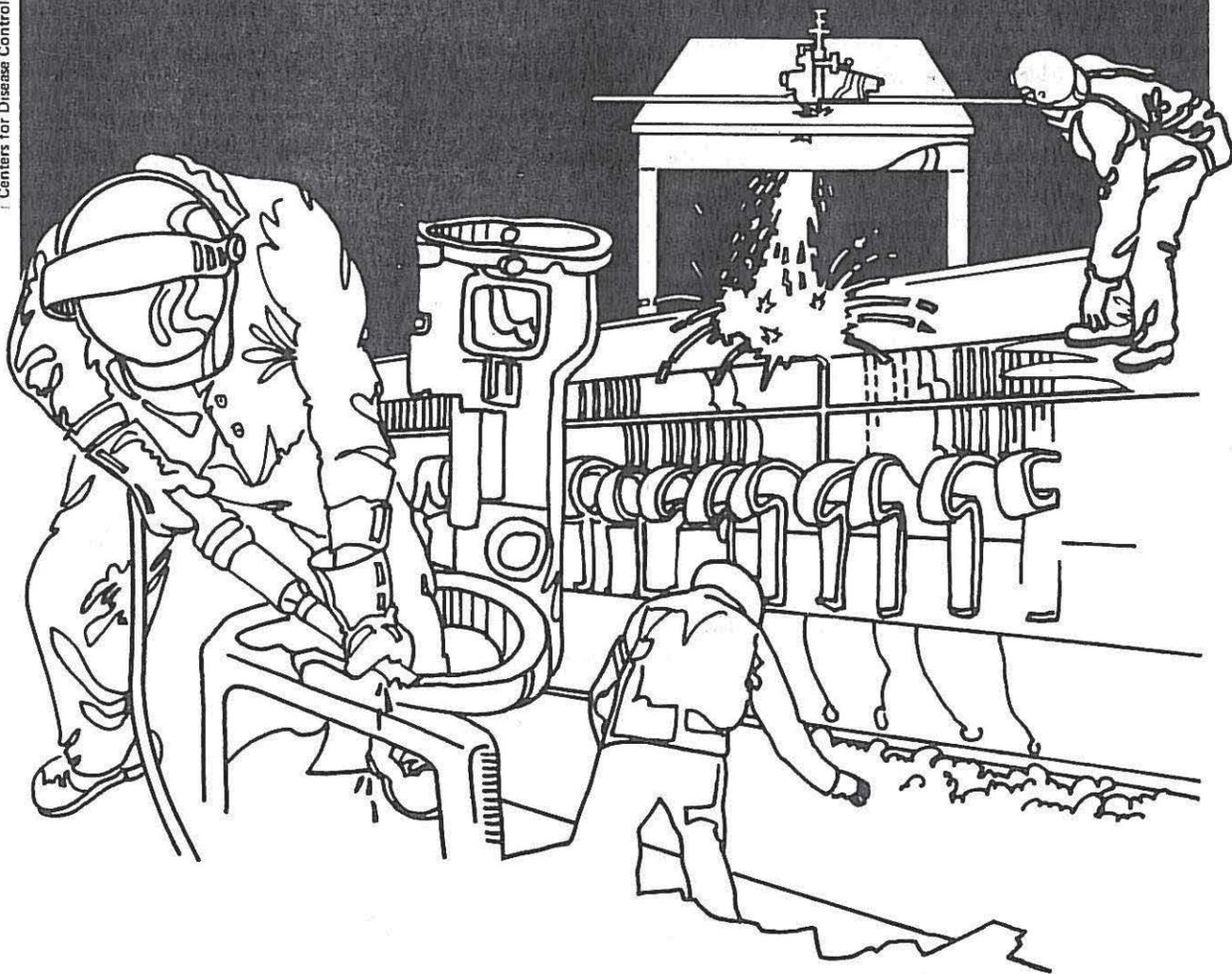


NIOSH



Health Hazard Evaluation Report

HHE 80-181-909
RALSTON PURINA COMPANY
CINCINNATI, OHIO

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.

