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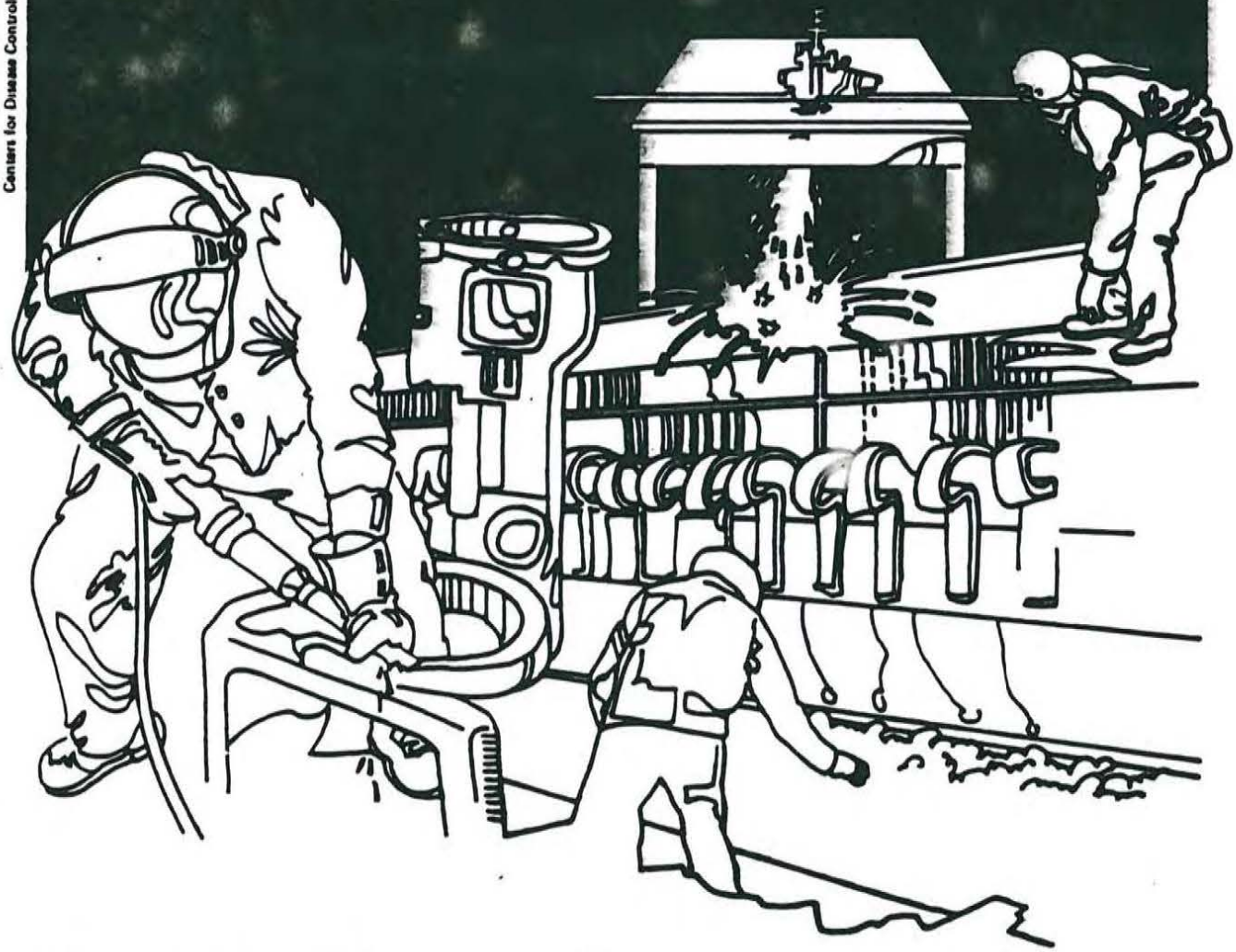

Health Hazard Evaluation Report

HETA 83-376-1556
PORTSMOUTH NAVAL SHIPYARD
PORTSMOUTH, NEW HAMPSHIRE

PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial hygiene technical and consultative assistance (TA) to Federal, state, and local agencies; labor; industry and other groups or individuals to control occupational health hazards and to prevent related trauma and disease.

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

HETA 83-376-1556
April 1985
PORTSMOUTH NAVAL SHIPYARD
PORTSMOUTH, NEW HAMPSHIRE

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I. SUMMARY

In August 1983, the National Institute for Occupational Safety and Health (NIOSH) received a request to evaluate occupational exposures during the system testing conducted as part of a submarine overhaul at Portsmouth Naval Shipyard, Portsmouth, New Hampshire. Employees reported experiencing headache, nausea, and eye, skin and mucous membrane irritation during this operation and believed these symptoms were due to exposures to substances released as a result of the heat produced by the operation.

