FINAL REPORT:
SPECIAL ANALYTICAL MEASUREMENTS
AND SHORT-TERM METHOD DEVELOPMENT

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The development of gas and high performance liquid chromatographic sampling and analytical procedures for methyl-isocyanate (624839), ethyl-isocyanate (109900), n-propyl-isocyanate (110781), isopropyl-isocyanate (1795488), n-butyl-isocyanate (111364), tertiary-butyl-isocyanate (1609865), cyclohexyl-isocyanate (3173533), caprolactam (105602), dimethylterephthalate (120616), bisphenol-A (80057), the diglycidyl ether of bisphenol A, polynuclear aromatic hydrocarbon compounds such as fluoranthene (206440), pyrene (129000), benz(a)anthracene (56553), benzo(a)pyrene (50328), benzo(e)pyrene (192972), chrysene (218019), benz(o)phenanthrene, and dibenz(a,h)anthracene (53703) are described. A selective ion electrometry method was developed for the analysis of fluoroboric-acid (16872110). The authors note that alkaline treated cellulose pads can be used for the collection of gaseous fluoroboric acid.

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ABSTRACT

This report summarizes analyses and analytical method development work accomplished by UBTL Division, University of Utah Research Institute, for the National Institute for Occupational Safety and Health under Contract Number 210-78-0087. This work was completed during the period September 28, 1978 - May 30, 1980.

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INTRODUCTION

On December 29, 1970, the Williams-Steiger Occupational Safety and Health Act (PL 91-596) became Federal Law. The primary purpose of this legislation is to assure safe and healthful working conditions for the labor force of the United States. Under the provisions of the law, the National Institute for Occupational Safety and Health (NIOSH) was established within the Department of Health, Education and Welfare and the Occupational Safety and Health Administration (OSHA) was organized in the Department of Labor (1). In connection with this legislation, both NIOSH and OSHA have been involved with programs designed to protect workers from deleterious effects of exposure to toxic materials. For example, since passage of the Act, OSHA has published in the Federal Register exposure standards for approximately 600 substances, and NIOSH regularly publishes a Toxic Substances List which provides toxicity data relevant to thousands of different types of materials. There were ~16,500 different chemical substances listed in the 1975 edition of this publication. Evaluations of compliance to the promulgated OSHA standards as well as assessments and research of potential hazards associated with exposure to agents for which there are no current standards requires reliable sampling and analytical procedures. NIOSH has established important programs designed to provide such procedures and to improve methodology which is currently in use. The contributions of NIOSH in this research field have been extraordinary during the past few years. However, exposure to agents for which sampling and analytical procedures are inadequate occurs on a regular basis. Quantitative measurement demands associated with such occurrences frequently arise in emergency situations requiring immediate action. Accordingly, NIOSH has required additional resources which can provide non-routine analysis (in support of increasing demands) of special samples as well as capability for quick response methods development. As a result, NIOSH established a contract agreement with the UBTL Division of the University of Utah Research Institute, to provide special analyses and short-term development of analytical methods. This document briefly summarizes the work accomplished under this contract agreement. The contract (210-78-0087) extended from September 28, 1978, to May 30, 1980.

ANALYSES

During the course of the project, a total of 249 samples were analyzed, representing 626 analyses. Of the samples analyzed, 142 were submitted from NIOSH field operations, and 107 were generated at UBTL for quality assurance purposes or research activities. Concerning the number of analyses, 364 analyses were accomplished for actual field samples and 262 were completed to support quality assurance and research. Table 1 provides a summary of these data.

Table 1. Summary of analytical work.

	Field Samples	Quality Assurance or Research	Total
Number of Samples	142	107	249
Number of Analyses	364	262	626

Compiled in Table 2 is detailed information relative to the specific substances (analytes) which were addressed by the analytical work as well as the types of samples and the methods involved.

Table 2. Summary of specific information related to analyses.

Sample Set	Analyte(s)	Number of Field Samples	Number of Analyses (Field samples)	Number of Support Samples	Number of Support Analyses	Sample Type	Analytical Method
1	Aromatic Hydrocarbons; MIBK	4	40	4	40	Charcoal Tube	GC
2	Aromatic Hydrocarbons; MIBK; Butyl Acetate; Cyclohexane	4	60	4	60	Charcoal Tube	GC/MS
3	Dimethylterephthalate	11	11	5	10	Filter (Glass Fiber)	GC
4	Caprolactam	13	13	5	10	Filter (Glass Fiber)	GC
5	Bisphenol A (BA); Diglycidyl Ether of Bisphenol A (DEB)	4	8	25	50	Bulk	HPLC
6	Particulate Weight; BA; DEB	14	42	10	10	Filter (PVC)	HPLC
7	Particulate Weight; BA; DEB	12	36	5	5	Filter (PVC)	HPLC
8	BA; DEB	14	28	14	28	Filter (Glass Fiber)	HPLC
9	Cyclohexane Solubles; Polynuclear Aromatic Hydrocarbons (PNA) (Eight Specific PNA Compounds)	2	18	0	0	Bulk	Extraction; HPLC

(Continued)

Table 2. Summary of specific information related to analyses (continued).