HE 80-181-909
July 1981
Ralston Purina Company
Cincinnati, Ohio

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I. SUMMARY

On July 1, 1980, the National Institute for Occupational Safety and Health (NIOSH) received a request to evaluate worker exposure to "EP Liquid", a chemical recently introduced into the work environment at Ralston Purina, Cincinnati, Ohio. Workers in the animal food extrusion room were concerned about potential safety and health hazards when working with this chemical due to the increased level of personal protective equipment required and the lack of specific ingredient information.

EP Liquid is a caustic (pH=1.0) cleaning and bacteriostatic agent that is pumped into the extruders each Friday and drained on Sunday. Four operators (2 on Friday and 2 on Sunday) at each Ralston Purina animal feed extrusion plant are potentially exposed.

Laboratory analysis of a bulk sample of the EP Liquid, in addition to confirming its acidic nature, indicated a potential for ethylene oxide exposure. Subsequent air sampling at the plant detected concentrations ranging from 2.0 to 4.5 parts per million (ppm) in particular areas, but all personal breathing zone samples were negative. One headspace sample, obtained from a 55 gallon drum of the concentrated EP Liquid, detected 7.5 ppm formaldehyde. Another survey was planned to further evaluate formaldehyde exposure, but the extrusion operation was shut down, due to a reported lack of production volume, before this could be accomplished. The OSHA standards for ethylene oxide and formaldehyde are 50 ppm and 3 ppm respectively. NIOSH recommends that both be handled as carcinogens and therefore, exposures should be minimized to the extent possible.

Symptoms reported by the 4 extruder operators were nonspecific, relatively mild (except during the performance of one task that requires looking into a mixing tank) and transient. They included eye and throat irritation, light-headedness, cough and noxious odor. Two workers described symptoms of first degree burns after spilling EP liquid on the arm.

The acute symptoms experienced by the workers are most probably due to exposure to mist and droplets of the EP Liquid during the performance of three or four specific tasks where the chemical is agitated. Ethylene oxide was not detected in personal breathing zone samples, however, it was detected in certain area samples. The source of the ethylene oxide should be identified and eliminated. Formaldehyde exposure also requires further evaluation. Recommendations are provided in Section VII that will reduce caustic emissions and minimize ethylene oxide exposure.

KEYWORDS: SIC 2048, Ethylene oxide, formaldehyde, citric acid, methylparaben

II. INTRODUCTION

On June 25, 1980 an authorized representative of AFL-CIO, Grain Millers Local Number 256, Cincinnati, Ohio requested a health hazard evaluation of worker exposure to Purina EP Liquid in the extruder room of Ralston Purina's Cincinnati plant. The extruder room houses 10 extruder machines that are used to process animal food. Each weekend, during a shutdown period, the extruders are filled with the EP Liquid, an acidic cleaning agent and bacteriocide. The EP liquid is, reportedly, more effective than the previous ES compound, a dry mixture of rice hulls and a bacteriostatic agent.

Accompanying the introduction of the new chemical was a requirement that extruder operators must use a face shield and chemical resistant aprons, gloves and gauntlets. This increased level of personal protective equipment along with complaints of mucous membrane irritation and the inability of the extruder operators to obtain what they viewed as sufficient ingredient information raised questions about potential safety and health hazards.

Three NIOSH representatives (2 medical officers and 1 industrial hygienist) visited the plant in July 1980 to observe conditions of exposure and interview workers. Qualitative analysis of a bulk sample of the EP liquid concentrate indicated a potential for exposure to ethylene oxide. This analysis, along with the finding of ethylene oxide in some area air samples (not detectable in breathing zone samples) obtained on a follow-up survey in October 1980, proved to be controversial in that both Ralston Purina and Wyandotte, a supplier of an ingredient of the EP liquid, could not explain its presence, and Ralston Purina did not detect it while sampling side-by-side with NIOSH. Sampling accomplished during the follow-up survey also indicated that formaldehyde may be evolving from the EP liquid.