In November and December 1983, NIOSH performed laboratory tests on numerous materials used during the submarine overhaul to identify possible substances released from the heating of these materials. As a result of these tests and information on the composition of the materials used, the following substances were chosen to be evaluated both prior to and during an actual system testing: acrolein, aldehydes, organics, acids and phthalates.

Area air samples for acrolein, aldehydes, acids and organic vapors were collected on December 14, 1983 in the affected compartment of the submarine USS Jack (SSN 605). These samples were collected to determine background concentrations of environmental contaminants prior to system testing. On December 30, 1983, approximately 8 hours after the maximum test temperature was reached and with ventilation to the affected areas isolated to maximize the concentration of vapors, samples were again collected.

Only low concentrations of three organic solvents were measured during background sampling. Numerous other compounds were detected during system testing. Acrolein levels ranged from 0.057 ppm to 0.085 ppm. Five different aldehydes were identified; acetaldehyde (range 1.1 ppm to 1.2 ppm), formaldehyde (range 0.21 ppm - .23 ppm), proprionaldehyde (0.07 ppm), butyraldehyde (0.07 ppm - 0.08 ppm) and valeraldehyde (0.04 ppm). Organic materials included butanol (0.24 ppm - 0.33 ppm), benzene (0.24 ppm - 0.29 ppm), toluene (0.09 ppm - 0.11 ppm), xylene (0.39 ppm - 0.44 ppm) and naphtha (12 mg/M^3 - 148 mg/M^3). Low levels of acetic acid (0.02 ppm - 0.11 ppm) and formic acid (0.02 ppm) were also measured.

Of nine workers involved in previous system tests, eight reported eye irritation. Five workers also reported throat irritation and four of them nasal irritation. Only two workers reported cough, but five reported other chest symptoms. Five reported headache and three nausea. All eight symptomatic workers said that irritative symptoms began within half an hour of entering the affected shipboard areas.

The NIOSH investigation concludes that the health effects experienced by workers during submarine system testing were a result of the combined effects of exposures to acrolein and other aldehydes. Considering the relatively low concentration of these substances measured and the episodic exposures during system tests, the risk of chronic health effects from these exposures is believed slight.

However, due to irritative effects and the potential for chronic effects at higher levels, steps should be taken to reduce exposures. Recommendations are presented in Section VII.

KEYWORDS: SIC 3731 (ship building and repairing), acrolein, aldehydes, formaldehyde, benzene, eye irritation

II. INTRODUCTION

In August 1983, NIOSH received a request for a health hazard evaluation at the Portsmouth, Naval Shipyard, Portsmouth, New Hampshire. The Portsmouth Federal Employees Metal Trades Council (AFL-CIO) requested that NIOSH evaluate workers' exposures during system testing performed during overhaul. Concern was expressed about the possible substances released into the working environment by the heat produced during the testing as workers reported experiencing a variety of symptoms including headache, nausea and eye, skin and mucous membrane irritation.

On December 14, 1983 an initial environmental and medical survey was conducted to collect background data. NIOSH investigators returned on December 30, 1983 to conduct environmental sampling and collect medical information during the initial phases of system testing.

Findings of these evaluations were reported in the letter of March 9, 1984 to the requestors and the Navy.

III. BACKGROUND

The Portsmouth Naval Shipyard was established in 1800 for designing, constructing and repairing ships. The Portsmouth Naval Shipyard was officially designated a submarine yard in 1923 and at present is exclusively dedicated to overhauling, repairing and refueling nuclear powered submarines.

The operation evaluated in this study is the testing of shipboard systems performed near the end of a submarine overhaul. During the test period the shipboard systems are heated and are exercised to demonstrate proper operation. The heat was believed by workers to cause the release of irritant vapors from paints, adhesives, insulation materials and other products installed during the earlier phases of the overhaul. These "unknown" substances were reportedly causing symptoms among workers present during this operation. The request for evaluation asked specifically for the identification of the substances causing these health effects and for an evaluation of the potential for chronic health problems.

