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# Characterization of nitrogen-containing aromatic compounds in soil and sediment by capillary gas chromatography–mass spectrometry after fractionation

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## ABSTRACT

Nitrogen-containing aromatic compounds (NCACs) are characterized in soil and sediment by full-scan capillary gas chromatography–mass spectrometry under electron ionization. The approach makes use of fractionation of methylene chloride extracts based first on partitioning of the basic compounds into acid. The neutral NCACs are then isolated by preparative thin-layer chromatography which serves to separate them from the bulk of the polynuclear aromatic hydrocarbons. NCACs can then be determined using deuterated internal standards to 100 μg/kg or below. Examples of determinations in sediment and creosote-contaminated soil are given. An advantage of the two-step fractionation scheme is the chemical separation of azaarenes and cyanoazaarenes of the same elemental composition which facilitates identification of compound class and simplifies chromatographic separations.

## INTRODUCTION

The occurrence of nitrogen-containing aromatic compounds (NCACs) as environmental pollutants has been the subject of growing concern [1–3]. Interest in NCACs parallels interest in polynuclear aromatic hydrocarbons (PNAs) [4–6] because many of these compounds are mutagenic, carcinogenic [7] and toxic, especially to marine biota [8].

The presence of NCACs in sediments and soils can often be attributed to creosote contamination [3]. Indeed, many designated Superfund sites are a result of wood treatment activities involving creosote [9]. Of 1207 recent sites listed by category, about 5% were concerned with wood preservation. Creosote itself has been the subject of analytical investigation by several workers [1,3,6]. In the context of determining NCACs in sediments of Eagle Harbor, Puget Sound, Krone *et al.* [3] compared analyses of sediment directly to analyses of creosote extracts. Wright *et al.* [1] compared NCACs in synthetic fuels to those found in creosote. Nestler [10] characterized the major compounds of creosote, a coal tar distillate, which included PNAs, NCACs, and oxygen-containing and sulfur-containing aromatic compounds.

Sediments have been the focus of investigation in the U.S. and in Canada [2,3].

The analytical problem presented by NCACs is their determination in the presence of hunderds of other compounds including PNAs and alkyl hydrocarbons. This problem has been approached by using column chromatography to produce fractions enriched in the NCACs [11]. Thus, Wright *et al.* [1] and Krone *et al.* [3] have employed silica and alumina columns to afford enriched fractions. The disadvantage of column chromatography is the time-consuming need to standardize the column and the large volume of solvents used [12]. Onuska and Terry [2] employed a simple chemical separation based on partitioning of the basic compounds into acid.

Identification and quantitation usually rely on capillary gas chromatography–mass spectrometry (GC–MS) with appropriate internal standards. Levels of NCACs in the range of 10 μg/kg to 20 mg/kg have been reported for sediments [2,3] with levels $10^2$–$10^3$ times greater in creosote itself [3]. Typically, three classes of functional groups are found among NCACs in the environment: (a) tertiary nitrogen in the aromatic ring (*e.g.*, acridine); (b) secondary nitrogen derived from indole/carbazole; and (c) nitrile-containing aromatics (*e.g.*, cyanonaphthalene). Primary amines such as anilines do not occur appreciably in the context of these investigations, and this is possibly due to their appreciable water solubility and to their low initial concentration in sources of contamination such as creosote.

Other instrumental and chromatographic methods have been applied to the determination of NCACs. GC–nitrogen-phosphorous detection has been effectively employed as a screening tool [2]. An alternative element-specific detection can be used that is based on atomic emission spectroscopy with a microwave-induced plasma (GC–AES or GC–MIP, respectively) [13]. High-performance liquid chromatography with UV–visible or fluorescent detection can also serve to quantitate PNAs and NCACs [14]. Thin-layer chromatography (TLC) has long been employed in monitoring PNAs and NCACs [15–17], and Snook *et al.* [18] have isolated NCACs from tobacco smoke using silicic acid and gel chromatographies.

Current methods promulgated in the US Environmental Protection Agency (EPA) SW-846 manual [14] do not address most of the NCACs routinely encountered in contaminated sediments and soils. In order to address this need, development and evaluation of methodology to determine NCACs is needed [9].