At the request of Ralston Purina, NIOSH representatives met with Ralston Purina representatives in Cincinnati in February 1981 to discuss the status of the project. Another survey was planned to evaluate worker exposure to formaldehyde. NIOSH laboratory personnel were researching available sampling and analytical techniques to select a primary and a backup method for use in April 1981 when notification was received from Ralston Purina that the extrusion operation at Cincinnati was no longer operational due to insufficient volume.

III. BACKGROUND

EP liquid is manufactured by Ralston Purina Company. One ingredient, Pluronic F108, is supplied by Wyandotte Chemical Company. The concentrated EP liquid is highly acidic (pH=1.0). Ingredients are confidential but reported as being "food grade" substances. Each Ralston Purina Plant that extrudes animal food uses this chemical. Exposure occurs at the Cincinnati plant for approximately 2 hours on Friday and 2 hours on Sunday. On Friday, two operators pump concentrated EP liquid from a 55 gallon drum into a closed mixing tank where 35 gallons of EP liquid is mixed with 165 gallons of water. An overhead piping system then allows

for each of the 10 extruders to be sequentially filled with approximately 20 gallons of diluted EP liquid. As each extruder is filled, an operator positions a 4-wheeled, plastic cart at the exit orifice to catch excess EP liquid. The extruder is then plugged and the process continues at the next extruder in line until all units are filled. The plastic cart which now contains a mixture of meal and EP liquid is moved to a small washroom where it is emptied into a floor drain by turning it on its side.

On Sunday evening, two extruder operators spend approximately 2 hours draining the extruders in preparation for the Monday production run. This process begins by preheating the extruders with 247⁰F steam. Then, each extruder is unplugged and the contents are drained into a plastic cart as it is moved down the line. After all units are empty, the extruders and the floor of the extruder room are hosed down with hot water to remove residual EP Liquid and meal.

IV. METHODS

1. Environmental

Ralston Purina supplied a list of the chemical ingredients of the EP Liquid. Laboratory analysis of the head space above a bulk sample of this chemical was accomplished to determine volatile components. Air samples were obtained on a Friday and Sunday to evaluate worker exposure to the volatile components of the EP Liquid.

a. Head Space Analysis (EP Liquid)

A sample of the head space above a liquid aliquot of the EP Liquid was collected by pulling air through a glass tube containing activated carbon. Samples were analyzed for organic volatiles by NIOSH Method Number P&CAM 127 using a gas chromatograph equipped with a flame ionization detector.

Samples of the head space were also collected on SKC, petroleum based, Qazi-Ketcham activated charcoal tubes (SKC Cat. #226-36). A gas chromatograph equipped with a flame ionization detector and a 550 Ucon column was used for the analysis.

b. Ethylene Oxide

Ten air samples (6 area, 4 personal breathing zone) were collected during a Friday and Sunday operation in the extruder room at the Ralston Purina plant. Air was pulled through the sampling media (SKC, petroleum based, Qazi-Ketcham, activated charcoal tubes) at a sampling rate of 100-500 cubic centimeters per minute (cc/min). Samples were analyzed by gas chromatography following a modification of NIOSH Method S-286 as explained in Appendix A(1).

c. Acetaldehyde

Attempts to confirm the presence of ethylene oxide in the head space analysis by a gas chromatography/mass spectrometry technique were unsuccessful because another chemical, acetaldehyde, which is an isomer of ethylene oxide, produces the same mass spectra. Therefore, air samples were collected and scanned for aldehydes as an aid in the analysis of ethylene oxide rather than as a potential exposure. Samples were collected using an impinger containing 10 milliliters of 1% Sodium Bisulfide and analyzed by direct injection into a gas chromatograph equipped with a flame ionization detector. A 3' x 1/8" stainless steel column packed with Chromosorb 10 was used. The oven temperature was programmed from 70°C to 150°C at a rate of 10°C/minute.

2. Medical

NIOSH medical personnel observed a Friday (7/11) and Sunday (7/13) EP Liquid operation and interviewed 4 extruder operators.

V. RESULTS AND DISCUSSION

1. Environmental

Ethylene oxide was detected in the head space of the EP Liquid sample.

