

7. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods that are available for detecting, measuring, and/or monitoring creosote, its metabolites, and other biomarkers of exposure and effect to creosote. The intent is not to provide an exhaustive list of analytical methods. Rather, the intention is to identify well-established methods that are used as the standard methods of analysis. Many of the analytical methods used for environmental samples are the methods approved by federal agencies and organizations such as EPA and the National Institute for Occupational Safety and Health (NIOSH). Other methods presented in this chapter are those that are approved by groups such as the Association of Official Analytical Chemists (AOAC) and the American Public Health Association (APHA). Additionally, analytical methods are included that modify previously used methods to obtain lower detection limits and/or to improve accuracy and precision.

The analytical methods used to quantify creosote and related mixtures in biological and environmental samples are summarized below. As noted in Chapter 4, coal-derived mixtures (creosote, pitch, tar) are chemically very similar; the methods used for their analysis are directed to the primary components of these mixtures. In most cases uncovered through a search of the recent literature, the methods used for coal-derived mixtures are based on analysis of high-pressure liquid chromatography (HPLC) with ultraviolet (UV) absorbance detection to nondestructively separate these compounds for collection and characterization.

The high resolving power of capillary gas chromatography (GC) is required for the successful analysis of coal-derived materials, since these mixtures can contain hundreds of components with very similar chemical properties. Guillen et al. (1992) and Blanco et al. (1992) have demonstrated the full power of capillary GC using both mass spectrometry (MS) and flame ionization detection (FID) for analyzing coal tar. Specific applications for biological and environmental analyses are described below.

7.1 BIOLOGICAL MATERIALS

The levels of creosote in biological materials can be estimated by measuring the PAH content in biological samples. Methods include GC/FID, GC/MS, and HPLC. Synchronous luminescence spectroscopy (SLS), ³²P-postlabeling, and immunoassay techniques, i.e., enzyme linked immunosorbent assays (ELISA) and ultrasensitive enzyme radio immunoassay (USERIA), are methods currently being developed to detect and quantify ultratrace levels of PAH adducts bound covalently to macromolecules

7. ANALYTICAL METHODS

(e.g., DNA). Table 7-1 lists the available analytical methods for determining creosote/coal tar-derived PAH components in biological samples. GC/MS and HPLC have been employed to detect creosote-derived PAH complexes at ppt (pg/g) levels in human tissues, including adipose tissue, blood, and urine (Liao et al. 1988; Obana et al. 1981). The detection and quantification of trace levels of PAHs in biological tissues involves extensive and rigorous clean-up procedures including Florisil, silica, and alumina column chromatography (Liao et al. 1988; Obana et al. 1981).

There is considerable evidence, both *in vitro* and *in vivo*, that PAHs are enzymatically converted to highly reactive metabolites that bind covalently to macromolecules such as DNA, thereby causing carcinogenesis and mutagenesis in mammalian systems. Thus, benzo[a]pyrene (a procarcinogenic PAH and the most thoroughly studied one) is converted by specific cellular enzymes to the syn- and anti-isomers of 7 β , 8 δ -dihydroxy-(9 δ , 10 δ)-epoxy-7,8,9,10-tetrahydro-benzo[a]pyrene (B[a]PDE) and binds covalently to DNA, resulting in formation of the putative B[a]PDE-DNA adduct (Autrup and Seremet 1986; Harris et al. 1985; Haugen et al. 1986; Santella et al. 1995).

In an analysis of B[a]P and coal tar pitch volatiles in workplace air conducted by Ny et al. (1993), urine samples were analyzed for the pyrene metabolite 1-hydroxypyrene, and a high correlation between levels of this biomarker and PAH air levels was observed. Analyses were also conducted by HPLC with fluorescence detection. Tolos et al. (1990) reported results of 1-hydroxypyrene urinalysis for aluminum reduction plant workers, and showed a strong positive correlation between the compound and 17 environmental PAHs. This work verified the choice by earlier researchers (Jongeneelen et al. 1988) of the pyrene metabolite as a useful marker of exposure to PAHs. Elovaara et al. (1995) also demonstrated the usefulness of 1-hydroxypyrene as a biomarker for exposure to naphthalene and 10 other PAHs for creosote impregnation plant workers. Particulate PAHs were Soxhlet extracted with cyclohexane and analyzed by HPLC with fluorescence detection.