In this paper we present the results of the analyses of sediments and soils for NCACs. After Soxhlet or sonication extraction, a separation scheme yielding two fractions is used. The basic fraction (class a) is prepared by extraction of the methylene chloride extract with HCl and subsequent repartitioning into methylene chloride after adjusting to a basic pH. The remaining neutral fraction (classes b and c) is isolated by preparative TLC and recovered into methylene chloride. The choice of internal standards is presented as well as compound structures likely to be encountered.

## EXPERIMENTAL

### *Sample preparation*

*Sediments.* Sediment samples from Eagle Harbor, Puget Sound, WA, were subjected to standard US EPA methodology, *i.e.*, SW-846 [14]. Briefly, this involves a hexane—acetone Soxhlet extraction and a gel permeation chromatography cleanup step. Final concentration of extracts of 20–100 g samples was to 0.5 ml methylene chloride.

*Soils.* Soil samples from Spotsylvania, VA (L. A. Clark site) were subjected to standard US EPA methodogy, *i.e.*, SW-846 [14]. Briefly, 2-g samples were extracted using either Soxhlet or sonication methods. Final concentration of methylene chloride extracts was to 5.0 ml.

*Fractionation*

Methylene chloride extracts (0.5 ml) were extracted three times with 0.5 ml of 6 *M* HCl. The HCl fraction was taken to pH 14 with 6 *M* NaOH and extracted three times with methylene chloride. This methylene chloride fraction was dried by passing it through a column of $Na_2SO_4$ and was then concentrated to 100 $\mu$l using nitrogen, and was fortified with internal standards. The neutral fraction was applied to a preparative TLC plate (1-mm film thickness, 20 × 20 cm, E. Merck) with preconcentration layer. Developing solvent was methylene chloride–hexane (30:70) after pre-equilibrating the tank. The appropriate $R_F$ range was defined by standards of 1,4-dicyanobenzene and 9-methylcarbazole as $R_F$ = 0.05–0.32 and scraped after evaporation of solvent. The scrapings were extracted with methylene chloride, filtered, and concentrated to 100 $\mu$l under a nitrogen steam. Internal standards were added to the final extract.

*Internal standards and response factors*

A spiking solution of nominally 20–40 ng/$\mu$l consisted of [$^2H_7$] 3-picoline, [$^2H_7$]quinoline, [$^{13}C_1$]indole, [$^2H_9$]acridine, [$^2H_8$]naphthalene and [$^2H_{10}$]phenanthrene. Response factors for available standards were determined using a series of standard solutions *versus* a spiking solution. Response factors for tentatively identified compounds not confirmed by standards were estimated using the available data and chemical reasoning based on similar structures.

*Chemicals*

[$^2H_7$]3-Picoline, [$^2H_7$]quinoline, [$^{13}C_1$]indole and [$^2H_9$]acridine were obtained from Cambridge Isotope Laboratories. [$^2H_8$]Naphthalene, [$^2H_{10}$]phenanthrene were obtained from the US EPA repository. The following compounds were obtained from Aldrich: quinoline, isoquinoline, 2-methylquinoline, benzonitrile, indole, 3-picoline, 2,4,6-collidine, 8-methylquinoline, 4-methylquinoline, 6-methylquinoline, 2,4-dimethylquinoline, 2,8-dimethylquinoline, 1-methylisoquinoline, 2-phenylpyridine, 3-methyl-2-phenylpyridine, 7,8-benzoquinoline, phenanthridine, carbazole, 9-cyanophenanthene, 2-phenylquinoline 2,4-lutidine, 2,6-lutidine, 1-cyanonaphthalene and 1,4-dicyanobenzene.

*GC–MS*

Electron impact mass spectra were obtained on a Finnigan-MAT 4023 repetitively scanned from $m/z$ 50 to 450 in 1 s under data system control of a INCOS 2300 (Nova 4X, software Rev. 6.1). Gas chromatography was accomplished with a DB-5 (J & W) column (30 m × 0.32 mm I.D.) programmed from 60 to 300°C at 20°C/min using splitless injection at 220°C. Emission current was 0.50 mA at 70 eV, temperature of the source was 270°C, while that of the transfer line and separator was 250°C; conversion dynode voltage was 3 kV, multiplier was set at 1000 V and preamplifier set at $10^{-8}$ A/V. Flow-rate was 38 cm/s He at 60°C oven temperature.

