation from such information. The employer may within that period submit a request to the Director, NIOSH, to reconsider this intention and may provide additional information in support of the trade secret designation. The Director, NIOSH, shall notify the employer in writing of the decision which will become effective no sooner than 15 days after the date of such notice.

(c) NIOSH officers are authorized to collect environmental samples and samples of substances or measurements of physical agents (including measurement of employee exposure by the attachment of personal sampling devices to employees with their consent), to take or obtain photographs related to the purpose of the investigation, employ other reasonable investigative techniques, including medical examinations of employees with the consent of such employees, and to question privately any employer, owner, operator, agent, or employee. The employer shall have the opportunity to review photographs taken or obtained for the purpose of identifying those which contain or might reveal a trade secret.

(d) NIOSH officers shall comply with all safety and health rules and practices at the place of employment being investigated, and they shall provide and use appropriate protective clothing and equipment. In situations requiring specialized or unique types of protective equipment, such equipment shall be furnished by the employer.

(e) The conduct of investigations shall be such as to preclude unreasonable disruption of the operations of the employer's establishment.

[37 FR 23640, Nov. 7, 1972, as amended at 46 FR 2653, Jan. 14, 1980; 49 FR 4739, Feb. 8, 1984]

§ 85.8 Provision of suitable space for employee interviews and examinations; identification of employees.

An employer shall, in request of the NIOSH officer, provide suitable space, if such space is reasonably available, to NIOSH to conduct private interviews with, and examinations of, employees. NIOSH officers shall consult with the employer as to the time and place of the medical examination and shall schedule such examinations so as to avoid undue disruption of the operations of the employer's establishment. NIOSH shall conduct, and assume the medical costs of, examinations conducted under this part.

§ 85.9 Representatives of employers and employees; employee requests.

(a) NIOSH officers shall be in charge of investigations. Where the request for a health hazard evaluation has been made by an authorized representative of employees, a representative of the employer and a representative authorized by his employees who is an employee of the employer shall be given an opportunity to accompany the NIOSH officer during the initial physical inspection of any workplace for the purpose of aiding the investigation by identifying the suspected hazard. The NIOSH officer may permit additional employer representatives and such additional representatives authorized by employees to accompany him where he determines that such additional representatives will further aid the investigation. However, if in the judgment of the NIOSH officer, good cause has been shown why accompaniment by a third party who is not an employee of the employer is reasonably necessary to the conduct of an effective and thorough investigation of the workplace, such third party may accompany the NIOSH officer during the inspection: *Provided, however,* That access by such persons to areas described in paragraph (d) of this section shall be in accordance with the requirements of such provision, and access to areas described in paragraph (e) of this section shall be with the consent of the employer. A different employer and employee representative may accom-

pany the officer during each different phase of an inspection if this will not interfere with the conduct of the investigation.

(b) NIOSH officers are authorized to resolve all disputes as to who is the representative authorized by the employer and employees for the purpose of this section. If there is no authorized representative of employees, or if the NIOSH officer is unable to determine with reasonable certainty who is such representative, he shall consult with a reasonable number of employees concerning matters directly related to the health hazard evaluation.

(c) NIOSH officers are authorized to deny the right of accompaniment under this section to any person whose conduct interferes with a fair and orderly physical inspection.

(d) With regard to information classified by an agency of the U.S. Government in the interest of national security, only persons authorized to have access to such information may accompany an officer in areas containing such information.

(e) Upon request of an employer, any representative authorized under this § 85.9 by employees in any area containing trade secrets shall be an employee in that area or an employee authorized by the employer to enter that area.

§ 85.10 Imminent dangers.

Whenever, during the course of, or as a result of, an investigation under this part, the NIOSH officer believes that there is a reasonable basis for an allegation of an imminent danger, NIOSH will immediately advise the employer and those employees who appear to be in immediate danger of such allegation and will inform appropriate representatives of the Department of Labor or the State agency designated under section 18(b) of the OSH Act.

[37 FR 23640, Nov. 7, 1972, as amended at 45 FR 2653, Jan. 14, 1980]

§ 85.11 Notification of determination to employers, affected employees and Department of Labor.