The ELISA technique has been employed for detecting antibodies in serum bound to B[a]PDE-DNA adducts. The USERIA method involves measuring the immunological response of B[a]PDE-DNA in the presence of rabbit anti-serum, alkaline phosphatase enzyme, and radiolabeled para nitrophenyl phosphate (PNPP). The radioactivity of the hydrolyzed tritiated PNPP is measured by a scintillation counter. Both ELISA and USERIA methods have been employed to detect PAH-DNA adducts at 10^{-15} mol levels in the blood and tissues of humans occupationally exposed to PAH (Amin et al. 1982; Harris et al. 1985;

7. ANALYTICAL METHODS

Table 7-1. Analytical Methods for Determining Creosote/Coal Tar-Derived PAH Components in Biological Samples

Form	Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Coal tar creosote, Coal tar	Adipose tissues	Benzene/hexane extraction of adipose tissue; addition of Na ₂ SO ₄ ; cleanup with Florisil column; elution of PAHs with 8% benzene in hexane, sample concentration.	GC/MS	5–50 ng/g	52–95% recovery	Liao et al. 1988
Coal tar creosote	Liver homogenate	Extraction of homogenate with ethyl acetate; water removal (Na ₂ SO ₄), concentration.	HPLC	No data	No data	Amin et al. 1982
		Saponification of minced tissue, extraction with hexane; clean up by solvent partition, concentration; purification by silica/alumina chromatography; concentration of eluent.	HPLC	0.006–0.46 ng/g	No data	Obana et al. 1981
Coal tar creosote	Blood	Separation of white cells; isolation of DNA by standard Rnase and phenol treatment.	ELISA	1x10 ⁻¹⁵ mol BPDE per µg DNA	No data	Perera et al. 1988

7. ANALYTICAL METHODS

Table 7-1. Analytical Methods for Determining Creosote/Coal Tar-Derived PAH Components in Biological Samples (continued)

Form	Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Coal tar creosote, Coal tar		Isolation of PAH-DNA adduct from white cells; digestion of adduct with radiolabeled (³² P)ATP; radiolabeled adduct resolution by TLC.	³² P-post-labeling	0.3x10 ⁻¹⁵ mol BPDE per µg DNA	No data	Phillips et al. 1988
Coal tar creosote		Separation of lymphocyte cells and isolation of BPDE-DNA adduct by standard treatments.	ELISA or USERIA and SLS	0.006–0.23x 10 ⁻¹⁵ mol BPDE per µg DNA	No data	Harris et al. 1985
Coal tar creosote	Urine	Animal dosing with radiolabeled B[a]P; collection of urine, addition of MeOH; c-18 Sep-Pak column cleanup; elution with aqueous MeOH.	HPLC	5x10 ⁻¹² mol 7-BPDE-Gua per µg of labeled B[a]P	No data	Astrup and Seremet 1986
Coal tar creosote, Coal tar pitch, Coal tar		Hydrolysis of conjugates enzymatically; isolation of 1-pyrenol using SPE column.	HPLC/FI	0.45 nmol/L	No data	Tolos et al. 1990
Coal tar creosote, Coal tar pitch		Hydrolysis of conjugates enzymatically; isolation of 1-pyrenol using SPE column	HPLC/FI	10 nmol/L	84–88%	Ny et al. 1993

BPDE benzo[a]pyrene diol epoxide; B[a]P = benzo[a]pyrene; DMSO = dimethyl sulfoxide; ELISA = enzyme linked immunosorbent assay; FI = fluorescence; Gua = guanine; GC/MS = gas chromatography/mass spectrometry; HPLC = high-performance liquid chromatography; NADP⁺ = oxidized nicotinamide adenosine dinucleotide; SLS = synchronous luminescence spectroscopy; SPE = solid phase extraction; USERIA = ultra-sensitive enzyme radioimmunoassay

7. ANALYTICAL METHODS

Haugen et al. 1986; Newman et al. 1988; Perera et al. 1988). The ^{32}P -postlabeling method involves a 5'-labeling of DNA adducts that have been digested with nuclease P_1 enzyme system to 3'-mononucleotides. Adducts present in the digest that were resistant to nuclease P_1 were thus labeled with ^{32}P , while unmodified nucleotides were not. The digested DNA adducts are separated by thin-layer chromatography (TLC) and quantified by scintillation counting. A detection limit of 0.3×10^{-15} mol of PAH adduct per μg of DNA (less than one adduct in 10^7 nucleotides) has been achieved (Philips et al. 1988).