Sample Set	Analyte(s)	Number of Field Samples	Number of Analyses (Field samples)	Number of Support Samples	Number of Support Analyses	Sample Type	Analytical Method
10	Cyclohexane Solubles; Benzo(a)pyrene	9	18	0	0	Filter (Glass Fiber)	Extraction; HPLC
11	Benzo(a)pyrene	4	4	5	5	Extract	HPLC
12	Caprolactam	12	12	6	6	Bulk; Hydrolysis Aliquot	GC
13	Lindane; Mirex	17	34	6	12	Extract	GC
14	Quinone; Hydroquinone	18	36	8	16	Porous Polymer Tube	HPLC
15	Triethylene Glycol Diacrylate	4	4	10	10	Wipe; Bulk	HPLC
	Total	142	364	107	262		

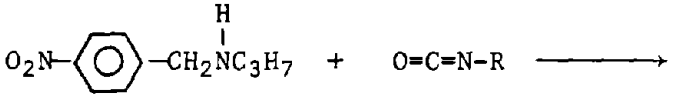
Abbreviations: MIBK - Methyl Isobutyl Ketone; GC - Gas Chromatography; MS - Mass Spectrometry; HPLC - High Performance Liquid Chromatography; BA - Bisphenol A; DEB - Diglycidyl Ether of Bisphenol A; PNA - Polynuclear Aromatic Hydrocarbon

METHOD DEVELOPMENT

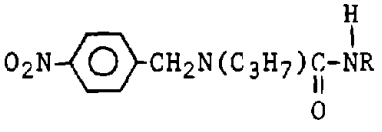
A majority of the effort expended in connection with this contract project involved attempts at developing sampling and analytical procedures. Methodology for each of the following was addressed: alkyl isocyanates (methyl isocyanate, ethyl isocyanate, n-propyl isocyanate, isopropyl isocyanate, n-butyl isocyanate, tertiary butyl isocyanate, and cyclohexyl isocyanate) by high performance liquid chromatography (HPLC); dimethylterephthalate by gas chromatography (GC); caprolactam by GC; bisphenol A by HPLC; the diglycidyl ether of bisphenol A by HPLC; polynuclear aromatic hydrocarbon (PNA) compounds (fluoranthene, pyrene, benz(a)anthracene, benzo(a)pyrene, benzo(e)pyrene, chrysene, benz(c)phenanthrene, dibenz(a,h)anthracene) by various chromatographic procedures including HPLC; and fluoroboric acid by selective ion electrometry. A brief summary of the results of each method development project follows:

ALKYL ISOCYANATES

The proposed approach for the collection and analysis of air samples containing alkyl isocyanates involved the formation of isocyanate-urea derivatives and the isolation and quantitation of the derivatives by HPLC. Samples are collected in impingers containing N-4-nitrobenzyl-N-n-propylamine (nitro reagent). Each alkyl isocyanate collected in the impinger reacts with the nitro reagent to form the corresponding urea derivative as follows:



(Nitro Reagent) (Alkyl Isocyanate)



(Urea Derivative)

R = alkyl group

In view of this proposed approach, the first part of this study was directed to the synthesis and characterization of the urea derivatives of each of the isocyanates listed in Table 3 which follows.

Table 3. Alkyl isocyanates

Methyl isocyanate
Ethyl isocyanate
n-Propyl isocyanate
Isopropyl isocyanate
n-Butyl isocyanate
t-Butyl isocyanate
Cyclohexyl isocyanate

Experimental Procedures

The synthesis of the alkyl isocyanate-urea derivatives in this study was based on the method of Vogt *et al.* (2) as originally applied to the synthesis of the urea derivative of 1,6-hexane diisocyanate. N-4-nitrobenzyl-N-n-propylamine, the nitro reagent (NR) used in this reaction, is available as the amine hydrochloride. Synthesis of isocyanate-urea derivatives required extraction of NR as the free amine followed by the direct reaction of this free amine in solution with the appropriate isocyanate. The urea derivatives of alkyl isocyanates were obtained as white amorphous solids. A typical preparation (that of the isopropyl isocyanate derivative) is described in detail in the following. The other derivatives were prepared in a similar manner.

To a 125-ml separatory funnel was added 0.150 g of nitro reagent (NR) (0.633 mmoles), 15 ml distilled water, and 9 ml 1 N sodium hydroxide solution. This mixture was shaken to release the amine, then extracted twice with 15 ml portions of benzene. The combined benzene extracts were dried over magnesium sulfate and the magnesium sulfate removed by filtration through a sintered glass filter funnel. A stoppered flask was used to wiegh 0.0490 g ($\sim$ 0.057 ml) isopropyl isocyanate (0.576 mmoles). Following weighing and as quickly as possible, 10 ml of acetone was added to the isocyanate; then the nitro reagent solution was also added. The mixture was allowed to stand for 15-30 minutes. The solvents were removed using a rotary evaporation apparatus and a water bath at 37°C. A white precipitate formed as the solvents were evaporated. The flask was cooled in an ice-water bath and 5 ml of hexane were added. The white precipitate was collected on a filter, rinsed with an additional 5 ml of chilled hexane, and dried under vacuum at room temperature.

With respect to the procedures detailed in the preceding, the following observations are noteworthy: (1) It is possible to extract a large quantity of nitro reagent for use in several different reactions. (2) The alkyl isocyanates are volatile and accurate weighing requires the use of a stoppered flask.

Following the synthesis of approximately 100 mg of each urea derivative, each compound was characterized by the determination of the melting point and by infrared (IR) spectroscopy. IR spectra were obtained on a Beckman Model IR 20-A used in the fast scan mode: 1200 cm^{-1}/min. Potassium bromide pellets were prepared with 1 mg of compound of interest per 200 mg potassium bromide.

Results

The melting points for each of the urea derivatives prepared in this study are summarized in Table 4.

Table 4. Melting points of urea derivatives of alkyl isocyanates.

Compound	Melting Point, °C	
	Run 1	Run 2
Methyl NCO Urea	138-140	139-140
Ethyl NCO Urea	139-140	139-140
n-Propyl NCO Urea	125-127	125-126
i-Propyl NCO Urea	141-142	140-141
n-Butyl NCO Urea	120-121	121-122
t-Butyl NCO Urea	114-115	115-116
Cyclohexyl NCO Urea	112-113	113-114

Discussion

The melting point range observed for each alkyl isocyanate-urea derivative was sufficiently narrow to indicate that the purity of each derivative was acceptable. Appropriate literature values with which these melting point data may be compared are not available. Similarly, there are apparently no IR spectra published in the literature for comparison with the observed spectral data. It is important to note, however, that the large band (at approximately 2275 cm^{-1}), which is characteristic of isocyanate spectra, was not observed in the IR spectra of the urea derivatives. This indicates that the derivatization reaction proceeded as anticipated in each case.