IV. EVALUATION DESIGN AND METHODS

A. Environmental

1. Laboratory Evaluation

In November and December, 1983, NIOSH performed laboratory tests on twelve bulk materials of construction used during the submarine overhaul to determine possible substances released as a result of exposure to heat. The samples were handled in the following manner:

a. Experimental-Sampling

Small amounts (less than 1 ml) of each of the bulks were coated on the inside of disposable glass pipettes, and allowed to air dry 2-4 days prior to any analyses. A tube furnace equipped with quartz tubing was set up to heat the samples. Nitrogen was used as the purge gas for the system. Although sampling conditions such as temperatures and times varied somewhat, the general procedure used for heating the materials and collecting samples was as follows:

1) With the oven temperature cool (20-40°C), a sample coated pipette from one of the bulks was placed in the oven tubing. A charcoal tube followed by a porous polymer tube in series was placed at the outlet of the oven tubing to collect the effluent. The oven temperature was turned up and the heated paint sampled for 30-45 minutes. Nitrogen purge flow was about 150-250 cc/min. The final temperature of the oven at this time was 140-160°C.

2) The sampling tubes described above were removed and replaced with a new series of sorbent tubes - a benzylethanol amine (BEA) coated Chromosorb 102 tube used to sample for formaldehyde, another charcoal tube, and a hydrogen chloride (HCl) detector tube. The oven temperature was again increased and another 30-45 minute sample collected. Final oven temperatures after this set ranged from 260-280°C.

b. Analyses

All charcoal tube samples were desorbed with carbon disulfide and screened by gas chromatography (FID) using 30 meter DB-1 bonded phase fused silica capillary columns (splitless mode). Selective samples were further analyzed by GC/MS to identify components. Both the front and back-up sections of the charcoal tubes were desorbed together for these analyses.

All the BEA coated tubes for formaldehyde were desorbed with isooctane and screened by gas chromatography (method P&CA 354) for formaldehyde. A 25 meter fused silica carbowax 20M capillary column was used. These samples were also screened on the 30M DB-1 column and selective ones reanalyzed by GC/MS.

Portions of the bulks were extracted directly (no heating or drying first) with carbon disulfide and screened by GC. A couple of these CS_2 extracts were further analyzed by GC/MS.

2. Initial Survey

Environmental air samples for acrolein, aldehydes, acids and organic vapors were collected on December 14, 1983 in the two affected areas aboard the submarine USS Jack (SSN 605). These samples were collected to determine background concentrations of environmental contaminants prior to system testing. Sampling and analytical methods are presented in Table 1.

3. Follow-up Survey

On December 30, 1983, approximately 8 hours after the maximum temperature was reached, environmental air samples were again collected for acrolein, aldehydes, acids and organic vapors in both of the affected areas. Sampling for phthalates was also conducted. Sampling duration was approximately 7 1/2 hours. Samples, for several of the substances being evaluated, were collected by two or more methods to eliminate data loss due to possible presence of interfering compounds (Methods - Table 1).

4. Medical

The NIOSH medical officer interviewed (a) the four workers identified by the requestor as having had symptoms during system testing, and (b) workers identified on ship access logs as working in or near affected areas during the first 48 hours in September 1982 aboard the USS James K. Polk (SSBN 645) or in May 1983 aboard the USS Billfish (SSN 676). He also reviewed the medical records of those interviewed workers who sought medical attention for their symptoms. (All interviews were private, except in the case of one worker who, despite his union steward's efforts to encourage him to have the interview privately, insisted that the steward be present.)

In addition to the four requestor-identified workers, five of the seven NIOSH-selected workers were interviewed. (One of the remaining two was on vacation, and the other no longer worked at the shipyard).

V. EVALUATION CRITERIA

A. Environmental Criteria

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy).

In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the evaluation criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: 1) NIOSH Criteria Documents and recommendations, 2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLV's), and 3) the U.S. Department of Labor (OSHA) occupational health standards. Often, the NIOSH recommendations and ACGIH TLV's are lower than the corresponding OSHA standards. Both NIOSH recommendations and ACGIH TLV's usually are based on more recent information than are the OSHA standards. The OSHA standards also may be required to take into account the feasibility of controlling exposures in various industries where the agents are used; the NIOSH-recommended standards, by contrast, are based primarily on concerns relating to the prevention of occupational disease. In evaluating the exposure levels and the recommendations for reducing these levels found in this report, it should be noted that industry is legally required to meet only those levels specified by an OSHA standard.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. Some substances have recommended short-term exposure limits or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from high short-term exposures.

Acrolein

Acrolein produces intense irritation to the eyes and mucous membrance of the respiratory tract. Because of acrolein's pungent, offensive odor and the intense irritation of the conjunctiva and upper respiratory tract, severe toxic effects from acute exposure are rare as workers will not tolerate the vapor even in minimal concentration. Acute exposure to acrolein may cause bronchial inflammation, resulting in bronchitis or pulmonary edema. The Federal OSHA standard for exposure to acrolein is 0.1 ppm.