*Accurate mass measurements*

A 1.0-$\mu$l sample was introduced by capillary GC–MS using a 30 m × 0.25 mm I.D. SPB-5 Supelco column with 0.25 $\mu$m film thickness operated at 60°C for 3 min followed by temperature programming at 20°C/min to 300°C; flow-rate was 40 cm/s He at 60°C; sample was injected on column using a deactivated 1 m × 0.53 mm I.D. column as a retention gap. Accurate mass measurements were made on a VG 7070 EQ operated at 3000 resolution (15% valley) scanned from 250 to 150 at 3 s/dec under data system control (11–250, 11/24 based system, version 3.0, B22 tasks) and the following conditions: emission current, 0.1 mA; electron energy, 70 eV; source temperature, 180°C.

## RESULTS AND DISCUSSION

### *GC–MS*

Fig. 1 and 2 illustrate the chromatograms of total-ion current for the HCl and neutral fractions of NCACs from a soil heavily contaminated by creosote. Selected compound classes are labeled in order to facilitate comparison of retention behavior and relative amounts of NCACs present. The major components of the HCl fraction are benzoquinoline, acridine, 2-methylquinoline, azapyrenes or isomers, methyl acridines or isomers and azachrysenes or isomers. The major component of the neutral fraction is carbazole with lesser amounts of 1-cyanonaphthalene, methylcarbazoles and cyanophenanthrenes or isomers.

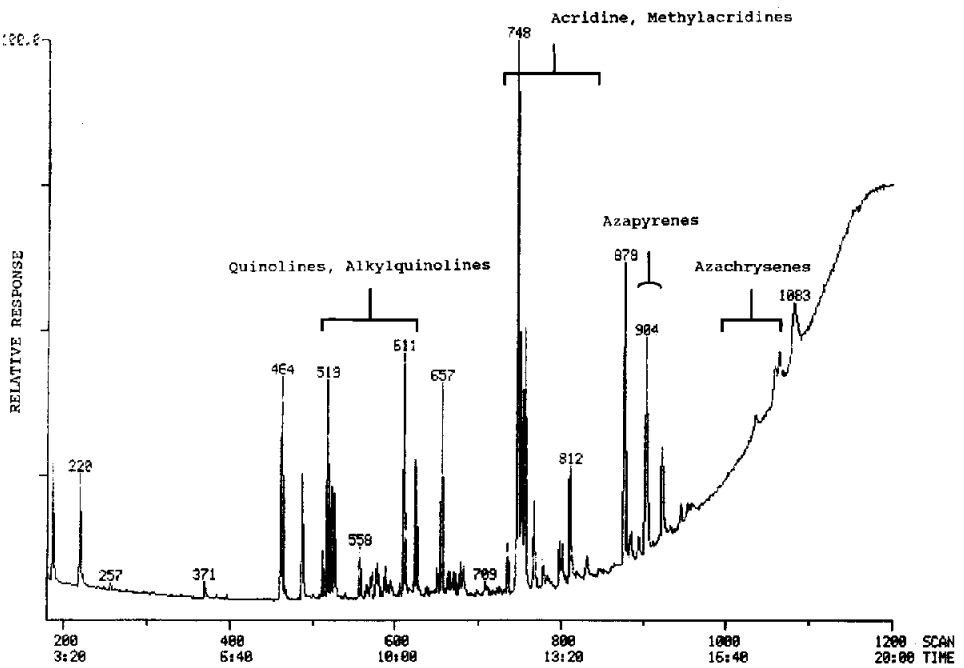


Fig. 1. GC–MS total-ion current chromatogram of the HCl fraction from a creosote-contaminated soil. Retention time in min:s.