(a) Upon conclusion of an investigation, NIOSH will make a determination concerning the potentially toxic

or hazardous effects of each substance or physical agent investigated as a result of the request for health hazard evaluation. At a minimum, the determination will: (1) Identify each substance or physical agent involved and describe, where appropriate, the concentrations or levels of the substance or physical agent found in the place of employment and the conditions of use, and (2) state whether each substance or physical agent has potentially toxic or hazardous effects in the concentrations or levels found, as well as the basis for the judgments.

(b) Copies of the determination will be mailed to the employer and to the authorized representatives of employees.

(c) Except as hereinafter provided, the employer shall post a copy of the determination for a period of 30 calendar days at or near the workplace(s) of affected employees. The employer shall take steps to insure that the posted determinations are not altered, defaced, or covered by other material during such period. The employer will not be required to post the determination if the employer requests that copies of the determination be mailed to affected employees and furnishes NIOSH with a list of the names and mailing addresses of the employees employed in the workplace(s) designated by the NIOSH Officer. In the latter event, NIOSH will mail such copies to affected employees at the mailing addresses provided by the employer.

(d) For purposes of this section, the term "affected employees" means those employees determined by NIOSH to be exposed to the substance(s) or physical agent(s) which is the subject of the health hazard evaluation.

(e) Copies of determinations made under the OSH Act will be forwarded to the Department of Labor and the appropriate State agency designated under section 18(b) of the OSH Act. Copies of determinations made under the FMSH Act will be forwarded to the Mine Safety and Health Administration of the Department of Labor; the Bureau of Mines, Department of the Interior; and the State agency which, in the judgment of NIOSH,

would benefit the most from the information. If NIOSH determines that any substance or physical agent has potentially toxic or hazardous effects at the concentrations or levels at which it is used or found in a place of employment, and the substance or physical agent is not covered by a safety or health standard established under section 6 of the OSH Act or section 101 of the FMSH Act, NIOSH will immediately submit the determination to the Secretary of Labor, together with all pertinent criteria.

[37 FR 23640, Nov. 7, 1972, as amended at 45 FR 2653, Jan. 14, 1980]

§ 85.12 Subsequent requests for health hazard evaluations.

If a request is received for a health hazard evaluation in a place of employment in which an evaluation under this part was made previously, NIOSH may make another investigation if, as a result of the passage of time or additional information, another investigation would be consistent with the purposes of the Acts.

[45 FR 2654, Jan. 14, 1980]

PART 85a—OCCUPATIONAL SAFETY AND HEALTH INVESTIGATIONS OF PLACES OF EMPLOYMENT

Sec.

85a.1 Applicability.

85a.2 Definitions.

85a.3 Authority for investigations of places of employment.

85a.4 Procedures for initiating investigations of places of employment.

85a.5 Conduct of investigations of places of employment.

85a.6 Provision of suitable space for employee interviews and examinations.

85a.7 Imminent dangers.

85a.8 Reporting of results of investigations of places of employment.

AUTHORITY: Sec. 8(g), 84 Stat. 1600; 29 U.S.C. 657(g) and sec. 508, 83 Stat. 803; 30 U.S.C. 957.

SOURCE: 41 FR 45002, Oct. 14, 1976, unless otherwise noted.

§ 85a.1 Applicability.

(a) Except as otherwise provided in paragraph (b) of this section, the provisions of this part apply to investigations of places of employment which

are conducted by NIOSH under sections 20 and 8 of the Occupational Safety and Health Act of 1970 and sections 501 and 103 of the Federal Mine Safety and Health Act of 1977.

(b) The provisions of this part do not apply to those activities covered by Part 85 of this chapter.

[41 FR 45002, Oct. 14, 1976, as amended at 45 FR 2654, Jan. 14, 1980]

§ 85a.2 Definitions.