High Performance Liquid Chromatography

Experiments were conducted to elucidate HPLC operating conditions with which the urea derivatives of the seven alkyl isocyanates listed in Table 3 could be resolved and identified. Such conditions were successfully determined in this study. These conditions comprise the essential components of an HPLC methodology for the determination of alkyl isocyanates. Accordingly, the potential of the method for quantitation of each alkyl isocyanate-urea derivative appears to be excellent. Data pertinent to this possibility (such as sensitivity and linearity of response) were not addressed in this study.

The liquid chromatography was accomplished using a Waters Model 660 solvent programmer with two Waters Model 6000A pumps, a Varian Vari-Chrom variable wavelength detector set at 254 nm and a Whatman Partisil PXS 10/25 column (Column No. 1B-1545).

A test mixture of the urea derivatives of the seven alkyl isocyanates of interest was prepared in dichloromethane. The concentrations were as follows: MeNCO-Urea, 112 ng/µl; EtNCO-Urea, 112 ng/µl; n-PrNCO-Urea, 87 ng/µl; n-BuNCO-Urea, 120 ng/µl; t-BuNCO-Urea, 92 ng/µl; and Cyclohexyl NCO-Urea, 87 ng/µl.

Two HPLC elution systems were evaluated. The first system was that of Vogt *et al*. (2). The most favorable HPLC conditions achieved in this study were

as follows: Gradient Program #10 (most concave); 20% B ——→ 100% B in ten minutes at 2 ml/min, solvent A = 100% dichloromethane, solvent B = 9.1% isopropanol in dichloromethane. The second solvent system investigated was hexane/isopropanol. After several experiments, optimal HPLC operating conditions were identified as follows: Gradient Program #10 (most concave); 10% B ——→ 100% B in 15 minutes at 2 ml/min; solvent A = 100% hexane, solvent B = 100% isopropanol.

Results

Only six of the urea derivatives could be resolved with the first HPLC system and it was considered unsatisfactory. Use of the second system resulted in resolution of each of the seven derivatives of interest, although baseline resolution of the n-butyl, isopropyl, and n-propyl compounds was not achieved. Repeated experimental runs involving several different systems did not produce better separation of the compounds than that obtained with the second system described in the preceding. Retention times observed with the application of the second solvent system are tabulated in Table 5.

Table 5. HPLC retention times for urea-derivatives of alkyl isocyanates.

Alkyl Isocyanate	Retention Time (Minutes)
t-Butyl	4.57
Cyclohexyl	5.59
n-Butyl	8.07
i-Propyl	8.66
n-Propyl	9.53
Ethyl	12.13
Methyl	14.17

It was discovered that the nitro reagent does not elute from the column with the second HPLC system tested, nor does it elute after the application of either dichloromethane or methanol. This observation merits further study because of the importance of separating the nitro reagent from the various analyte components in a chromatographic run of field samples.

The second solvent system offers an acceptable HPLC approach for the analysis of specific alkyl isocyanates collected in nitro reagent and thereby converted to the corresponding urea derivatives. The specific urea compounds separated by this method are those derived from methyl isocyanate, ethyl isocyanate, n-propyl isocyanate, isopropyl isocyanate, n-butyl isocyanate, tertiary butyl isocyanate, and cyclohexyl isocyanate.

CAPROLACTAM

A gas chromatographic method was developed for the analysis of caprolactam collected as particulate on glass fiber filters (Gelman Type A-E or equivalent). Details of the method are provided in the following.

A known volume of air is drawn through a 37-mm glass fiber filter to trap particulate matter containing caprolactam. The glass fiber filter is transferred to a 2-dram vial and extracted with 5 ml dichloromethane. Each vial is tightly capped and placed in an ultrasonic bath for thirty

(30) minutes. An aliquot of the extract is injected into a gas chromatograph. Typical operating conditions for the gas chromatograph are as follows: stainless steel column, 12' x 1/8", packed with 20% SP-2100/0.1% Carbowax 1500 on 100/120 Supelcoport or equivalent; flame ionization detector; helium carrier gas flow: 50 ml/min.; hydrogen gas flow to the detector: 50 ml/min.; air flow to the detector: 200 ml/min.; injector temperature: 200°C; detector temperature: 250°C; programmed oven temperature: 185°C for two minutes, increased to 230°C at the rate of 4°/minute, returned immediately to initial temperature upon reaching 230°C. The area of the caprolactam peak is determined and compared with areas obtained from the injection of solutions of standards. The lower limit of detection is 0.5 mg/sample; the upper limit of the method is 50 mg/sample.

DIMETHYLTEREPHTHALATE

A gas chromatographic method was developed for the analysis of dimethylterephthalate collected as particulate on glass fiber filters (Gelman Type A-E or equivalent). Details of the method are provided in the following.

A known volume of air is drawn through a 37-mm glass fiber filter to trap particulate matter containing dimethylterephthalate. The glass fiber filter is transferred to a 2-dram vial and extracted with 5 ml of dichloromethane. Each vial is tightly capped and placed in an ultrasonic bath for thirty (30) minutes. An aliquot of the extract is injected into a gas chromatograph. Typical operating conditions for the gas chromatograph are as follows: stainless steel column, 12' x 1/8", packed with 20% SP-2100/0.1% Carbowax 1500 on 100/120 Supelcoport or equivalent; flame ionization detector; helium carrier gas flow: 50 ml/min.; hydrogen gas flow to detector: 50 ml/min.; air flow to detector: 200 ml/min.; injector temperature: 200°C; detector temperature: 250°C; programmed oven temperature: 185°C for 2 minutes, increased to 230°C at the rate of 4°/minute, returned immediately to initial conditions upon reaching 230°C. The area of the dimethylterephthalate peak is determined and compared with areas obtained from the injection of solutions of standards. The lower limit of detection is 0.1 mg per sample; the upper limit of the method is 50 mg/sample.