Table 1 presents Ethylene Oxide results for the follow-up air sampling accomplished at the plant on October 3 and 5, 1980. Area samples ranged from 2.0 ppm to 4.5 ppm and represent the time-weighted-average concentration at that location for the period of time sampled (10 minutes to 2 hours). They do not represent personal exposures since the breathing zone of the operators did not correspond to the location of the area sample media. No detectable levels of ethylene oxide were found in breathing zone samples. Considering the analytical detection limit which was reported by the laboratory to be 0.02 milligrams per sample and a sample volume of from 6 to 12 liters of air, the lower limit of detection ranged from 0.9 to 1.9 ppm. Although confirmation of the presence of ethylene oxide was not possible by a second analytical method as mentioned in Section IV, a remark was included in the laboratory report to the effect that the retention time for acetaldehyde, was approximately 0.5 to 1 minute earlier than that of ethylene oxide. The fact that Ralston Purina did not detect ethylene oxide is unexplained. Although an attempt was made to duplicate sampling and analytical procedures, it is not clear whether analytical methods were the same.

Aldehyde results are presented in Table 2. The only aldehyde detected was Formaldehyde (7.5 ppm) in the EP Liquid drum headspace sample. This was an unexpected finding that warranted further evaluation in light of the fact that NIOSH recommends that formaldehyde be handled as a potential occupational carcinogen.⁽²⁾

A primary and backup sampling/analytical method was selected to confirm and quantify formaldehyde exposure at the plant. However, the extruder operation was shut down due to a reported lack of production volume before the survey could be conducted. The extruder equipment is still in place but there are no immediate plans to resume production.

2. Medical

Extruder operators were aware of the caustic nature of the EP Liquid and the consequences of direct contact with the skin. Two operators described symptoms of first degree burns after spilling some of the EP Liquid on their arms. Each operator reported symptoms typical of mucous membrane irritation, including irritation of the throat and/or redness of the eyes. Other symptoms reported included cough, noxious odor and light-headedness. The symptoms noted by the operators were nonspecific and relatively mild. They may have been due to exposure to one or more of the components of the EP Liquid or to a combination of those ingredients. The following chemicals are contained in the EP Liquid and may be responsible for some of the symptoms the workers have reported:

Citric acid, which is the acid contained in citrus fruits like oranges, can have a direct irritating effect on the mucous membranes of the mouth.

Methylparaben and other parabens can cause contact dermatitis, a type of skin irritation.

Ethylene oxide can cause irritation of eyes, nose, and throat and a peculiar taste. Skin contact may cause burns.

Formaldehyde is not an ingredient of EP Liquid, but it was found in small quantities in the sampling done by NIOSH. Formaldehyde can cause burning and tearing of the eyes and irritation of the upper respiratory tract.

High-dose exposures to some of the chemicals mentioned above can result in more serious adverse health effects, but the production processes which we observed involved relatively brief and intermittent exposure to the EP Liquid. For most of these chemicals, such exposure would not be likely to cause adverse health effects more serious than the irritative symptoms which the employees have experienced. Two of the chemicals, however, are considered to be potential carcinogens. Formaldehyde has been demonstrated to cause cancer in experimental animals⁽²⁾, and ethylene oxide has been shown to cause mutations in experimental animals^(3,4). Safe levels of exposure to carcinogens have not been demonstrated, but the potential for developing cancer should be minimized by reducing exposure as much as possible.

Operators reported that there were 3 steps in the process when they were most likely to notice symptoms. A fourth step was later included in this list as a result of discussions during the environmental sampling phase of the study.

a. Mixing Operation

In order to check fluid mixing levels the operator had to open the lid on the tank exposing himself to an extremely irritating atmosphere.

b. Extruder Filling/Draining Operation

The operator is positioned adjacent to the cart to monitor the draining/filling operation. He occasionally uses a stick to unplug the extruder orifice. The pressure that has built up can cause the EP Liquid to spurt out and splash on the operator. Additionally, as the EP Liquid empties into the plastic cart the agitation causes irritating emissions.

c. Washroom Operation

The washroom is a small (6'x9'), non-ventilated area. The plastic cart is emptied by turning it on its side and then hosed down with hot water. The emissions generated by this activity are a source of upper respiratory tract irritation.

d. Hose-down Operation

The surface of the extruders and the floor of the extruder room are hosed down with hot water to remove residual EP Liquid and animal feed residue. Workers reported that this activity occasionally produced irritating emissions.