Any term defined in the Occupational Safety and Health Act of 1970 or the Federal Mine Safety and Health Act of 1977 and not defined below shall have the meaning given it in the Acts. As used in this part:

(a) "OSH Act" means the Occupational Safety and Health Act of 1970 (29 U.S.C. 651 et seq.) and "FMSH Act" means the Federal Mine Safety and Health Act of 1977 (30 U.S.C. 801 et seq.).

(b) "Assistant Regional Director" means any one of the ten Occupational Safety and Health Administration Assistant Regional Directors for Occupational Safety and Health.

(c) "Informed consent" means the knowing consent of an individual or his legally authorized representative, so situated as to be able to exercise free power of choice without undue inducement or any element of force, fraud, deceit, duress, or other form of constraint or coercion. The basic elements of information necessary to such consent include:

(1) A fair explanation of the procedures to be followed, and their purposes, including identification of any procedures which are experimental;

(2) A description of any attendant discomforts and risks reasonably to be expected;

(3) A description of any benefits reasonably to be expected;

(4) A disclosure of any appropriate alternative procedures that might be advantageous for the subject;

(5) An offer to answer any inquiries concerning the procedures; and

(6) An instruction that the person is free to withdraw his consent and to discontinue participation in the investigation any time without prejudice to the subject.

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(d) "Investigation" means research projects, experiments, demonstrations, studies, and similar activities of NIOSH which are conducted under section 20 of the OSH Act and section 501 of the FMSH Act.

(e) "Legally authorized representative" means an individual or judicial or other body authorized under applicable law to consent on behalf of a prospective subject to such subject's participation in the particular activity or procedure.

(f) "NIOSH" means the National Institute for Occupational Safety and Health of the Center for Disease Control, Public Health Service, Department of Health and Human Services.

(g) "NIOSH authorized representative" means a person authorized by NIOSH to conduct investigations of places of employment, including any person that is fulfilling a contract agreement with NIOSH or is serving as an expert or consultant to NIOSH pursuant to the Act.

(h) "NIOSH Regional Office" means any one of the ten Department of Health and Human Services Regional Offices, the addresses of which are specified in § 5.31 of Title 45, Code of Federal Regulations.

(i) "Place of employment" means any coal or other mine, factory, plant, establishment, construction site, or other area, workplace or environment where work is performed by any employee of an employer.

(j) "MSHA District Office" means any one of the Mine Safety and Health Administration's District Offices.

(k) "BOM" means the Bureau of Mines, Department of the Interior.

(l) "Employee" has the same meaning as stated in the OSH Act and for the purposes of this part includes "miner" as defined in the FMSH Act.

(m) "Employer" has the same meaning as stated in the OSH Act and for the purposes of this part includes "operator" as defined in the FMSH ACT.

[41 FR 45002, Oct. 14, 1976, as amended at 45 FR 2654, Jan. 14, 1980]

§ 85a.3 Authority for investigations of places of employment.

(a) NIOSH authorized representatives who have been issued official

NIOSH credentials are authorized by the Director, NIOSH, under sections 20 and 8 of the OSH Act, sections 501 and 103 of the FMSH Act, and this part. To enter without delay any place of employment for the purpose of conducting investigations of all pertinent processes, conditions, structures, machines, apparatus, devices, equipment, and materials within the place of employment; and to conduct medical examinations, anthropometric measurements and functional tests of employees within the place of employment as may be directly related to the specific investigation being conducted. Such investigations will be conducted in a reasonable manner, during regular working hours or at other reasonable times and within reasonable limits. In connection with any investigations, such NIOSH authorized representatives may question privately any employer, owner, operator, agent, or employee from the place of employment; and review, abstract, or duplicate employment records, medical records, records required by the Act and regulations, and other related records. In those instances where systems of records subject to review, abstraction or duplication are of a confidential nature, such as medical records, and are abstracted or duplicated, NIOSH will maintain such systems in accordance with the Privacy Act of 1974 (5 U.S.C. 552a) and the implementing regulation of the Department of Health and Human Services (45 CFR Part 5b).

(b) Areas under investigation which contain information classified by any agency of the United States Government in the interest of national security will be investigated only by NIOSH authorized representatives who have obtained the appropriate security clearance and authorization.