BISPHENOL A AND THE DIGLYCIDYL ETHER OF BISPHENOL A

Sampling and analytical methods were successfully developed for the determination of airborne concentrations of bisphenol A (BA) and its diglycidyl ether (DEB). The approach for the determination of each of these compounds is similar. Therefore, a combined summary is provided in this section.

A known volume of air is drawn through a glass fiber filter (Gelman Type A or equivalent) to collect BA or DEB as particulate from the air. The exposed filter is transferred to a capped tube and extracted with 2 ml of acetonitrile. A 50-µl aliquot of the extract is injected into a high performance liquid chromatograph (HPLC). Chromatographic conditions are as follows: column - prepacked µBondapak C_{18}, 0.63 cm i.d. by 30 cm long, Waters Associates or equivalent; linear gradient elution from 100% Solvent A to 100% Solvent B over a thirty minute period. Solvent A is 60%

acetonitrile, 40% water (v/v), Solvent B is 100% acetonitrile; solvent flow rate - 1.0 ml/min.; detection - UV absorbance at 230 nm, 0.02 AUFS sensitivity. Peak areas are determined for each analyte on each sample and compared with calibration curves derived from peak areas obtained from injections of standard solutions. The detection limits for the determination of BA and DEB are 0.4 µg/filter and 0.6 µg/filter, respectively. These limits were determined using a 2-ml acetonitrile extraction volume and a 50-µl aliquot for injection into the HPLC. The working range for each analyte is as follows: 0.4-511 µg bisphenol A per sample; 0.6-513 µg DEB per sample. Samples with levels greater than 511 µg bisphenol A or 513 µg DEB can be analyzed by increasing the volume of the extraction solvent or by decreasing the sensitivity setting of the HPLC detector or the quantity of the aliquot injected into the HPLC. The coefficient of variation for the analytical method is as follows: for bisphenol A in the range 127-511 µg/filter - 1.8%; for DEB in the range 127-513 µg/filter - 2.7%. Recoveries for bisphenol A and DEB were 99.5% and 99.3%, respectively, based on eighteen fortified glass fiber filters, six replicates at each of three loading levels: ∿ 125 µg, ∿ 250 µg, and ∿ 500 µg. The efficiency for the collection of bisphenol A or DEB as particulate by the glass fiber filter was not determined.

POLYNUCLEAR AROMATIC HYDROCARBONS

Several experiments were conducted in an attempt to develop a convenient method for the analysis of selected polynuclear aromatic hydrocarbon (PNA) compounds in petroleum base asphalt pitch. The PNA compounds of interest were: fluoranthene, pyrene, benz(a)anthracene, benzo(a)pyrene, benzo(e)pyrene, chrysene, benz(c)phenanthrene, and dibenz(a,h)anthracene. The specific experimental approaches investigated were designed to eliminate interferences prior to identification and quantitation of specific PNA compounds by high performance liquid chromatography (HPLC). None of the methods investigated were entirely successful.

The intent of this report is to provide only a brief description of the work which was accomplished and the conclusions derived from the study.

The objective of each of several experiments is outlined in the following along with procedural details and conclusions. Unless otherwise indicated, a cyclohexane extract of bulk asphalt pitch was the initial sample in each case.

Experiment 1: Florisil Column Chromatography

Objective--
The purpose of this experiment was to investigate the use of Florisil in open column chromatography with various eluting solvents as a means of removing the interference encountered in the reverse phase HPLC analysis of petroleum asphalt pitch bulk samples for PNA compounds. Specifically, the recovery of PNA from the Florisil column using a standard solution of benzo(a)pyrene and fluoranthene in cyclohexane was investigated.

Procedure--
Eight columns were prepared (14 cm x 1.6 cm) with a layer of Na_2SO_4 both preceding and following 8 ml of dry Florisil. The following procedures were employed: 1) application of standard solution; 2) pentane wash; 3) elution with one solvent: iso-octane, ethyl ether, carbon disulfide, toluene, acetonitrile, methanol, nitromethane or ethyl acetate; 4) analysis of the collected eluant for each PNA by reversed phase HPLC and estimation of percent recovery.

Samples were analyzed by reversed-phase high pressure liquid chromatography, utilizing a Waters Associates HPLC System equipped with a Vydac 201 TP column. Analytical procedures involved application of a methanol/water solvent gradient. The UV detector monitors the sample at 365 nm and 280 nm simultaneously, which aids in compound identification. Detection by fluorescence was also utilized.

Retention times of specific peaks in the chromatograms derived from the samples were compared with those of known standard compounds for analyte identification. Peak areas of several concentrations of each compound of interest were measured and standard curves were constructed. Quantitative data were obtained by a comparison of the peak areas in the chromatograms of the samples with the standard curves.

Results and Discussion--
Methanol and ethyl acetate yielded the best recoveries. Acetonitrile did not elute fluoranthene well (very poor recovery); the recovery for fluoranthene in toluene was also low.

Conclusion--
The PNA compounds tested can be recovered from Florisil columns by elution with methanol or ethyl acetate. The highest recovery was estimated to be $\sim$ 80% (ethyl acetate).

Experiment 2: Florisil Column Chromatography

Objective--
The purpose of this experiment was to continue the Florisil column investigation by repeating Experiment #1 using a solution of the petroleum asphalt pitch bulk fortified with benzo(a)pyrene and fluoranthene to determine if the interference in the HPLC analysis is removed.

Procedure--
The procedure for this experiment was the same as that for Experiment #1 except for the presence of the asphalt bulk.

Results and Discussion--
The interference was present in all cases where the recovery for the PNA compounds was acceptable. In addition, the interference appeared to carry over from one sample to the next in the HPLC analysis unless the column was flushed with 100% methanol after each sample. The chromatograms for this experiment were recorded with an attenuation five times larger than that used for succeeding experiments. The concentration of bulk in the final

solutions was, at most, about one-third of that normally present in a routine analysis.

Conclusion--
The interference is not separated from the PNA compounds of interest by Florisil. This implies that the interference has similar polarity to that of the PNA's.

