U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES ■ Public Health Service
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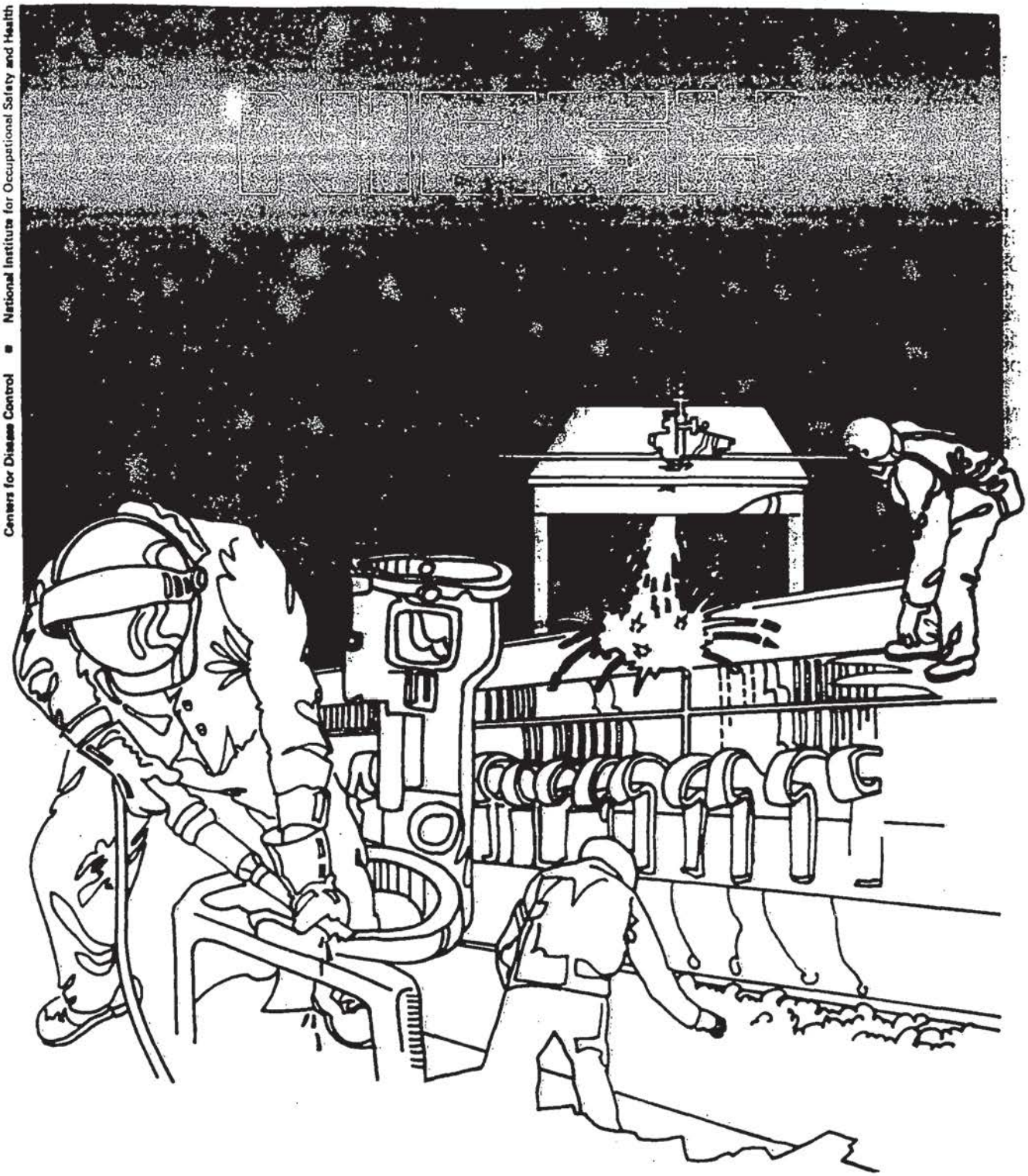

Health Hazard Evaluation Report

HETA 81-031-1209
GULF OIL CORPORATION
BELLE CHASSE, LOUISIANA

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.

HETA 81-031-1209
OCTOBER 1982
GULF OIL CORPORATION
BELLE CHASSE, LOUISIANA

NIOSH INVESTIGATORS:
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I. SUMMARY

In October 1980, the National Institute for Occupational Safety and Health (NIOSH) received a request from an authorized representative of employees to evaluate the exposures of approximately twenty-four (24) employees to phenol (Fluid Catalytic Cracking Unit #1291) and hydrogen fluoride (Alkylation Unit #491) at the Gulf Oil Corporation Alliance Refinery, Belle Chasse, Louisiana.