[41 FR 45002, Oct. 14, 1976, as amended at 45 FR 2654, Jan. 14, 1980]

§ 85a.4 Procedures for initiating investigations of places of employment.

(a) Except as otherwise provided in paragraph (b) of this section, NIOSH authorized representatives will contact an official representative of the place of employment prior to any site visits

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and will provide the details of why an investigation of the place of employment is being conducted. Prior to the initiation of a site visit of a place of employment, representatives of the following organizations will be advised of the site visit and the reason for its conduct:

(1) The appropriate State agency designated under section 18(b) of the OSH Act, or if no State agency has been designated under the OSH Act and in the case of the FMSH Act, the State agency which, in the judgment of NIOSH, would benefit the most from the investigation's findings;

(2) If there is a local union at the place of employment, the local president, business manager or other appropriate individual;

(3) The appropriate Assistant Regional Director, when investigations are conducted under the OSH Act;

(4) The appropriate MSHA District Office; the Director, BOM, and the Assistant Director for Mining, BOM, when investigations are conducted under the FMSH Act.

(b) Advance notice of site visits will not be given to the place of employment or local union at the place of employment when, in the judgment of the NIOSH authorized representatives, giving such notice would adversely affect the validity and effectiveness of an investigation. Those individuals and organizations specified in § 85a.4(a)(1), (a)(3) and (a)(4) will be notified prior to the initiation of such a site visit. After the site visit has been initiated, and, as soon as possible thereafter, the NIOSH authorized representatives will contact those individuals specified in § 85a.4(a)(2) concerning the nature and details of the site visit.

(c) In those instances where site visits are not necessary to the conduct of an investigation, the NIOSH authorized representatives will contact an official representative of the place of employment either verbally or through a written communication and provide the details of why an investigation of the place of employment is being conducted. If appropriate, the NIOSH authorized representatives will contact those individuals stipulated in paragraphs (a)(1), (a)(2), (a)(3), and

(a)(4) of this section about the nature and details of the investigation.

[41 FR 45002, Oct. 14, 1976, as amended at 45 FR 2654, Jan. 14, 1980]

§ 85a.5 Conduct of investigations of places of employment.

(a)(1) Prior to beginning a site visit, NIOSH authorized representatives will present their credentials to the employer, owner, operator or agent in charge at the place of employment, explain the nature, purpose and scope of the investigation and the records specified in § 85a.3 which they wish to review, abstract or duplicate.

(2) In those instances where site visits are not necessary to the conduct of an investigation and the initial contact is made verbally, NIOSH authorized representatives will, at the request of the employer, owner, operator or agent in charge at the place of employment, provide a written explanation of the nature, purpose and scope of the investigation and the records specified in § 85a.3 which they wish to review, abstract or duplicate.

(b)(1) At the commencement of an investigation, the employer, owner, operator or agent in charge at the place of employment shall precisely identify that information which is trade secret and might be seen or obtained by the NIOSH authorized representatives during the investigation. If the NIOSH authorized representatives have no clear reason to question such identification, such information will not be disclosed by NIOSH in accordance with the provisions of section 15 of the OSH Act. Generally, NIOSH will not question trade secret designations; however, if NIOSH at any time does question such identification, not less than 15 days' notice to the employer, owner, operator or agent will be given of the intention to remove the trade secret designation from such information. The employer, owner, operator or agent may within that period submit a request to the Director, NIOSH, to reconsider this intention and may provide additional information in support of the trade secret designation. The Director, NIOSH, will notify the employer, owner, operator or agent in writing of the decision

which will become effective no sooner than 15 days after the date of such notice.

(2) In those instances where the NIOSH authorized representative is a person fulfilling a contact agreement with NIOSH or is serving as an expert or consultant to NIOSH pursuant to the Act, the employer, owner, operator or agent in charge at the place of employment may, after advising the NIOSH contractor or consultant in writing, elect to withhold information deemed to be a trade secret from such a NIOSH authorized representative or prohibit entry into the area of the place of employment where such entry will reveal trade secrets. In those instances, where the subject information is needed or access to the area of the place of employment is necessary, in the judgment of NIOSH, to fulfill the goals of the investigation, NIOSH regular employees will then obtain the information or enter the subject area of the place of employment.