Experiment 3: Solvent Extraction and Gel Permeation Chromatography

Objective--
The purpose of this experiment was to investigate the separation of PNA's from the interference by 1) extraction into a solvent after deposition of dissolved sample material onto the inside surface of a screw-cap tube by evaporation and 2) open column gel permeation chromatography (GPC).

Procedure--
Two types of GPC column packings were used: Biobeads SX-2 for use with nonpolar solvents, and Sephadex LH-20 for use with polar solvents. Eight solvents or solvent mixtures were investigated in the extraction step using standard BaP/fluoranthene solutions. Four of these (ethyl acetate, nitromethane, 1:1 methanol-toluene, 1:1 acetonitrile-toluene) were not considered useful because of unsatisfactory HPLC results (e.g., poorly resolved or broadened peaks or solvent interference). The remaining solvents were used to extract, apply, and elute bulk samples fortified with BaP and fluoranthene using the appropriate GPC column. Toluene and tetrahydrofuran (THF) were used with Biobeads; methanol and acetonitrile were used with Sephadex. An ultraviolet (UV) light was used to determine the time of elution of the PNA compounds. Several eluant fractions (cuts) were collected from the eluant from each of the four columns. Each fraction was analyzed by HPLC.

Results and Discussion--
Some separation of the interference from the PNA peaks was apparent. However, the interference was not eliminated. The results for toluene were best, followed by those for acetonitrile. Part of the bulk appeared to elute earlier than the PNA's. This is consistent with the fact that PNA's are not only separated by size on GPC columns but also interact with the columns, possibly by adsorption. The amount of bulk present in the final solutions was at most, about one-tenth in the best toluene fraction and about one-thirtieth in the best acetonitrile fraction of that normally present in a routine HPLC analysis.

Conclusion--
The amount of interference appeared to be reduced by the GPC separation, but by no means was eliminated. The solubility and size characteristics of PNA and interfering compounds appear to be similar.

Experiment 4: Gel Permeation Chromatography

Objective--
The objective of this experiment was to repeat Experiment #3 using improved techniques and to reinvestigate (in detail) the use of toluene with Biobeads SX-2 and acetonitrile with Sephadex LH-20. The effect of using a longer column was also addressed.

Procedure--
Bulk samples dissolved in a small amount of solvent and fortified with BaP and fluoranthene were applied to each of 4 columns: 16cm x 8mm and 26cm x 8mm Biobead columns; 11cm x 8mm, and 28cm x 8mm Sephadex columns. The sample prepared in acetonitrile was processed by evaporating (with nitrogen) an aliquot of the original bulk sample dissolved in toluene, extracting the resulting dry film with acetonitrile (using sonication), then fortifying with benzo(a)pyrene (BaP) and fluoranthene. The sample prepared in toluene was processed by first fortifying the toluene solution of the sample with the PNA compounds, then processing through the GPC column. Fractions were collected from all GPC columns, evaporated with nitrogen, then reconstituted with acetonitrile for final HPLC analyses. If bulk sample was present, the last step would be an extraction since much of the bulk sample is not soluble in acetonitrile.

Results and Discussion--
All fractions and standards were reconstituted to the same volume of acetonitrile so that direct comparisons could be made between quantities of PNA recovered and the amount of interference present. The fluoranthene recovery was poor in each case. The BaP recovery was better for toluene/Biobeads than for acetonitrile/Sephadex. The acetonitrile sample contained HPLC peaks approximately twice as large as those observed for toluene. This may be attributed, in part, to incomplete extraction of PNA by acetonitrile. Narrowing the fraction volumes in an attempt to exclude as much interference as possible resulted in PNA's occurring in other fractions. This indicates that the PNA band is wide and overlaps the interference band. The results for the longer columns showed that interference was not significantly reduced when the PNA bands were collected in different fractions. The concentration of bulk in the final solutions was, at most, about one-fourth that normally present in a routine analysis.

Conclusion--
Fluoranthene recovery from Biobead or Sephadex columns is poor. Acetonitrile did not extract the PNA's quantitatively from a thin layer of fortified petroleum asphalt bulk. Individual PNA's are separated from one another before the interference is reduced to an acceptable level when column length is increased. At least a significant fraction of the interference is similar to the PNA's with respect to molecular size and adsorption characteristics.

Experiment 5: High Performance Liquid Chromatography

Objective--
The purpose of this experiment was to separate the PNA compounds of interest from the interference using only HPLC techniques. Specifically, use of a high performance GPC column in series with the usual Vydac TP analytical column was investigated.

Procedure--
A Waters μPorasil GPC 60Å column was used alone and in series with (following) the Vydac column. Various gradient programs and solvent mixtures were investigated and results were compared in an attempt to identify a set of conditions yielding the best separation of PNA's of interest from the interference.

Results and Discussion--
Under the solvent conditions used for routine analysis, no significant improvement (attributable to the addition of the GPC column) was observed. The optimum conditions for separating the interference from the PNA's appeared to be obtained by using a linear gradient rather than an exponential one and starting with a higher percentage of methanol. These conditions broadened the PNA peaks; but at a final bulk concentration of about one-fifth that normally present in a routine PNA analysis by HPLC, the conditions appeared to shift the interference to a later retention time relative to the BaP peak. This result was obtained with the Vydac column alone as well as with the GPC column succeeding it.

When this experiment was repeated with a final concentration of bulk sample similar to that used in routine PNA analyses, it was determined that the conditions noted in the preceding do not solve the problem. The interference is simply broadened (as are the PNA peaks). However, at normal sample concentrations, the interference is still a recalcitrant problem.

Conclusion--
The HPLC manipulations did not succeed in removing the interference.

Experiment 6: Application of μC_{18} Sep-Paks

Objective--
The objective of this experiment was to remove the interference by retaining it on a μC_{18} Sep-Pak (Waters Associates), while eluting the PNA's with a suitable solvent. An investigation of the following possibility was also conducted: The interference is a long-retained peak in the HPLC analyses caused by precipitation of methanol/water insolubles on the head of the column upon injection of the sample.