7.2 ENVIRONMENTAL SAMPLES

As with biological samples, the PAH component fraction is most often used as an indicator of creosote contamination of environmental media. For example, screening for total PAHs is often used at hazardous waste sites when creosote contamination is suspected. The PAH fraction (neutral) is used in these analyses because it is more persistent than the acidic or basic fractions, which tend to be more mobile and biodegradable. The methods used to measure total PAHs can also be used to detect the nitrogen, oxygen, and sulfur heterocyclic components of the mixture. Table 7-2 lists the available analytical methods for determining creosote/coal tar-derived PAH components in environmental samples.

The efficacy of supercritical fluid extraction was demonstrated to be a promising technique for coal tar pitch (Camel et al. 1993). Extraction procedures for coal tar pitch volatiles on air sampling filters have been compared by Hekmat et al. (1994). Methylene chloride was shown to be superior as an extracting solvent to cyclohexane. For coal tar pitch volatiles collected on poly(tetrafluoroethylene) filters or glass fiber filters and extracted with benzene, cyclohexane, or dichloromethane, Hekmat et al. (1994) found that the highest recoveries were achieved with collection on poly(tetrafluoroethylene) filters, desorption with dichloromethane, and analysis using spectrophotometry (UV quantification). Cyclohexane was not found to be a suitable substitute for benzene. These authors also concluded that spectrophotometric methods were superior to gravimetric methods of measurement of coal tar pitch volatiles.

Hale and Aneiro (1997) reviewed recent progress made in improving analytical techniques for determining components of creosote in environmental media. The multiple extraction and purification steps required prior to chromatographic analysis is problematic in that compounds may be lost through volatilization or transformed through photodegradation. More efficient extraction procedures include supercritical fluid extraction, accelerated solvent, and microwave, and solid-phase extraction. Newer

7. ANALYTICAL METHODS

Table 7-2. Analytical Methods for Determining Creosote/Coal Tar-Derived PAH Components in Environmental Samples

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Wooden sleepers (railroad crossties) in playground	Extraction of sample with ether; filtration through anhydrous sodium sulfate and evaporation of solvent; acid/base/neutral liquid-liquid partition.	GC/MS	1–3 ng/sample	No data	Rotard and Mailahn 1987
Coal tar creosote	Dissolution of sample in cyclohexane and extraction with 90% ethanol; evaporation of extract to dryness; dissolution of residue in cyclohexane, extraction with nitromethane; evaporation of extract to dryness and dissolution of residue with small amount of benzene.	GC	10 ppm	No data	Lijinsky et al. 1963
	Dissolution of sample in methylene chloride at a concentration of . 10% (w/w).	GC	No data	No data	Nestler 1974a
River sediments	Digestion of wet sediment sample in boiling EtOH/KOH; extraction of hydrocarbons into cyclohexane; extract concentration and Florisil column cleanup; elution of PAH complex with 50% methylene chloride/hexane; concentration of sample.	HPLC	No data	No data	Black 1982

7. ANALYTICAL METHODS

Table 7-2. Analytical Methods for Determining Creosote/Coal Tar-Derived PAH Components in Environmental Samples (*continued*)

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Contaminated groundwater	Filtration through prebaked glass-fiber filters to remove suspended sediments; cleanup with bonded-phase extraction column; elution of organics from column with acetonitrile followed by methylene chloride; water removal (Na ₂ SO ₄); concentration by nitrogen blow-down.	GC/MS	50 µg/L	95%	Rostad et al. 1984
Groundwater	pH to 12. Extraction with CH ₂ Cl ₂ . Drying and concentration of organic phase (containing neutral and bases). Adjustment of aqueous phase pH to 7 and extraction; then to pH 2 and extraction. Both extracts derivatized to TMS esters/ethers.	GC/FID	100 ppb	>90% for PAHs; . 30–50% for phenols; . >70% for bases	Mueller et al. 1991
Impregnated wood (workplace)	Heating of sample at 60 EC in a chamber; cleanup with XAD-2 column; extraction with ether.	GC/MS	0.07–0 µg/L using ITMS (α, β, and sulfate)	116–128%	Heikkilä et al. 1987
	Collection of heated sample on a prewashed (cyclohexane) glass fiber filter; extraction of sample with cyclohexane and evaporation to dryness; dissolution of residue in acetonitrile/water (85/15).	HPLC	8 ng/m ³	No data	