VI. CONCLUSIONS

1. The symptoms reported by the workers are nonspecific, relatively mild (except when looking into the mixing tank) and transient. They are most probably the result of exposure to the droplets and mist of the EP Liquid and are most often associated with the four operations described in Section V. These acute health effects can be minimized, and perhaps eliminated, through the implementation of engineering controls to reduce exposure during these operations. Recommendations are provided in Section VII.

2. Low concentrations (2.0-4.5 ppm) of ethylene oxide were detected in area samples but, due to the fact that it was not detectable in personal breathing zone samples and considering an exposure time of 2 hours or less per week, the occurrence of chronic health effects would be extremely unlikely for the work situation evaluated.

3. Evaluation of worker exposure to formaldehyde is inconclusive. The finding of 7.5 ppm in the head space of a drum of the EP Liquid suggests that it may be present in the work environment.

4. The finding of ethylene oxide in the work environment and the indication that formaldehyde may be present warrants further investigation by Ralston Purina for the following reasons:

a. NIOSH recommends that ethylene oxide and formaldehyde be handled as potential human carcinogens. Therefore, exposures should be minimized to the extent possible. (2)(3)

b. Neither ethylene oxide nor formaldehyde is intended to be a component in the finished EP Liquid. Ethylene oxide is a reactant chemical, but a vacuum distillation process is supposed to remove residual ethylene oxide.

c. EP Liquid is currently used for only 2 hours on Friday and 2 hours on Sunday. The extent of future use is uncertain. Increased usage may result in exposures of longer duration, and more people would be affected if this product is eventually marketed by Ralston Purina.

VII. RECOMMENDATIONS

1. Implementation of the following recommendations which were forwarded to management and labor by letter, dated January 12, 1981, should significantly reduce exposures responsible for the reported symptoms and even further minimize the potential for long term health effects. They are presented in the order of their significance.

a. The mixing tank should be equipped with an external sight gauge that is not affected by entry, water-line flow.

b. The plastic cart should be equipped with a drain plug so the cart could be emptied by positioning it over the floor drain in the washroom and pulling the plug.

c. The feasibility of covering the cart and adding a clear plastic cover to connect the cart to the exit part of the extruders should be considered.

d. The use of cold water instead of hot may reduce the level of emissions generated during washdown.

NOTE: Correspondence received from Ralston Purina (dated February 2, 1981) indicated that recommendation (a) had been implemented and (b) was in the planning stage. Recommendations (c) and (d) will not be implemented because (c) may create a potential safety hazard and cold water (d) will not adequately remove fat residue.

2. The use of disposable/reusable dust/mist respirators as an interim measure will help reduce mucous membrane irritation, however, the fact that they offer no protection against vapors requires that they be used with caution.
3. Further testing should be done by Ralston Purina to determine the source of the ethylene oxide vapors. Samples of the head space of the Pluronic F108 should be obtained and analyzed for ethylene oxide. Head space samples of the Pluronic F108 and EP Liquid should be analyzed for the presence of formaldehyde. Appendix A and B contain ethylene oxide and formaldehyde sampling and analytical methods that are recommended by NIOSH for this purpose.

VIII. REFERENCES

1. Qazi, A.H., Ketcham, N.H.: A New Method for Monitoring Personal Exposure to Ethylene Oxide in the Occupational Environment. AIHA Journal, Volume 38, November, 1977.
2. NIOSH Current Intelligence Bulletin 34: Formaldehyde - Evidence of Carcinogenicity, April 15, 1981.
3. DHEW (NIOSH) Publication No. 77-200: Special Occupational Hazard Review with Control Recommendations - Use of Ethylene Oxide as a Sterilant in Medical Facilities, August, 1977, pg. 38.
4. NIOSH Current Intelligence Bulletin 35: Ethylene Oxide, Evidence of Carcinogenicity, May 22, 1981.