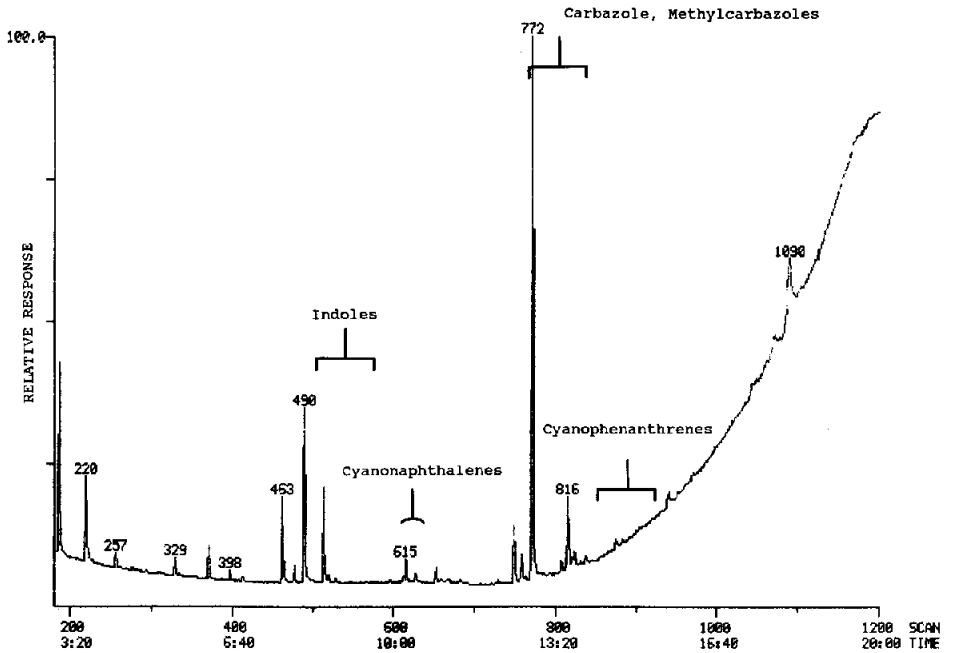


Fig. 2. CG–MS total-ion current chromatogram of the neutral fraction of a creosote-contaminated soil. Retention time in min:s.

A broad spectrum of NCACs was considered in characterizing samples. Table I summarizes compound classes divided into the HCl fraction and the neutral fraction. A minor number of NCACs containing sulfur or oxygen are included. One advantage of the fractionation is the ability to chemically separate isobaric and isotopic ions such as cyanophenanthene and azapyrene (molecular mass, $M_r$ = 203). Not all of these classes are found as significant components in samples. A routine monitoring program will likely be limited to representative compounds or to those that are of special interest because of their extreme toxicity.

*Quantitative results*

Table II presents quantitative results for the compounds monitored using a contaminated soil sample as an example. These data are again divided into the HCl and neutral fractions.

In the HCl fraction quinoline and isoquinoline ($M_r$ = 129) were found. About eight isomers of methylquinolines, six isomers of dimethylquinolines and eight isomers of trimethylquinolines ($M_r$ = 171) were observed. Four compounds of $M_r$ = 179 were observed including 7,8-benzoquinoline, acridine, phenanthridine, and presumably, another benzoquinoline. Usually, three isomers of $M_r$ = 203 and two isomers of $M_r$ = 229 were observed in sample extracts. Azafluorene, azabenzofluorenes, phenylpyridine and methylphenylpyridines, and phenylquinolines were found. Quinolinol and methylquinolinol were oxygen-containing NCACs discovered.

In the neutral fraction, 1-cyanonaphthalene and 2-cyanonaphthalene were found. Benzothiazole was observed in this fraction as well. Usually, three isomers of

TABLE I

KINDS OF NCACs CONSIDERED FOR TARGETS OF GC–MS

Representative compounds are given. Other isomers are implicit.

| HCl fraction | $M_r$ (with alkyl derivatives) | Neutral fraction |
|---|---|---|
| Pyridine | 79 (93, 107, 121) | |
| Quinoline | 129 (143, 157, 171) | |
| Benzoquinoline, acridine, phenanthridine, | 179 (193, 207) | Cyanobiphenyl |
| Azapyrene, azafluoranthene | 203 (217) | Cyanophenanthrene |
| Azachrysene | 229 (243) | Cyanophenylnaphthalene |
| Phenylpyridine | 155 (169) | |
| Phenylquinoline | 205 (219) | |
| Diphenylpyridine | 231 | |
| Azafluorene | 167 (181, 195) | Carbazole |
| Dibenzoacridine | 279 | |
| Quinolinol | 145 (159) | |
| Acridone | 195 | |
| | 103 (117, 131) | Benzonitrile |
| | 153 (167) | Cyanonaphthalene |
| | 227 | Cyanopyrene |
| | 253 | Cyanochrysene |
| | 117 (131) | Indole |
| | 217 (231) | Benzocarbazole |
| | 267 | Dibenzocarbazole |
| | 135 | Benzothiazole |
| | 185 | Dibenzothiazole |
| | 235 | Naphthobenzothiazole |
| | 191 | Benzo[*def*]carbazole, cyanofluorene |

methylcarbazole were present in sample extracts but no 9-methylcarbazole. In addition, cyanophenanthrene/anthracenes, cyanopyrenes and cyanofluorene compounds were observed. Benzocarbazole responses were noted as well as a $M_r$ = 229 compound of unknown structure not expected in this fraction (*i.e.*, an azachrysene would be in the HCl fraction). This $M_r$ could represent a cyanophenylnaphthalene for example. On a weight basis, these responses are individually about 1–10% relative to carbazole.