Procedure--
A PNA-fortified bulk sample was dissolved in toluene and applied directly to a μC_{18} Sep-Pak. Methanol and water were added to the sample to precipitate dark material (but not so much as to cause immiscibility of the solvents) before applying to a Sep-Pak. Eluant was collected, evaporated to dryness, and reconstituted in methanol before analyzing by HPLC.

Results and Discussion--
The interference was not removed by use of the μC_{18} Sep-Pak. We concluded that the interference is not attributable to a solubility problem since all methanol-insolubles were removed by "filtering" with the Sep-Pak. Peaks apparently introduced by the Sep-Pak itself were seen in the HPLC chromatogram. The final bulk concentration was about one-fourth of that normally used in routine PNA analyses.

Conclusion--
The interference and PNA's have like solubilities in methanol and are too similar to separate with a μC_{18} Sep-Pak.

Experiment 7: Solvent-Solvent Partitioning

Objective--
The objective of this experiment was to separate the interference from the PNA's with a solvent-solvent partition, using carbon disulfide and acetonitrile.

Procedure--
A solution of the bulk asphalt sample (fortified with BaP and fluoranthene) in toluene (0.5 ml) was shaken with 5 ml CS_2 and 5 ml acetonitrile and allowed to settle repeatedly. An aliquot of each fraction (CS_2 and acetonitrile) was analyzed by HPLC.

Results and Discussion--
Both the interference and the PNA's partitioned into the CS_2 fraction; no separation was achieved.

Conclusion--
The observed result is not surprising since a solvent-solvent partition is only one theoretical plate and the interference is not separated from the PNA's by thousands of theoretical plates on the HPLC column.

Experiment 8: Additional Application of μC_{18} Sep-Paks

Objective--
The purpose of this investigation was to check the results obtained for μC_{18} Sep-Paks in Experiment #6 using a cyclohexane solution of fortified petroleum asphalt bulk at the concentration level used in routine HPLC analyses of PNA and with more control samples.

Procedure--
Methanol was added to the cyclohexane sample solution until a fine precipitate was observed. The mixture was eluted through a μC_{18} Sep-Pak. The eluant was evaporated to dryness and reconstituted in methanol before analysis by HPLC. A blank was prepared in a like manner.

Results and Discussion--
Results for the blank sample showed that μC_{18} Sep-Paks contribute foreign peaks to the HPLC chromatogram when used with the solvents studied. At the final concentration level used (approximately the same as for routine HPLC

analyses), it was evident that the interference was not significantly reduced by the Sep-Paks. These results (at high concentrations) cast doubt on some of the earlier hopeful conclusions that had been based on results from lower final concentrations of bulk sample.

Conclusion--
Conclusions derived from Experiment #6 were confirmed. Results based on final bulk concentrations lower than that used for routine analysis may lead to overly optimistic conclusions regarding the separation of the interference from PNA compounds of interest.

Experiment 9: Additional High Performance Liquid Chromatography

Objective--
In this experiment, an attempt was made to separate the interference into peaks and resolve such from those of PNA compounds of interest by increasing the resolving power in HPLC.

Procedure--
Two analytical columns were connected in series in an attempt to increase resolving power. In an additional experiment, a GPC 60 Å column was connected in series to the two analytical columns, the GPC column last in the series.

Results and Discussion--
Two columns in series resulted in somewhat better resolution (visible in chromatograms of standards). However, all three columns connected in series not only elevated the system pressure to $\sim$ 4000 psi, but also effected no increase in resolution (possibly due to limitations imposed by the dead volume of the connections). In any case, neither arrangement was able to resolve the interference from the PNA compounds of interest.

Conclusion--
The HPLC conditions applied do not have the capability to resolve the interference into peaks and to separate it from PNA compounds of interest.

General Conclusion

The information derived from these experiments coupled with the observations of other investigators as well as evidence compiled in the literature indicate that the interference is not a single type of compound sufficiently different from the PNA's of interest to be separated from them in a simple one or two step process. Rather, it is likely that the interference is comprised of many compounds very similar to the PNA analytes. It appears that several separation steps using several different techniques will be required to effect the required separation.

FLUOROBORIC ACID

The development of a sampling and analytical method for the determination of airborne concentrations of fluoroboric acid (HBF_4) was addressed. Sufficient time was not available to realize development of a successful method.

Several important experimental observations were obtained, however. A summary of the work accomplished follows.

Literature Review

A literature review was conducted via computerized data bases for the period 1972 to 1980. This computerized search was current through Volume 92 (Number 12) of Chemical Abstracts. The search strategy addressed both fluoroboric acid (HBF_4) and tetrafluoroborate ion (BF_4^-). It was restricted to scientific articles written in the English language. As a result of the literature review, several pertinent publications were found, the most useful summarizing methods for the analysis of fluoroborate ion by either specific ion electrometry or ion chromatography. The literature search was not confined to analytical methods; possible entries for applications, sampling, and properties of HBF_4 were also addressed by the computer. Interestingly, no publications were identified for sampling the acid or its conjugate base.

The direct potentiometric determination of tetrafluoroborate ion employing a liquid ion exchange membrane electrode has been reported by several investigators (3-9). Also of interest is the paper by Hill and Lash (10) which summarizes a method for the ion chromatographic determination of boron as tetrafluoroborate. In this methodology, borate is concentrated on Amberlite XE-243 ion exchange resin, converted to BF_4^- with 10% HF, eluted from the column with NaOH, and the tetrafluoroborate determined by ion chromatography. These publications provided the basis for the experimental work reported in the following.

Experimental Work

The experimental research conducted involved the use of specific ion electrometry. As noted previously, ion chromatography is a potentially promising technique for effecting the analysis of fluoroboric acid. This method was not investigated because required ion exchange resin was not available until shortly before the expiration date of the contract. An Orion Model 93-05 fluoroborate electrode and an Orion Model 90-02 double junction reference electrode with Orion 900002 filling solution in the inner chamber and 0.1 M ammonium fluoride in the outer chamber were used in the studies reported in the following.