IX. AUTHORSHIP/ACKNOWLEDGEMENTS

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X. DISTRIBUTION AND AVAILABILITY

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Copies of this report have been sent to:

1. Ralston Purina Company
Director, Corporate Regulatory Compliance
2. Ralston Purina Company, Cincinnati, Ohio.
3. AFL-CIO, Grain Millers Local Number 256, Cincinnati, Ohio.
4. OSHA, Region V
5. NIOSH, Region V

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

TABLE 1

ETHYLENE OXIDE

RALSTON PURINA COMPANY
CINCINNATI, OHIO
HE 80-181

October 3 and 5, 1981

<u>Date</u>	<u>Job/Location</u>	<u>Sample Type⁽¹⁾</u>	<u>Sample Volume (L)</u>	<u>Sampling Time</u>	<u>Ethylene Oxide (ppm)⁽²⁾</u>
10/3	Extruder Op. #1	P	12	8:55am-10:50am	ND
10/3	Extruder Op. #2	P	12	8:55am-10:50am	ND
10/3	Drum Headspace	A	12	9:00am-10:55am	2.8
10/3	Plastic Cart	A	7	9:20am-10:15am	ND
10/3	Washroom	A	5	10:15am-10:25am	4.5
10/5	Extruder Op. #3	P	6	5:57pm-7:05pm	ND
10/5	Extruder Op. #4	P	6	6:00pm-7:05pm	ND
10/5	Plastic Cart	A	6	6:03pm-7:05pm	3.7
10/5	Extruder Exit Port ⁽³⁾	A	6	6:05pm-7:10pm	2.0

- NOTE: (1) P = Personal Breathing Zone Sample, A = Area Sample
 (2) Time-Weighted-Averages for the period of time sampled. ND means ethylene oxide was not present in high enough concentrations to be detectable. Considering an analytical limit of detection of 0.02 mg/sample, ND can be interpreted as <0.9 ppm for a 12 liter sample and <1.9 ppm for a 6 liter sample.
 (3) This sampling apparatus was moved from extruder to extruder as each was emptied and positioned so that the sampling media was within 12 inches of the exit port.

TABLE 2

ALDEHYDES

RALSTON PURINA COMPANY
CINCINNATI, OHIO
HE 80-181

October 3 and 5, 1981

<u>Date</u>	<u>Sample Location</u>	<u>Air Sample Volume (L)</u>	<u>Sampling Time</u>	<u>Impinger Volume (mL)</u>	<u>Formaldehyde ppm</u>	<u>n-Valeraldehyde ppm</u>	<u>Acetaldehyde ppm</u>	<u>Pioprionaldehyde ppm</u>	<u>n Butraaldehyde ppm</u>
10/3	Drum head space	115	9:00am-10:55am	13.3	7.5(1)	ND	ND	ND	ND
10/3	Plastic Cart	55	9:20am-10:15am	8.9	ND(2)	ND	ND	ND	ND
10/5	Plastic Cart	60	6:05pm-7:05pm	4.2	ND	ND	ND	ND	ND
10/5	Extruder Exit Port	65	6:05pm-7:10pm	6.2	ND	ND	ND	ND	ND

NOTE: (1) Time-Weighted-Average concentration for the period sampled.
 (2) ND means that the particular substance identified was not present in high enough concentrations to be detectable. The analytical detection limit for Formaldehyde was 0.04 mg/ml. Therefore, the lower limit of detection for the three samples where Formaldehyde was ND ranged from 2-5 ppm.

APPENDIX A

ETHYLENE OXIDE ANALYSIS

Sampling and analysis was performed in accordance with NIOSH Method S-286 with the following modifications.

Sampling Modification

The sampling media was a single SKC, petroleum-based, Qazi-Ketchum, activated charcoal tube (SKC catalog # 226-36). Sampling flow rate was 100 cc/min except for one short term sample at 500 cc/min.

Analytical Modification

A 12'x1/8" stainless steel column packed with 20% UCON LB 550-x on 50/100 mesh Chromosorb P(AW) was used with oven temperature programming from 70°C to 120°C at a rate of 5°C/minute.