The retention time and internal standard reference are also included in Table II. In general, response factors for available standards exhibited relative standard deviations of less than 15%. A typical response factor plot of analyte *versus* internal standard is shown in Fig. 3 for acridine [$^2H_9$]acridine. In all cases, the area of the molecular ion was used for quantitation. Additional internal standards would be useful for late-eluting NCACs as additional analyte standards become available for further study. For example, an azachrysene standard and labeled compound would be expected to improve quantitation of similar compounds.

NCACs with similar chemical structures were found in some sediment samples from Eagle Harbor. Levels were generally 10–100 times lower than those in the con-

TABLE II

THE GC–MS DETERMINATION OF NCACs IN A CREOSOTE-CONTAMINATED SOIL

| Compound | $M_r$ | Retention time (min:s) | Amount detected (μg/g) | I.S.[a] |
|---|---|---|---|---|
| *HCl fraction* | | | | |
| 3-Picoline | 93 | 3:40 | – | 1 |
| 2,4-Lutidine | 107 | 5:09 | 0.603 | 1 |
| 2,6-Lutidine | 107[b] | 5:17 | 0.296 | 1 |
| 2,4,6-Collidine | 121[b] | 5:48 | 0.149 | 1 |
| Quinoline | 129 | 8:10 | 0.624 | 2 |
| Isoquinoline | 129 | 8:22 | 0.699 | 2 |
| Methylquinoline | 143 | 8:39 | 2.30 | 2 |
| 2-Methylquinoline | 143[b] | 8:44 | 13.3 | 2 |
| Methylquinoline | 143 | 8:48 | 1.74 | 2 |
| 8-Methylquinoline | 143[b] | 8:54 | 0.262 | 2 |
| 1-Methylisoquinoline | 143[b] | 9:00 | 0.816 | 2 |
| 6-Methylquinoline | 143[b] | 9:06 | 0.212 | 2 |
| 2,8-Dimethylquinole | 157[b] | 9:17 | 1.71 | 2 |
| Dimethylquinoline | 157 | 9:29 | 1.27 | 2 |
| 2,6-Dimethylquinoline | 157[b] | 9:37 | 4.43 | 2 |
| 2,4-Dimethylquinoline | 157[b] | 9:48 | 3.83 | 2 |
| Dimethylquinoline | 157 | 9.52 | 1.66 | 2 |
| Dimethylquinoline | 157 | 9:57 | 0.595 | 2 |
| Trimethylquinoline | 171 | 10:06 | 0.622 | 2 |
| Trimethylquinoline | 171 | 10:18 | 1.06 | 2 |
| Trimethylquinoline | 171 | 10:23 | 0.399 | 2 |
| Trimethylquinoline | 171 | 10:27 | 0.201 | 2 |
| Trimethylquinoline | 171 | 10:38 | 0.634 | 2 |
| Trimethylquinoline | 171 | 10:44 | 0.548 | 2 |
| Trimethylquinoline | 171 | 10:52 | 0.106 | 2 |
| Trimethylquinoline | 171 | 10:58 | 0.313 | 2 |
| 2-Phenylpyridine | 155[b] | 9:55 | 2.25 | 2 |
| Methylphenylpyridine | 169 | 10:21 | 2.16 | 2 |
| Methylphenylpyridine | 169 | 10:48 | 1.22 | 2 |
| Methylphenylpyridine | 169 | 11:11 | 2.19 | 2 |
| Quinolinol | 145 | 11:40 | 1.49 | 4 |
| Methylquinolinol | 159 | 11:58 | 0.307 | 4 |
| 7,8-Benzoquinoline | 179 | 12:32 | 20.5 | 4 |
| Acridine | 179 | 12:37 | 30.8 | 4 |
| Phenanthridine | 179 | 12:48 | 1.94 | 4 |
| Benzoquinoline/isomer | 179 | 13:04 | 2.49 | 4 |
| Methylacridine/isomer | 193 | 12:59 | 4.67 | 4 |
| Methylacridine/isomer | 193 | 13:07 | 1.49 | 4 |
| Methylacridine/isomer | 193 | 13:18 | 9.63 | 4 |
| Methylacridine/isomer | 193 | 13:32 | 6.14 | 4 |
| Methylacridine/isomer | 193 | 13:42 | 3.57 | 4 |
| Azafluorene | 167 | 11:22 | 6.84 | 4 |
| Azapyrene/isomer | 203 | 14:46 | 3.11 | 4 |
| Azapyrene/isomer | 203 | 14:55 | 2.23 | 4 |
| Azapyrene/isomer | 203 | 15:24 | 10.8 | 4 |
| Phenylquinoline | 205 | 13:51 | 0.387 | 4 |
| 2-Phenylquinoline | 205[b] | 14:07 | 0.497 | 4 |
| Azachrysene/isomer | 229 | 17:16 | 7.53 | 4 |
| Azachrysene/isomer | 229 | 17:38 | 6.36 | 4 |