Specific Ion Electrometry Calibration Curves--

A comparison of calibration curves over the concentration range 0.1 - 200 ppm BF_4^- prepared from stock solutions of the sodium and potassium salts was made. Stock solutions at a concentration of 1000 ppm of BF_4^- were prepared by weighing out 0.6324 g $NaBF_4$ and 0.7252 g KBF_4 (available from Alpha Inorganics), by dissolving each portion of weighed salt in approximately 50 ml of deionized water, filtering, transferring filtrates to 500-ml volumetric flasks, and diluting to volume with deionized water. Solutions were stored in polyethylene bottles and discarded after one week to avoid errors introduced by hydrolysis of tetrafluoroborate. The sodium salt was much more water soluble than the potassium salt. Working standards were prepared by appropriate dilutions of the stock solutions. For a decade change in BF_4^-

concentration, a slope averaging 54 millivolts at 22°C adjusted to 0.1 M NH_4F was typically observed using the sodium salt stock solution. This slope approximates Nernstian behavior (approximately 57 mv for 10-fold change in concentration). Therefore, the sodium salt was used to prepare stock and standard solutions used in these studies.

To assure a constant ionic strength background (ISA), 1 ml of 10 M NH_4F was added to each 100 ml of sample and standard for a final background concentration of 0.1 M NH_4F. It may be noted from the data in Table 6 that a change in the concentration of BF_4^- from 0 to 200 ppm did not appreciably affect the pH of the solution. This is indicative of the buffering effect of NH_4F.

Table 6. Effect of BF_4^- concentration on pH of solutions of constant ionic strength.

Standard Concentration (µg/ml BF_4^-)	pH
0	6.04
0.1	6.02
1.0	6.01
10	6.02
50	6.03
100	6.00
200	5.93

Recovery of BF_4^- from Alkaline-Treated Cellulose Pads--
One possible approach to the collection and analysis of airborne fluoroboric acid is to adapt the methodology of NIOSH procedure P&CAM 212, which addresses the analysis of gaseous and particulate fluorides collected, respectively, on a membrane filter and an alkaline-treated cellulose backup pad. This was investigated in the laboratory.

Cellulose pads were treated with alkaline fixative solution according to the procedures of NIOSH Method P&CAM 212. Six replicates at each of the following loading levels were prepared: 250 µg/pad; 500 µg/pad. Each pad was placed in 50 ml of deionized water and magnetically stirred to produce a pulp. After filtering the samples, adjusting the ionic strength of the filtrate with NH_4F and the solution pH to ~6 with HCl, and allowing the solution to equilibrate to room temperature, the analyst measured the sample potentials. Presented in Table 7 are the results of the fluoroborate recovery.

Eleven additional samples were prepared at a loading level of 500 µg. These samples were processed as described previously, excepting they were stored in a desiccator for one week prior to the initiation of analytical procedures. The results (also tabulated in Table 7) for these samples indicate that BF_4^- did not undergo hydrolysis on the pad during the one-week storage period. The high recoveries obtained in these studies are indicative that the alkaline-treated cellulose pads may be useful for sample collection. Collection efficiencies, however, have not yet been determined. Recovery

studies involving a longer storage period and the simulation of sampling conditions by placing test samples in sealed cassettes should be pursued as a continuation of the present study.

Table 7. Recovery of BF_4^- from alkaline-treated cellulose pads.

Loading Level (μg BF_4^-/pad)	Number of Replicates	Average Recovery (%)	Relative Standard Deviation (%)
250 (No Storage)	6	99	6.8
500 (No Storage)	6	102	4.6
500 (1-Week Storage)	11	109	7.1

Recovery of BF_4^- from Membrane Filters--
Membrane filters (Millipore Type AA; 37 mm) were fortified with known amounts of tetrafluoroborate ion. For analysis, each sample was placed in a nickel crucible and 0.5 g of equi-molar fused K_2CO_3 - Na_2CO_3 was added on top of the filter. Each filter was charred on a hotplate; then ashed in a fusion mixture. Each sample was transferred to a plastic beaker and the pH was adjusted to 5-6 with 1:1 HCl. Following the pH adjustment, 2.5 ml of 10 M NH_4F (ISA) was added and the sample volume adjusted to 50 ml with deionized water. Each sample was analyzed by specific ion electrode. No significant recovery of BF_4^- was observed for any of the fortified samples. The possible loss of BF_4^- during the ignition of the membrane filters was considered. To investigate this possibility, a known quantity of fluoroborate was added to each of several fusion mixtures. These preparations were treated as described previously for the ashed filters. Recovery for each fortified fusion mixture was less than ten percent. Therefore, the analytical method, as investigated for the filters, is not acceptable. Additional developmental work is required for the analysis of fluoroborate collected on membrane filters. For example, standards prepared on the carbonate fusion mixture and adjusted with NH_4F and 1:1 HCl should be prepared and processed concurrently with fortified samples. Note that aqueous standards were used in this recovery study without regard for matching matrices of standards and samples. However, several blanks were treated and analyzed for the fortified samples; their potential readings were comparable to those of the samples.

Other possible approaches to the determination of fluoroborate on membrane filters should be investigated.

Effect of pH on Electrode Potentials--
A study by Duhart (5) of the U.S. Environmental Protection Agency indicated little change in the BF_4^- specific ion electrode potentials over the pH range 3-10. We investigated the pH effects (pH range 2-10) on electrode potentials. In this study, ten replicate solutions at a concentration of 10 ppm BF_4^- were prepared. The fluoroborate potential and pH of each solution was recorded. The pH of each of various solutions was adjusted with the addition of 1:1 HCl or 0.1 M NaOH. The fluoroborate selective ion potential was determined following adjustment of the pH to a specific target value. The results summarized in Table 8 indicate that the pH range of stability is less than seven full pH units. At pH less than three and

greater than six, higher BF_4^- concentrations were observed compared to that obtained at pH 3. The conclusion is that pH control is important in analysis of aqueous samples for BF_4^- by selective ion electrometry.