On January 22, 1981, a walk-through survey was performed of the above-described areas. The NIOSH evaluation of employee exposures was based on a review of results of early January 1981, Gulf Oil Corporation environmental monitoring for phenol and hydrofluoric acid (HF), responses from directed questionnaires administered to twenty-four employees on two of the four shifts in FCCU-1291 and AU-491. One worker, reported to have had a severe allergic reaction was interviewed by telephone. Appropriate medical records were obtained from both Gulf Oil Corporation and private physicians.

Results of the company's environmental monitoring for phenol and HF were below OSHA's permissible exposure limits. Levels of exposure to chemicals in the FCCU-1291 and AU-491 areas appeared relatively low and restricted to occasional episodes. It is generally felt that workers are not being excessively exposed to applicable chemicals.

One employee, who had not worked at the refinery since July 1980, had probably developed an occupational allergy to a substance in the workplace. None of the workers noted any frequent symptoms. Eighty-three percent of those interviewed noted occasional eye irritation, sometimes accompanied by nasal irritation and cough, when HF fumes escaped from AU-491, not all workers were aware of that fact, or knowledgeable as to its proper use.

Based on the results of the environmental/medical evaluation, NIOSH determined that a potential health hazard did not routinely exist for Fluid Catalytic Cracking Unit/Alkylation Unit employees from exposures to phenol and hydrogen fluoride. However, occasional episodes involving the release of HF have resulted in eye, nose and throat irritation in a substantial percentage of the exposed workers.

Recommendations relating to this evaluation are presented in Section VIII of this report.

KEYWORDS: SIC 2865 (Cyclic Crudes, Cyclic Intermediates); Phenol; Hydrogen fluoride; Allergies

II. INTRODUCTION

On October 27, 1980, NIOSH received an employee request to evaluate exposures to phenols (Fluid Catalytic Cracking Unit #1291) and hydrogen fluoride (Alkylation Unit #491) at the Gulf Oil Alliance Refinery, Belle Chasse, Louisiana. One worker at the refinery was reported to have experienced a severe allergic reaction.

III. BACKGROUND

The Alliance Refinery is designed on the basis of a single train of units -- in essence, the crude enters one end of the refinery, travels through a series of processing units and flows from the other end in the form of refined products. Only one unit, the two-stage distillation unit, actually processes the total crude oil received. From there, the various separated components of crude pass on to other units (naphfining unit, sulfur unit, etc.).

As applied to this evaluation, the Fluid Catalytic Cracking Unit (FCCU-1291) is involved with the thermal cracking of gas oil into gasoline, heating oils, olefins and lighter hydrocarbons. The Alkylation Unit (AU-491) utilized hydrogen fluoride as a catalyst in the reaction of olefins and isobutane to form alkylate, a high octane gasoline blending stock.

IV. EVALUATION DESIGN AND PROCEDURES

Environmental/Medical

A walk-through survey was performed at the refinery on January 22, 1981. An opening conference was conducted with management representatives and a walk-through of the FCCU-1291 and AU-491 was performed.

Results of recently conducted phenol and hydrogen fluoride monitoring by company personnel were reviewed.

The Occupational Safety and Health Administration Injury/Illness Log (OSHA-200) was reviewed and a directed questionnaire was administered to 24 FCCU-1291 and AU-491 day and night shift employees. The questionnaire elicited information on smoking history, allergic history, seniority at the plant, and the occurrence, within the preceeding six (6) months, of symptoms such as burning eyes, headache, stuffy nose, cough, shortness of breath, nausea, blurry vision, dizziness and ringing of the ears. The individual who reported having a severe allergic reaction was interviewed, and medical records were obtained from various physicians whom he had visited.

V. EVALUATION CRITERIA

A. Environmental

Environmental standards and criteria applicable to this evaluation are a follows:

Substance	NIOSH, 8-10 hr. TWA Recommendation (mg/M^3)*	ACGIH, TLV Committee, 8-hr. TWA (mg/M^3)*	OSHA,8 hr. TWA Standard (mg/M^3)*
Phenol	20.0/60-C	19.0	19.0
Hydrofluoric Acid	2.5/5-C	3.0	2.5

*Eight or ten-hour, time-weighted average (TWA) concentration in milligrams of substance per cubic meter of air sampled. Ceiling "C" limit based on 15 minute sample.

ACGIH - American Conference of Governmental Industrial Hygienists, Threshold Limit Value Committee;
OSHA - Occupational Safety and Health Administration.