(c)(1) NIOSH authorized representatives will be in charge of site visits conducted pursuant to this part.

(2) Where there is a request by the representative of the State agency and/or employees, who were notified pursuant to § 85a.4(a)(1) or § 85a.4(a)(2) to accompany the NIOSH authorized representatives during the site visit of the place of employment, the NIOSH authorized representatives will allow this request if they determine that this will aid the investigation; or where, in the judgment of the NIOSH authorized representatives, good cause has been shown why accompaniment by a third party who is not an employee of the employer is reasonably necessary to the conduct of an effective and thorough site visit, they may permit such third party to accompany them during the site visit: *Provided, however,* That access by such person(s) to areas described in § 85a.5(c)(4) shall be in accordance with the requirements of such provision and access to areas containing trade secrets shall be with the consent of the employer, owner, operator or agent in charge at the place of employment.

(3) NIOSH authorized representatives are authorized to deny the right

of accompaniment under this paragraph to any person whose conduct in their judgment interferes with a fair and orderly site visit. In all instances, a representative of the employer shall be permitted to accompany the NIOSH authorized representatives during the site visit of the place of employment.

(4) With regard to information classified by an agency of the United States Government in the interest of national security, only persons authorized to have access to such information may accompany NIOSH authorized representatives in areas containing such information.

(d)(1) NIOSH authorized representatives are authorized: To collect environmental samples and samples of substances; to measure environmental conditions and employee exposures (including measurement of employee exposure by the attachment of personal sampling devices to employees with their consent); to take or obtain photographs, motion pictures or videotapes related to the purpose of the investigation; to employ other reasonable investigative techniques, including medical examinations, anthropometric measurements and standardized and experimental functional tests of employees with the informed consent of such employees; to review, abstract, and duplicate such personnel records as are pertinent to mortality, morbidity, injury, safety, and other similar studies; and to question and interview privately any employer, owner, operator, agency, or employee from the place of employment. The employer, owner, operator, or agency shall have the opportunity to review photographs, motion pictures, and videotapes taken or obtained for the purpose of identifying those which contain or might reveal a trade secret.

(2) Prior to the conduct of medical examinations, anthropometric measurements or functional tests of any employees, the NIOSH authorized representatives will obtain approval of the procedures to be utilized from the NIOSH Human Subjects Review Board and no employee examination, measurement or test will be undertaken without the informed consent of such employee.

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(e) NIOSH authorized representatives will comply with all safety and health rules and practices at the place of employment and all NIOSH, Occupational Safety and Health Administration, and Mine Safety and Health Administration regulations and policies during a site visit and will provide and use appropriate protective clothing and equipment. In situations requiring specialized or unique types of protective equipment, such equipment shall be furnished by the employer, owner, operator or agent in charge at the place of employment.

(f) The conduct of site visits will be such as to preclude unreasonable disruption of the operations of the place of employment.

[41 FR 45002, Oct. 14, 1976, as amended at 45 FR 2654, Jan. 14, 1980; 49 FR 4739, Feb. 8, 1984]

§ 85a.6 Provision of suitable space for employee interviews and examinations.

An employer, owner, operator or agent in charge at the place of employment shall, on request of the NIOSH authorized representatives, provide suitable space at the place of employment, if such space is reasonably available, to NIOSH to conduct private interviews with, and medical examinations, anthropometric measurements and functional tests of employees. NIOSH authorized representatives will consult with the employer, owner, operator or agent as to the time and place of the private interviews, medical examination, anthropometric measurements and functional tests and will schedule same so as to avoid undue disruption of work at the place of employment. NIOSH will conduct the medical interviews, measurements, examinations and tests specified under this part at its own expense.

§ 85a.7 Imminent dangers.