Aldehydes

The effects of acute exposure to aldehydes are primarily mucous membrane irritation (burning, tearing eyes, nose and throat irritation). These symptoms can occur with exposures as low as about 0.1 ppm.

At the present time there are no exposure criteria for either proprionaldehyde or butyraldehyde. The American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) for acetaldehyde is 100 ppm and for valeraldehyde 50 ppm. The current OSHA standard for formaldehyde is 3 ppm as an 8-hr TWA. However, a study conducted by the Chemical Industry Institute of Toxicology (CIIT), in which mice and rats exposed to formaldehyde vapors developed nasal cancer, has raised concerns about its carcinogenic potential in humans. On the basis of the CIIT study findings, ACGIH and NIOSH currently recommend that formaldehyde be treated as a potential human carcinogen. NIOSH recommends that exposures be reduced to the lowest feasible level.

Benzene

Acute exposure to benzene can cause central nervous system depression resulting in such symptoms as headache, vertigo (dizziness), lightheadedness, drowsiness, confusion and incoordination. Chronic exposure to benzene can cause decreased production of red blood cells, white blood cells and platelets, resulting in pallor and shortness of breath, impaired ability to fight infections and bleeding problems. Benzene can also cause leukemia. In order to reduce the risk of leukemia, NIOSH recommended in 1977 that exposure to benzene not exceed

1 ppm. This criterion, initially a 2-hour TWA, then later a 1-hour TWA as analytical sensitivity improved, was chosen because it represented the limit of analytical reliability. As with other carcinogens, NIOSH recommends that employee exposure to benzene be reduced to the lowest feasible level.

VI. RESULTS

A. Environmental

1. Bulk Sample Testing

Volatile materials identified in the bulk materials tested included mineral spirit-type naphthas (composed mainly of C_9-C_{12} aliphatics and some alkyl substitued benzenes), toluene, xylene, cellosolves, butyl cellosolve, butanol, methyl ethyl ketone, alkyl substituted dioxan and methyl pentanediol.

Although the BEA coated Chromosorb 102 tubes have been evaluated only for formaldehyde, they were used in this study as indicators of other aldehydes present based on the reaction products observed by GC/MS. Formaldehyde was detected in ten of the twelve heated bulk material samples. In addition to formaldehyde, various other aldehydes were also indicated in the samples, some in fairly large amounts. The largest single aldehyde present in most of the samples was suspected to be acetaldehyde based on the m/e 176 ion detected by GC/MS. The aldehydes possibly present were propionaldehyde, butyraldehyde, valeraldehyde and furfural.

One of the paint samples also gave a positive indication on the HCl detector tube (entire indicating layer changed to positive yellow color). Other materials identified on the sample bulk included butyl acetate, 2-chloroethylacetate and other acetate-type compounds such as acetol acetate, butenes, butanol and benzene.

2. Survey Results

As a result of the bulk material tests and general knowledge of the composition of the materials used, the following classes of compounds or substances were chosen to be evaluated both prior to and during system testing: acrolein, aldehydes, organics, acids and phthalates.

Table II contains the environmental results from the air samples collected for background determination and those collected during system testing. A review of the data shows that only low concentrations of three organic solvents were measured during background sampling. The substances identified were toluene, xylene, and naphtha. These substances are all common solvents used in paints, adhesives, etc. and their presence under the above described construction condition would be predictable.

A review of the data collected during system testing shows the presence of numerous other compounds not detected during the background monitoring. Acrolein levels ranged from 0.057 ppm to 0.085 ppm. Five different aldehydes were identified as being present in measurable concentrations: acetaldehyde (1.1 ppm to 1.2 ppm), formaldehyde (0.21 ppm to 0.23 ppm), proprionaldehyde (0.07 ppm), butyraldehyde (0.07 ppm to 0.08 ppm) and valeraldehyde (0.04 ppm). Organic materials present included butanol (0.24 ppm - 0.33 ppm), benzene (0.24 ppm - 0.29 ppm), toluene (0.09 ppm - 0.11 ppm), xylene (0.39 ppm - 0.44 ppm), and naphtha (12 mg/m^3 - 14.8 mg/m^3). Low concentration of acetic acid (0.02-0.11 ppm) and formic acid (0.02 ppm) were measured. No hydrochloric acid or phthalates were found.

3. Medical

All but one of the interviewees reported eye irritation during system testing. Five workers also reported throat irritation, and four of them nasal irritation. Two persons reported facial skin irritation. Only two workers reported cough, but five (including the two with cough) reported other chest symptons (tightness, soreness, shortness of breath). Five persons reported headache, and two of them reported addition neurologic symptoms (lightheadedness, dizziness, confusion). Three workers reported nausea; none had vomiting. The requestor-referred workers, as a group, were no more likely to report multiple, non-irritative symptoms than the NIOSH-selected interviewees.