7. ANALYTICAL METHODS

Table 7-2. Analytical Methods for Determining Creosote/Coal Tar-Derived PAH Components in Environmental Samples (*continued*)

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Creosote treated wood	Heating of sample in injection port of GC.	GC	No data	No data	Lorenz and Gjovik 1972
Gas and particulate matter (workplace)	Pumping sample through a glass fiber filter-XAD-2 adsorbent sampling system; extraction with ether in ultrasonic bath; concentration of extract and dilution with acetonitrile.	HPLC	0.005–2.5 mg/m ³	87–102%	Andersson et al. 1983
Breathing zone air (workplace)	Pumping air through Teflon filters and sorbent tubes. Extraction of particulate and tubes with benzene. Concentration of extracts.	GC	0.05 mg/sample	No data	Tolos et al. 1990
Breathing zone air (workplace)	No information.	HPLC/FI	No data	No data	Rogaczewska and Ligocka 1991
Breathing zone air (workplace)	Pumping air through filters and XAD resin. Extraction of both with benzene. Concentration.	HPLC/UV-FI	No data	No data	Ny et al. 1993
Creosote	Dissolution in cyclohexane; washing with H ₂ SO ₄ ; neutralization of acid fraction and extraction with cyclo-hexane; alumina column cleanup.	HPLC/UV or GC/MS	No data	No data	Galceran et al. 1994

7. ANALYTICAL METHODS

Table 7-2. Analytical Methods for Determining Creosote/Coal Tar-Derived PAH Components in Environmental Samples (*continued*)

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Water and sediment	Extraction (Soxhlet for sediment only) of PAHs with methylene chloride.	HPLC/ spectro-fluorometric detection	No data	Water - 74.4± 7.8% to 103± 1.1%; Sediment - 71.3± 2.9% to 105± 3.1%	Bestari et al. 1998
Creosote-treated wood	Soxhlet extraction of PAHs with dichloromethane; concentration of extracts and cleanup on silica column eluted with hexane; drying with anhydrous sodium sulfate; extraction in series with hexane, hexane: DCM (60:40); elution with hexane: DCM (60:40).	GC/FID	No data	HMW PAHs - 104±0.9% LMW PAHs - 84±5%	Gevao and Jones 1998
Sediment pore water and elutriate	Drying with anhydrous sodium sulfate; Soxhlet extraction with acetone:hexane (59:41); concentration of extract; cleanup on silica column eluted in series with hexane and dichloromethane; concentration and redissolution in hexane.	GC/FID	2–5 ng/g	No data	Hyötyläinen and Oikari 1999b

7. ANALYTICAL METHODS

Table 7-2. Analytical Methods for Determining Creosote/Coal Tar-Derived PAH Components in Environmental Samples (*continued*)

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Coal tar pitch volatiles on glass filters	Soxhlet extraction with dichloromethane; cleanup on silica columns eluted with cyclohexane; concentration; HPLC separation using backflush.	GC/S-selective AED	4 ng/m ³	Cleanup recoveries were estimated at 97–100%	Becker et al. 1999

AED = atomic emission detection; FI = fluorescence; FID = flame ionization detection; GC = gas chromatography; HMW = high molecular weight; HPLC = high-performance liquid chromatography; LMW = low molecular weight; MS = mass spectrometry; PAH = polycyclic aromatic hydrocarbon; UV = ultraviolet

7. ANALYTICAL METHODS

methods also include on-line purification and coupling of extraction and chromatography. These authors found that MS use has increased, especially since ion traps and mass selective detectors have become more available. Other increasingly common methods are HPLC with fluorescence and diode array UV; and C-, S-, and N-selective GC detectors. The use of HPLC with fluorescence detection allows for a lower limit of detection for some PAHs than does GC/FID.

GC/FID or GC/MS are the most widely employed analytical techniques for the determination of coal-derived PAHs in contaminated ground water, railroad cross ties, and impregnated wood (Gevao and Jones 1998; Heikkilä et al. 1987; King and Barker 1999; Lijinski et al. 1963; Lorenz and Gjovik 1972; Nestler 1974a; Rostad et al. 1984; Rotard and Mailahn 1987). GC/FID is one of the methods recommended by EPA for detection of PAHs in waste water and solid waste (EPA 1986c). GC/FID was utilized by Bieniek (1997) to determine the breathing-zone air concentration of naphthalene in a coking plant. Hyötyäinen and Oikari (1999b) utilized GC/FID to determine PAHs in sediment pore water and elutriates.