Whenever, during the course of, or as a result of, an investigation under this part, the NIOSH authorized representatives believe there is a reasonable basis for an allegation of an imminent danger, NIOSH will immediately advise the employer, owner, operator or agent in charge at the place of employment and those employees who

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appear to be in immediate danger of such allegation and will inform the agencies identified in § 85a.4(a)(1), (a)(3), and (a)(4).

[41 FR 45002, Oct. 16, 1976, as amended at 45 FR 2654, Jan. 14, 1980]

§ 85a.8 Reporting of results of investigations of places of employment.

(a)(1) Specific reports of investigations of each place of employment under this part, with identification of the place of employment, will be made available by NIOSH to the employer, owner, operator or agent in charge at the place of employment, with copies to the appropriate officials and Agencies notified pursuant to § 85a.4(a). Prior to release of such reports, a preliminary report will be sent by NIOSH to the employer, owner, operator or agent for review for trade secret information and technical inaccuracies that may inadvertently be presented in the report. If requested in writing, the data used to compile the reports will be made available by NIOSH to the employer, owner, operator or agent in charge at the place of employment, except that data will not be released in a form that is individually identifiable.

(2) All specific reports of investigations of each place of employment under this part will be available to the public from the NIOSH Regional Consultant for Occupational Safety and Health in the appropriate NIOSH Regional Office.

(3) In certain instances, specific reports of investigations of each place of employment will not be prepared. In such instances, a closing conference at the place of employment will be conducted by the NIOSH authorized representatives and those individuals participating in the site visit to discuss the findings of the site visit and appropriate recommendations.

(b)(1) Any specific findings of individual employee medical examinations, anthropometric measurements and functional tests will be released by NIOSH authorized representatives to the company physician, private physician, or other person only pursuant to the written authorization of the employee; otherwise, the specific findings and other personal records concerning

individuals will be maintained in accordance with 45 CFR Part 5b and section 3 of the Privacy Act of 1974 (5 U.S.C. 552a). Notice of all NIOSH systems of records as defined in 45 CFR 5b.1(n) as a result of the investigations of places of employment pursuant to this part will be published in the FEDERAL REGISTER under Notices of Systems of Records for the Department of Health and Human Services.

(2) In cases where an employee shows positive significant medical findings, the employee and the physician(s) designated by the employee under § 85a.8(b)(1) will be immediately notified by NIOSH.

(3) A summary of the findings of the examinations for each employee will be sent by NIOSH to the individual.

(c) The findings of a total investigation generally will be disseminated as part of NIOSH criteria documents, NIOSH technical reports, NIOSH information packets, scientific journals, presentations at technical meetings, or in other similar manners. These findings of a total investigation will be presented in a manner which does not identify any specific place of employment; however, it should be noted that the specific reports of investigations of each place of employment under this part are subject to mandatory disclosure, upon request, under the provisions of the Freedom of Information Act (5 U.S.C. 552).

PART 86—GRANTS FOR EDUCATION PROGRAMS IN OCCUPATIONAL SAFETY AND HEALTH

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AUTHORITY: Sec. 8(g), 84 Stat. 1600, 29 U.S.C. 657(g); sec. 21(a), 84 Stat. 1612, 29 U.S.C. 670(a).

SOURCE: 40 FR 29076, July 10, 1975, unless otherwise noted.

Subpart A—General

§ 86.1 Applicability.

The regulations of this part are applicable to the award of training grants and direct traineeships pursuant to section 21(a)(1) of the Occupational Safety and Health Act of 1970 (29 U.S.C. 670(a)(1)) to assist in providing an adequate supply of qualified personnel to carry out the purposes of the Act.

§ 86.2 Definitions.

Any term not defined herein shall have the same meaning as given it in the Act. As used in this part:

(a) "Act" means the Occupational Safety and Health Act of 1970 (29 U.S.C. 651 et seq.).

(b) [Reserved]

(c) "Secretary" means the Secretary of Health and Human Services and any other officer or employee of the Department of Health and Human Services to whom the authority involved has been delegated.

(d) "State" means a State of the United States, the District of Columbia, Puerto Rico, the Virgin Islands,