All eight symptomatic workers said that irritative symptoms began within half an hour of entering the affected areas; four of them said that the onset occurred within a few minutes. Four of the affected workers said that recovery from the irritative symptoms took only a few minutes. Two others said that recovery took an hour or two, and the remaining two said that it took until the next day. Respiratory symtpoms tended to last an hour or so after exposure ended. One worker claimed residual respiratory impairment.

Two workers sought medical attention for symptoms related to system testing; they were working on the USS James K. Polk, (SSBN 645) at the time. Their medical records indicated eye, nose, throat, and/or chest symptoms, and noted redness of the nose or throat on examination.

All six symptomatic workers who recalled working during system testing both on the USS James K. Polk (SSBN 645) and on other submarines said that symptoms were more severe or occurred only on USS James K. Polk (SSBN 645). Three workers recalled symptoms recurring over at least several days; the others either could not remember or were not assigned to system testing long enough to know.

VII. DISCUSSION AND RECOMMENDATIONS

The irritative symptoms reported from previous system testing operations are compatible with the effects of exposure to aldehydes and acrolein. NIOSH's environmental measurements cannot determine whether concentrations of air contaminants were higher earlier (as suggested by the Naval Research Laboratory data) or later in the testing, nor whether they were higher during previous system tests. The headaches and neurologic symptoms reported during previous system tests are compatible with the effects of exposure to aldehydes, and the respiratory symptoms and nausea are compatible with the effects of exposure to acrolein. While none of these effects, with the exception of mild irritation, would be expected at the concentrations measured by NIOSH, even when the substances are considered in combination, they suggest the possibility of exposure to higher concentrations during previous system tests.

Except for acrolein, benzene, and formaldehyde, none of the substances measured by NIOSH are known to cause chronic health effects, even at concentrations much higher than NIOSH found. Benzene is a known human carcinogen, and formaldehyde is an animal carcinogen and therefore a suspect human carcinogen. Considering the relatively low concentrations of these compounds at the time of the NIOSH study, though, the health risk from the episodic exposures during system testing is believed slight.

Acrolein can cause permanent pulmonary damage, but this ordinarily requires exposure to a concentration higher than that which usually causes intolerable eye irritation. Thus, the circumstances of such an exposure would generally involve an inability to remain in an area where the acrolein concentration has suddenly increased, as from a spill or leak, for example. These conditions apparently would not normally occur during system testing, but NIOSH has no way of determining whether individual cases of excessive exposure to acrolein occurred in the past.

NIOSH investigators believe that the health effects being experienced by workers during system testing are a result of the combined effects of exposures to acrolein and other aldehydes. Based on the laboratory testing of the construction materials, the majority of them release one or more of the aldehydes when heated, thus making elimination and substitution a difficult or impossible task. It is therefore recommended that during system testing, affected areas be properly ventilated to reduce acrolein, aldehyde and benzene levels or appropriate eye and respiratory personal protective equipment be provided to all individuals entering the affected areas. Additional monitoring for these substances should be performed to determine duration of release and also the effectiveness of the control measures used in reducing exposures.

IX. AUTHORSHIP AND ACKNOWLEDGEMENTS

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X. DISTRIBUTION AND AVAILABILITY OF REPORT

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1. Department of the Navy, Portsmouth Naval Shipyard, Portsmouth, N.H.
2. Portsmouth Federal Employee Metal Trades Council, Portsmouth, N.H.
3. NIOSH, Region I
4. OSHA, Region I
5. Commander, Naval Sea Systems Command, Washington, D.C.

For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

Table I

Sampling and Analytical Methods

Portsmouth Naval Shipyard
Portsmouth, New Hampshire

Substance	Sampling Media	Flow Rate	Analytical Method	Reference
Acrolein	2-(hydroxymethyl)Piperidine coated XAD-2 tubes	100 cc/min	GC (FID)	NIOSH Method 2501
Aldehydes	N-benzylethanolamine coated XAD-2 tubes	50 cc/min	GC (NPD)	P&CAM 354
	2,4-dinitrophenylhydrozine coated silica gel tubes	200 cc/min	IC	Anal. Chem (1980) 52, 1110-1114
Organics	Charcoal tube	100 cc/min	GC (FID)	P&CAM 127
Acids	Silica gel tube	200 cc/min	IC	P&CAM 339
	Chromosorb 103 tubes	200 cc/min	IC	Method Development
Phthalates	Teflon Filter	1.5 liters/min	GC (FID)	S-33 (Modified)

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