*(Continued on p. 230)*

TABLE II *(continued)*

| Compound | $M_r$ | Retention time (min:s) | Amount detected (μg/g) | I.S.[a] |
|---|---|---|---|---|
| Benzoazafluorene/isomer | 217 | 15:51 | 1.96 | 4 |
| Benzoazafluorene/isomer | 217 | 15:59 | 2.66 | 4 |
| Acridone | 195 | – | – | 4 |
| Diphenylpyridine | 231 | – | – | 4 |
| Benzothiazole | 135 | 8:04 | 0.119 | 3 |
| Dibenzothiazole | 185 | 12:24 | 1.04 | 4 |
| *Neutral fraction* | | | | |
| Benzonitrile | 103 | 5:53 | – | 1 |
| Methylbenzonitrile | 117 | 7:06 | – | 1 |
| Benzothiazole | 135 | 8:05 | 0.079 | 3 |
| 1-cyanonaphthalene | 153 | 10:15 | 3.54 | 2 |
| 2-Cyanonaphthalene | 153 | 10:28 | 1.51 | 2 |
| Carbazole | 167 | 12:52 | 34.8 | 6 |
| Methylcarbazole | 181 | 13:28 | 0.924 | 6 |
| Methylcarbazole | 181 | 13:44 | 2.02 | 6 |
| Methylcarbazole | 181 | 13:51 | 0.433 | 6 |
| Cyanophenanthrene/isomer | 203 | 15:00 | 0.404 | 4 |
| Cyanophenanthrene/isomer | 203 | 15:05 | 0.402 | 4 |
| Cyanopyrene/isomer | 227 | 17:00 | 0.567 | 4 |
| Cyanopyrene/isomer | 227 | 17:05 | 0.790 | 4 |
| Cyanobiphenyl | 179 | 12:44 | 0.182 | 4 |
| Dibenzothiazole | 185 | 12:24 | 1.01 | 4 |
| Benzo[*def*]carbazole, cyanofluorene | 191 | 15:40 | 1.63 | 6 |
| Benzocarbazole | 217 | 15:53 | 0.117 | 6 |
| Benzocarbazole | 217 | 16:02 | 0.184 | 6 |
| Cyanophenylnaphthalene | 229 | 17:23 | 2.81 | 4 |

[a] Internal standards (I.S.): 1 = [$^2H_7$]3-picoline; 2 = [$^2H_7$]quinoline; 3 = [$^{13}C_1$]indole; 4 = [$^2H_9$]acridine; 5 = [$^2H_8$]naphthalene; 6 = [$^2H_{10}$]phenanthrene.

[b] Since not all isomers were available to us for investigation, the possibility exists that another isomer could coelute with the assigned compound. These identifications, therefore, must be considered tentative.

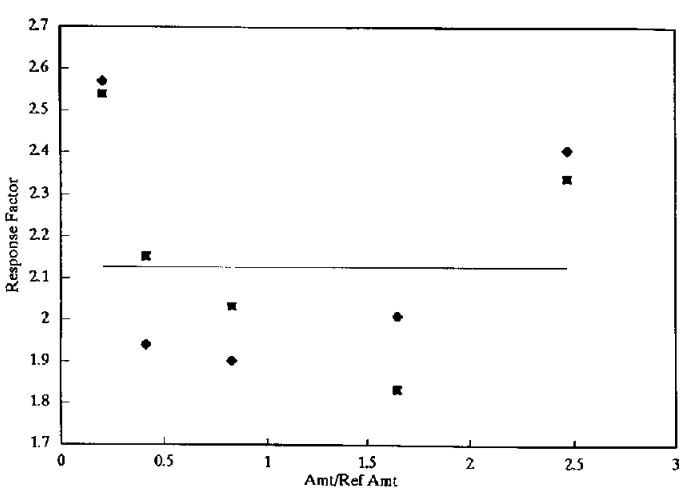


Fig. 3. Calibration plot of acridine response *versus* response of its internal standard ([$^2H_9$]acridine). Relative standard deviation = 11.9%. Amt/Ref Amt = ng of analyte/ng of I.S. ◆ and ■ are duplicate injections of the same solution.