Heikkilä et al. (1987; 1997), employed GC/MS to determine creosote levels in workplace air from impregnated wood. Detection limits of 10×10^{-6} to 50×10^{-6} g of creosote per m^3 of sample and recoveries of 82 and 102% were achieved. Heikkilä and co-workers measured the components of PAHs with reverse-phase HPLC using fluorescence detection. A similar study was conducted by Heikkilä et al. (1995) for a worker exposed to coal tar pitch. For the detection of creosote vapors, naphthalene was used as an indicator since it constitutes about 18% by weight of total PAHs in creosote (Andersson et al. 1983; Heikkilä et al. 1987). Rotard and Mailahn (1987) used a modified sample extraction procedure to identify various components of creosote extracts in railroad cross ties. The procedure involved the separation of compounds by functional group using acid, base, and neutral conditions. Detected compounds included phenanthrene, anthracene, and naphthalene (neutral extractions), quinoline, and isoquinoline (basic extraction), cresols, and phenols (acidic extraction). Mohammed et al. (1998) used GC/MS to determine creosote-derived PAHs in aquifer materials. Recent literature has shown that GC with (sulfur selective) atomic emission detection (CG/AED) is successful in determining the thiaarene fraction of total PAHs in the atmosphere without prior separation of the thiaarenes from the PAHs (Becker et al. 1999).

Grimmer et al. (1997) developed a technique using GC/MS for simultaneously determining 25 urinary metabolites as a measure for exposure to individual PAHs. Samples are treated enzymatically with glucuronidase and arylsulfatase and extracted with benzene or toluene; the extract is then divided and one part is treated with diazomethane to convert phenols into methylethers and the other part is used to convert dihydrodiols into phenols. Following further purification, individual metabolites are determined

7. ANALYTICAL METHODS

using GC/MS. The detection limit for various compounds is approximately 0.01 ng. Inter-individual variation was significant. These authors determined that the correlation between inhaled PAHs to their urinary metabolites will vary with the individual, but appeared to be linear for an individual.

Rostad et al. (1984) developed a method for the isolation and detection of creosote in contaminated ground water. This method involved passage of the sample through a small column containing a solid-bonded phase sorbent, which retained the organic compounds. The authors indicated that this method is simple, faster, and cheaper to perform than the acid/base/neutral extraction procedure. It effectively isolated all organic compounds from contaminated ground water regardless of polarity, functional group, or water solubility in one step, thereby minimizing hazardous exposure to sample.

A study on the spatial and temporal distribution of PAHs from various sources (wood-preserving facilities, refineries, chemical manufacturers, etc.) was reported by Huntley et al. (1995). The concentrations of PAHs were shown to increase with sediment depth from analysis of core samples. Samples were analyzed using EPA Method 8310 (GC/MS).

HPLC with fluorescence detection has been used to identify coal-derived PAHs in river sediments (Black 1982). Andersson et al. (1983) employed an Amberlite XAD-2 adsorbent for isolating organic compounds from gas and particulate matter in a creosote impregnating plant. Good sample recoveries and detection limits were achieved. HPLC, with either fluorescence or UV detection, is an EPA-recommended method for the analysis of both solid and liquid hazardous waste (EPA 1986c). At present, HPLC cannot achieve the high resolution capability of capillary GC. HPLC, however, does offer some advantages for the determination of coal-derived PAHs in environmental samples. HPLC offers a variety of stationary phases capable of providing unique selectivity for the separation of PAH components and/or isomers that are often difficult to separate by GC. In addition, UV absorption and fluorescence detection provide sensitive and selective detection of PAHs. Rogaczaska and Ligocka (1991) reported results of a study of occupational exposure to coal tar pitch volatiles, including benzo[a]pyrene (B[a]P), by measuring B[a]P in air using HPLC with fluorescence detection.