B. Toxic Effects

Phenol[1,2]

Phenol is highly irritating to, and easily absorbed through, the skin. It does not frequently constitute a serious respiratory hazard in industry, owing, in large part, to its low volatility. The vapor readily penetrates the skin with an absorption efficiency equal to that for inhalation. Acute poisoning by ingestion can result in muscular weakness. Chronic effects of phenol include mental disturbances, skin depigmentation, and liver/kidney damage.

Hydrogen Fluoride[3,4]

Hydrogen fluoride (HF) is highly irritating -- causing skin burns, eye irritation, and nosebleeds -- and its burns are especially painful and slow to heal. It can also cause perforation of the nasal septum. HF is a respiratory irritant and instances of acute exposure have caused pulmonary edema and death. Chronic absorption of fluoride can cause osteosclerosis, which is, however, seldom disabling.

VI. RESULTS/DISCUSSION

A. Environmental

The results from environmental monitoring of the affected areas conducted by company personnel in early-January 1981 indicated that

all three samples collected for phenol evaluation showed non-detectable levels. and that the four samples collected for HF ranged from 0.02 - 0.46 mg/M^3, with an average concentration of 0.16mg/M^3. All samples were well below both NIOSH recommended levels and OSHA standards.

Based on results from the company's environmental monitoring program (see Appendix A), visual observation of the closed systems in the two units, and the lack of frequent employee symptoms in the completed questionnaires, the decision was made that a follow-up visit for environmental monitoring was not warranted.

B. Medical

Table 1 summarizes the results of the questionnaire survey. Of the 24 employees interviewed over two shifts, 11 were performing duties on FCCU-1291, and 13 were working in the group which includes AU-491 as part of the normal rotation. These two groups were comparable in age, years of employment at the refinery, and smoking history. Five of 12 employees on AU-491 and one of 9 employees on FCCU-1291 reported a history of allergy, but this difference is not statistically significant. Workers on both units spend an average of 60 percent of their working time outside.

None of the workers noted any frequent symptoms. However, 77% of AU-491 workers and 91% of FCCU-1291 workers observed eye irritation on an occasional basis, generally stated to be once or twice each month. This eye irritation, sometimes accompanied by nasal irritation and cough, was associated by these workers with the release of HF from AU-491. Most directly affected were AU-491 workers, despite the availability of protective equipment such as body suits. Many employees stated that they were not always fully prepared for the release of HF, and some of those interviewed were unsure as to the availability of respirators. Those on FCCU-1291 were also subjected to HF fumes, due to the proximity of their unit to AU-491, whenever the wind blew from the direction of AU-491. They also noted sulfur fumes from the desulfuration unit and fumes from a nearby boiler. Workers on FCCU-1291 have less personal protective equipment available than do those on AU-491. Workers in both units stated that they are able to leave the site if fumes become troublesome.

There were 13 episodes of skin and eye burns listed on the OSHA-200 (Inquiry/Illness Log) for 1980. Most of these appeared to result from HF exposures.

Medical records were reviewed for the individual noting allergic symptoms. He was also interviewed by telephone. Symptoms apparently started in the fall of 1979, while he he was working in the FCCU-1291 area. Symptoms included stuffy nose, swelling of the

backs of his hands and feet, and bumps on his arm -- believed by him to be urticaria (hives). These symptoms occurred intermittently, with questionable response to antihistamines. Results of scratch and patch tests, using the light catalytic gas oil and carbon black feedstock, were negative. The swelling persisted, and by the spring of 1980, he noted tingling of the tongue. When he moved to AU-491 unit in June 1980, he also noted tongue and lip swelling, as well as some wheezing. He further stated that he had not had such symptoms before, that he had them only at work, and that they resolved upon leaving work.

No physician had reported having observed these symptoms; however, several of the workers interviewed observed this individual when he was having his reaction. Symptoms and signs described by these workers included tongue swelling (it looked like "a piece of meat"), hand and facial swelling, and hives. An IgE level performed in September 1980 was within normal limits. A complete blood count, performed by an independent laboratory in July 1980, had an eosinophil count of 539 per cubic millimeter, which is above the listed normal upper limit of 424 per cubic millimeter.

Accurate diagnosis of occupational allergy requires determination of the offending allergen. In most cases where the suspected allergen is a chemical, skin and scratch testing is very unreliable, and an inhalation study would generally be required. Given this individual's history, as corroborated by his fellow workers, and considering the elevated eosinophil count, a diagnosis of occupational allergy would be highly probable in this instance -- making inhalation studies a logical next step for definitive diagnosis. Unfortunately, there in no easy, quick way of identifying the allergen, since a great many substances at both AU-491 and FCCU-1291 might be capable of causing allergy.[5]

Two other workers interviewed during the NIOSH evaluation reported urticaria. In one case, the reaction occurred only at home; in the other, the reaction occurred only once and had no time relation to working. Thus, in neither instance did the allergy seem occupationally related.