taminated soils. As a typical example of contamination levels in one of these sediments, the following major components are reported in μg/kg: acridine (43.7), methylacridine (6.0), azapyrene (12.0), carbazole (463.0) and methylcarbazole (61.5). Other compounds were often below 5 μg/kg. Results varied depending on sampling site.

*Interferences*

The removal of PNAs is complete enough to allow concentration of fractions to below 100 μl. In heavily contaminated samples, the methylene chloride solution afforded by the HCl fractionation procedure (with subsequent repartitioning to organic phase) may be taken through a second round of HCl fractionation to remove any PNAs that had appreciable aqueous solubility in 6M HCl due to their initial high concentration.

The neutral fraction afforded by preparative TLC is satisfactorily free of interfering PNAs. Most PNAs and alkyl hydrocarbons had an R greater than 0.32. The TLC isolate does contain several oxygenated compounds along with NCACs. These are listed in Table III for reference purposes, and are tentatively identified as 9,10-anthraquinone ($M_r$ = 208), a 4,5-carbonylphenanthrene ($M_r$ = 204), two aceanthrenones ($M_r$ = 218), and benzoanthrone ($M_r$ = 230). To further characterize these compounds, accurate mass measurements were obtained by capillary GC–MS at 3000 resolution. The elemental compositions thus inferred were consistent with the proposed strutures. In addition, the loss of CO or CHO$^{\cdot}$ from $M^{+\cdot}$ was also confirmed in each case by accurate mass measurement.

TABLE III

OXYGEN-CONTAINING AROMATIC COMPOUNDS FOUND IN THE PREPARATIVE TLC SEPARATION

| Compound | $M_r$ | Retention time (min:s) | Confirmed elemental composition |
|---|---|---|---|
| 9,10-Anthraquinone or isomer | 208 | 14:01 | $C_{14}H_8O_2$ |
| Cyclopentanone[*def*]phenanthrene or isomer (4,5-carbonylphenantrene) | 204 | 14:39 | $C_{15}H_8O$ |
| Aceanthrenone or isomer | 218 | 15:35; 15:44 | $C_{16}H_{10}O$ |
| Benzofluorenone, benzanthrone, or isomer | 230 | 17:03 | $C_{17}H_{10}O$ |

*Recovery*

Recovery studies of the common extraction techniques used for these samples have been published [14]. Recovery of analytes using the HCl fractionation has been shown to be variable but usually within the 50–90% range [2]. Initial experiments within our laboratory indicate that recovery of analytes in both the HCl and neutral fractions can be quantitative (50–90%). Further studies of analyte recovery and of potential surrogates will be published separately.

## CONCLUSIONS

NCACs can be isolated and quantitated in soils and sediments using a two-step fractionation scheme based on acid–base partition of basic compounds and prepara-

tive TLC isolation of neutral compounds followed by capillary GC–MS. Co-extractives such as alkyl hydrocarbons and PNAs and effectively removed as interferences from both fractions. Major percentage contribution of reported compounds in the HCl fraction include 7,8-benzoquinoline (12%), acridine (18%), 2-methylquinoline (8%), and azapyrene (6%). With the reported compounds found in the neutral fraction, carbazole constituted 68%; 1-cyanonaphthalene, 7%; and a methylcarbazole, 4%. These compounds are implicated in toxic, teratogenic and carcinogenic effects in fish and mammals.

Future work could be addressed to a more complete investigation of various isomers of azaarenes. The application of solid-phase extraction to simplifying cleanup is also of interest. The use of TLC as a screening method for NCACs is an area largely neglected in environmental analysis. Automated sample appplication and quantitation in TLC are attractive capabilities. Finally, the information provided in this paper should help to define monitoring needed during the cleanup of designated sites by supplying the identities and the quantitative levels of compounds found in creosote-contaminated soil and sediment.

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