Table 8. Effect of pH on BF_4^- selective ion electrode potentials.

Sample Number	pH	Change in BF_4^- Electrode Potential (mv)
1	2.01	-4.5
2	3.00	0
3	3.95	0
4	5.08	0
5	6.37	-3.5
6	7.96	-3.8
7	8.96	-13.9
8	10.00	-26.6

Stability of Tetrafluoroborate Ion in Aqueous Solution--
The degree of hydolysis of tetrafluoroborate ion in aqueous solution could influence the efficacy of the selective ion electrode method for analysis of BF_4^-. Therefore, a kinetic study was conducted to ascertain the stability of BF_4^- in aqueous solution. Three unbuffered samples were prepared at BF_4^- concentrations of 1, 10, and 100 ppm. An additional sample of 10 ppm BF_4^- buffered with 0.1 M NH_4F was also prepared. The concentration of BF_4^- was determined for each solution, after which the samples were placed in a controlled temperature bath maintained at 31 ± 1°C. Periodically, potential measurements and corresponding BF_4^- concentrations were obtained during a ten-day period. Results are presented in Table 9. Following the ten-day period, each of the four solutions was heated to and maintained at 70°C for six and one-half hours, after which the BF_4^- concentration was determined by selective ion electrometry. The results of these determinations are also presented in Table 9.

The use of the NH_4F buffer decreases the rate of hydrolysis of BF_4^-. After ten days, the original concentration of 10 ppm tetrafluoroborate was found to decrease by only 11% in the buffered solution compared to a decrease of 31% for the unbuffered sample. The use of a buffer would be prudent with respect to the development of a successful selective ion electrode analytical method.

Recovery of Hydrolyzed Tetrafluoroborate Ion--
The work of Carlson and Paul (3) suggests that hydrolyzed BF_4^- may be recovered by employing appropriate techniques involving special ion exchange resins. This is an important consideration because use of these methods could make it possible to determine BF_4^- which has undergone hydrolysis during sample collection or during sample storage. Accordingly, we attempted to duplicate the results of these workers. These attempts were unsuccesful.

Partially hydrolyzed, alkaline solutions of BF_4^- were introduced to a boron

TABLE 9. Time Dependence of Tetrafluoroborate Ion Concentrations in Aqueous Solutions Maintained at 31°C.

Time (hours)	Observed Tetrafluoroborate Ion Concentration (ppm)			
	1 ppm BF_4^- (Unbuffered)	10 ppm BF_4^- (Unbuffered)	10 ppm BF_4^- (Buffered)	100 ppm BF_4^- (Unbuffered)
0	1.0	10.	10.	100.
66	0.94	9.2	8.3	92
115	0.57	6.6	8.2	77
140	0.55	6.8	8.1	80
163	0.66	6.8	9.0	80
238	0.67	6.9	8.9	79
238 + Heated at 70°C for 6.5 Hours	0.58	6.5	7.9	57

specific ion exchange column packed with Amberlite IRA-743 (Rohm and Haas Co.). Selective conversion of boron-containing species to tetrafluoroborate ion is presumably effected by the addition of 10% HF. The tetrafluoroborate ion is eluted from the column with 0.3 N NaOH. Excess fluoride and sodium hydroxide are removed from the solution with a strong acid column packed with Dowex 50W-XA ion exchange resin converted to the calcium form. Fluoride ion concentration in the solution is reduced by precipitation of calcium fluoride in the column. Tetrafluoroborate ion is converted to fluoroboric acid by this process. The eluent could be analyzed by quantitative conversion of the fluoroboric acid to BF_4^- followed by analysis by specific ion electrometry or by ion chromatography. As noted previously, this approach is desirable because all boron-containing species would be recovered. Unfortunately, our experiments resulted in recoveries of BF_4^- of less than ten percent. Additional work with this method is recommended.

Conclusions

The following conclusions were derived from the experimental results obtained.

(1) Alkaline-treated cellulose back-up pads represent a feasible, albeit onerous, collection procedure for gaseous fluoroboric acid. Following sample collection, the pad is reduced to a pulp by placing it in 50 ml deionized water and stirring for ∿15 minutes. The solution is filtered, adjusted to a pH of 6 with 1:1 HCl and the potential obtained with a fluoroborate anion selective electrode. Recoveries of BF_4^- for eleven replicate samples averaged ∿109% after a storage period of one week.

(2) Unexpectedly high BF_4- concentrations were obtained for samples below pH 3 and above pH 6. Little change in tetrafluoroborate potentials was noted in the pH range 3-6. These results indicate the necessity of buffering the samples; 0.1 M NH_4F served this purpose throughout the study.

(3) The calibration curve of the tetrafluoroborate electrode was determined. The slope of the curve was ∿54 millivolts and was Nernstian to a low value of 1 ppm BF_4^-. Lower standards (0.5 and 0.1 ppm) resulted in a nonlinear calibration curve. The curve was linear over the concentration range 1-100 ppm.

(4) Tetrafluoroborate ion recoveries of less than 10% were obtained from membrane filters fortified with 250 µg or 500 µg BF_4^-. These filters were alkali-fused in nickel crucibles. The BF_4^- in the melt was determined by use of a specific ion electrode.

SUMMARY

A wide variety of special analytical measurements and determinations were successfully achieved during the tenure of this project. Analytical work involved several different analytes, sample types, and instrumental techniques. In addition, methods were developed for the sampling and analysis of alkyl isocyanates, caprolactam, dimethylterephthalate, bisphenol A, and the diglycidyl ether of bisphenol A. Significant research was also accomplished pertinent to the analysis of selected polynuclear aromatic hydrocarbons in a bulk sample of petroleum base asphalt pitch and to the determination of airborne concentrations of fluoroboric acid.

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