VII. CONCLUSIONS

A. Enviromental

Results of Gulf Oil Corporation's environmental monitoring program for phenol and HF were well below applicable NIOSH recommended exposure limits and OSHA standards. An adequate on-going monitoring program is currently in effect for all chemicals/compounds currently used/produced in the refinery work environment.

B. Medical

Exposure to chemicals at FCCU-1291 and AU-499 appears relatively small and restricted to occasional episodes. One employee, who has not worked at the refinery since July 1980, has probably developed an occupational allergy to a substance in the workplace.

In conclusion, and based on the findings obtained during the preliminary investigation, it is felt that the need for further NIOSH environmental/medical evaluation does not exist.

VIII. RECOMMENDATIONS

1. An audible alarm system should be installed to alert employees in AU-491 and FCCU-1291 when protective measures should be taken as the result of an unplanned release of HF.

2. Adequate personal protective equipment should be made available to employees in AU-491 and FCCU-1291 to facilitate protection from HF.

3. An employee training program should be provided to include the following: (a) identify hazards from HF exposure; (b) procedures to be taken during an accidental release of HF, and (c) identify available personal protective equipment, and provide full instructions on its use and maintenance.

4. An agressive program by management should ensure that required personal protective equipment is used, and established procedures followed when HF leaks occur.

IX. REFERENCES

1. National Institute for Occupational Safety and Health, U.S. Department of Health, Education and Welfare: Criteria for a Recommended Standard.....Occupational Exposure to Phenol, Publication No. 76-196, U.S. Government Printing Office, Washington, D.C., 1976.

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4. American Conference of Governmental Industrial Hygienists: Hydrogen Fluoride as HF, Documentation of TLV's for Substances in Workroom Air. 3rd Edition (1976) p. 131, Cincinnati, Ohio.

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X. AUTHORISHIP AND ACKNOWLEDGEMENTS

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XI. DISTRIBUTION AND AVAILABILITY OF REPORT

Copies of this report are currently available upon request from NIOSH, Division of Standards Development and Technology Transfer, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days, the report will be available through the National Technical Information Service (NTIS), 5285 Port Royal, Springfield, Virginia 22161. Information regarding its availability through NTIS can be obtained from NIOSH Publications Office at the Cincinnati address. Copies of this report have been sent to:

1. Gulf Oil Corporation, Alliance Refinery
2. Authorized Representative of Employees
3. NIOSH, Region VI
4. OSHA, Region VI
5. Louisiana State Department of Health

For the purpose of informing the approximately twenty-four (24) affected employees, a copy 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 1

Results of Questionnaire

Gulf Oil Corporation
Alliance Refinery
Belle Chasse, Louisiana

January 1981

	Unit 1291 (11 Workers)	Unit 491 (13 Workers)
Mean age (years)	33	32
Mean seniority (years)	9	7
Smoking	3 (27%)	5 (38%)
History of allergies	1 (11%)	5 (42%)
Eye irritation (occasional)	10 (91%)	10 (77%)
Nasal irritation (occasional)	5 (45%)	3 (23%)
Cough (occasional)	1 (9%)	2 (15%)
Percent of time spent outside	60%	60%

[1] Nine (9) workers on Unit 1291 and twelve (12) workers on Unit 491 responded to this question. The difference is not statistically significant.

Appendix A

GULF SCIENCE AND TECHNOLOGY COMPANY
INDUSTRIAL HYGIENE LABORATORY

1. COMPOUND

Airborne Acid Fume

2. PROCEDURE

Sampling frequency - once each year, four shifts during a consecutive 48 hour period; both shifts (12 hours) are monitored; both personal and area samples are collected.

3. PRINCIPLE

Airborne acid fume (HF, HNO_3, H_2SO_4 and HCl) is determined by collection of the fume in a solid sorbent tube containing granular sodium acetate. The sample is analyzed by placing the sorbent in a 100-ml beaker, dissolving in water and analyzing by an appropriate technique (ion-selective electrode).

4. PROCEDURE

In the case of HF, the sample is dissolved in 25 ml H_2O. A 10-ml aliquot of sample solution is added to 10 ml of TISAB solution. The resulting solution is stirred with a magnetic stirrer. The fluoride ion-selective electrode is inserted into the solution and the mV reading is obtained. This reading is compared to a previously-prepared calibration curve (mV vs concentration). The concentration of fluoride is determined from the curve.