An acid partition and alumina column clean-up procedures were used to analyze for several acridines (HPLC/UV) in creosote by Galceran et al. (1994). HPLC with fluorescence detection was used for analysis of the PAH components from a coal tar sample (NIST SRM 1597) as reported in a review article by Wise et al. (1993). Since fluorescence detection affords more selectivity than UV absorbance detection, less clean-up is required for certain sample types. This study also showed the utility of a multi-dimensional approach to PAH analysis from complex samples. This methodology involves use of normal

7. ANALYTICAL METHODS

phase liquid chromatography (LC) to separate PAH fractions, which can then be analyzed by reverse phase LC with fluorescence. Coal tar pitch has also been analyzed using planar chromatography as an initial fractionation technique (Herod and Kandiyoti 1995). The resultant fractions were analyzed either directly on the silica by MS, or were extracted from the silica for further fractionation using size exclusion chromatography. The approach yielded structural information not readily available from direct characterization of the original mixture.

7.3 ADEQUACY OF THE DATABASE

Section 104(I)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of creosote is available. Where adequate information is not available, ATSDR, in conjunction with the National Toxicology Program (NTP), is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of creosote.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

7.3.1 Identification of Data Needs

Methods for Determining Biomarkers of Exposure and Effect. Wood creosote and coal-derived tars are complex mixtures of organic compounds. Virtually all potential human and ecological exposures in the natural environment are limited to the coal-derived tars and not wood creosote, which is used medicinally. Sensitive methods exist for measuring components of the coal-derived mixtures in biological media. Most of these methods involve detection of PAHs, the predominant components of creosote, and their metabolites (Amin et al. 1982; Harris et al. 1985; Haugen et al. 1986; Newman et al.

7. ANALYTICAL METHODS

1988; Ny et al. 1993; Perera et al. 1988; Tolos et al. 1990). These analytical methods can reliably detect trace levels of PAHs in human tissues and body fluids, making them sensitive enough to measure background levels in the population, as well as levels at which biological effects might occur. PAHs, however, are not unique to creosote exposure. Analytical methods currently exist which are sensitive and selective enough to measure possibly unique or unusual components of creosote, and are capable of yielding a unique "fingerprint" for the mixture. These would be useful in monitoring exposures that might occur in work environments and near hazardous waste sites where creosote has been detected. Although these capabilities exist, they have not been applied except in the case of the pyrene biomarker discussed earlier.

The analytical methods for measuring PAHs and their metabolites in biological tissues and fluids are sensitive enough to measure levels at which health effects might occur, as well as background levels in the population. Methods also exist for measuring PAH-DNA adducts (Harris et al. 1985; Phillips et al. 1988), and research efforts are underway to develop methods that will detect ultratrace levels of these adducts in biological media. The increased sensitivity may allow correlation between levels of these adducts and observed health effects of PAH exposure related to coal products. There is also a need for methods to quantitatively correlate monitored levels of various PAHs in biological tissues or fluids to toxic effects in humans. Methods dependent on monitoring PAHs, however, are not specific for coal-derived products exposure. Methods sensitive and selective enough to detect a unique component or group of components making up the mixture would allow a more accurate assessment of the health effects associated with exposure to monitored levels of creosote and tars. The use of 1-pyrenol as illustrated above is an example of such an approach. Additional methods, targeting the detection of unique components of coal tar, coal tar creosote, and coal tar pitch in biological samples, would facilitate detection of exposure to these mixtures.

Methods for Determining Parent Compounds and Degradation Products in Environmental Media. Reliable and sensitive methods are available for measuring PAHs from creosote and tars in soil or sediments (Black 1982), water (Mueller et al. 1991; Rostad et al. 1984), air (Ny et al. 1993; Rogaczewska and Ligocka 1991; Tolos et al. 1990), and other environmental media. Exposure to such materials is most likely to occur in industrial settings where coal-derived tars are manufactured or used. Creosote-contaminated water and soil are a concern in areas near hazardous waste sites and other areas where creosote might be concentrated. The analytical methods available are accurate and sensitive enough to quantitatively detect PAHs from creosote and tars in these and other environmental media, and are effective for estimating creosote levels in media known to be contaminated with this substance. There is a lack of sensitive and reliable methods for detecting and measuring creosote and coal tar degradation

7. ANALYTICAL METHODS

products in environmental media. Development of such methods would allow assessment of the potential exposure to these products.

The minimal use of wood creosote for other than medicinal purposes probably argues against a pressing need for analytical methods for environmental monitoring of this substance. The rather short half-life of phenolic substances under most environmental conditions increases the difficulty of developing such assay methods.

7.3.2 Ongoing Studies

No ongoing studies concerning techniques for measuring and determining creosote in biological and environmental samples were reported.