APPENDIX A

GULF SCIENCE AND TECHNOLOGY COMPANY
INDUSTRIAL HYUGIENE LABORATORY

1. COMPOUND

Phenol

2. PROCEDURE

No "routine" phenol monitoring is conducted at the Alliance Refinery. There is no phenol as a product or intermediate. Should phenol be present, it is strictly in low-level impurity type quantities.

3. PRINCIPLE

Airborne phenol concentrations are determined by the collection of phenol in 0.1 N NaOH. acidification with perchloric acid and extraction of the phenol with isopropyl ether. The isopropyl ether layer is analyzed for phenol by gas chromatography. The TLV for phenol is 19 mg/m^3 (or 5 ppm).

4. APPARATUS

1. Gas chromatograph equipped with flame ionization detection.
2. Gas Chromatographic Column: 13.5% DC 550 on Gas Chrom C 80/100), 10 ft. by 1/8 in.
3. Volumetric flasks, 25 ml, with glass stoppers, one per sample.
4. Volumetric flasks, 100 ml, with glass stoppers, three for the phenol standards.
5. Pipets, volumetric, two 1-ml, two 2-ml, one 3-ml, and two 10-ml and 15-ml pipets for the samples.

5. REAGENTS

1. Hydrochloric Acid, sp. gr. 1.64.
2. Isopropyl Ether, reagent grade.
3. Phenol, p = 1.072 g/ml, white loose crystals, reagent grade, MW 94.11.

4. Stock standard A, S-A, 10.72 mg/m. Pipet 1 ml of phenol into a 100-ml volumetric flask and dilute to the mark with 0.1 N NaOH.

5. Stock Standard B, S-B, 1.072 mg/ml. Pipet 10 ml of S-A into a 100 ml volumetric flask and dilute to the mark with 0.1 N NaOH.

6. Stock Standard C, S-C, 0.107 mg/ml. Pipet 10 ml of S-B into a 100-ml volumetric flask and dilute to the mark with 0.1 N NaOH.

7. Working Standards. Prepare three working standards in 25-ml volumetric flasks from S-C according to the following table:

No.	Vol. of S-C (ml)	Phenol (mg)	Vol. 0.1 N NaOH (l)
S-1	1	0.107	14
S-2	2	0.214	13
S-3	3	0.321	12

Standardization

Acidify the three working standards, S-1, S-2, and S-3 with 2 ml of HCl, 70 percent, immediately pipet 5 ml of isopropyl ether into each of the 25-ml volumetric flasks, and stopper.

Extract the phenol by shaking the flasks vigorously for one to two minutes.

Allow the phases to separate and add sufficient distilled water to bring the ether layer up into the neck of the flask and stopper tightly.

Analyze the ether layer by gas chromatography using the following chromatographic conditions:

1. Dual FID

2. Column: 13.5% DC 550 on 80/100 Gas Chrom C (10 ft. by 1/8 in.)

3. Temperature Program: initial temperature 130°C; hold for 2 min. increase temperature at 8°/min. up to 170°C; hold at 170°C.

4. Injection Port Temperature: 200°C

5. Detector Temperature: 300°C

6. Carrier Gas Flowrater: 50 ml He/min. at 60 psi

7. Observed Elution Time: 270 sec.

Prepare a calibration curve by plotting peak area (or peak height) vs total mg of phenol.

Sample Analysis

Pipet 15 ml of each sample into numbered 25-ml volumetric flasks. Add 2 ml of concentrated HCl to each to acidify the samples and to each flask add 5 ml of isopropyl ether. Extract the phenol into the ether layer by vigorously shaking the flasks. Allow the layers to separate, add sufficient distilled water to bring the ether layer up into the neck of the flask and stopper tightly.

Analyze the ether layer of each sample by gas chromatography using the chromatographic conditions described for the standards.

6. CALCULATIONS

Plot peak area (or peak height) vs total phenol content (in mg). Draw the best straight line through the data points and derive an equation of the form $y + mx + b$.

From the observed peak areas (y) for each of the samples, calculate the total phenol content (x) for each sample and report as mg of phenol.

$$X = (y - b)/m$$

or
Total mg Phenol = (peak area - y-intercept)/slope of calibration curve

7. REFERENCES

1. R.J. Sherwood and F.W.G. Carter, Ann. of Occup. Hygiene, April 1970.

2. Determination of Phenol and Cresol in Urine, Analytical Method, Environmental Health Laboratory, United States Steel Corp. Monroeville, Pa. August 1976.