

## 6. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods that are available for detecting and/or measuring and monitoring JP-4 and JP-7 in environmental media and in biological samples. The intent is not to provide an exhaustive list of analytical methods that could be used to detect and quantify JP-4 and JP-7. Rather, the intention is to identify well-established methods that are used as the standard methods of analysis. Many of the analytical methods used to detect JP-4 and JP-7 in environmental samples are the methods approved by federal 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 refine previously used methods to obtain lower detection limits, and/or to improve accuracy and precision.

### 6.1 BIOLOGICAL SAMPLES

No analytical methods were located for detecting either JP-4 or JP-7 in biological samples. For analytical methods information on some hydrocarbon components of jet fuels, see the ATSDR toxicological profiles for benzene (ATSDR 1991a), toluene (ATSDR 1990), xylenes (ATSDR 1991c), and polycyclic aromatic hydrocarbons (ATSDR 1991b).

### 6.2 ENVIRONMENTAL SAMPLES

Since JP-4 and JP-7 are composed of a complex mixture of hydrocarbons, there are few methods for the analysis of all of these components in environmental samples, but methods are reported for the analysis of some of the individual components or the amount of total hydrocarbon in the mixture (IARC 1989). The analysis of individual components usually involves separation of the components by column chromatography (i.e., packed or capillary column) followed by a suitable quantification method. These methods included gas chromatography (GC) and high-resolution gas chromatography (HRGC) combined with flame ionization detector (FID), or infrared (IR) spectroscopy. GC combined with mass spectrometry (MS) has been used to identify the principal hydrocarbon components present in jet fuels. Nuclear magnetic resonance (NMR), supercritical fluid chromatography (SFC)/FID, and laser raman spectroscopy can be used specifically to characterize the aromatic hydrocarbon makeup for

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JP-4 and JP-7 (Clarke et al. 1991; Di Sanzo and Yoder 1991; DOE 1981). Although no methods were located specifically for analyzing JP-7 in environmental samples, the methods used to measure the hydrocarbon components of JP-4 can be used for measuring the hydrocarbon components of JP-7. The few analytical methods that have been used are summarized in Table 6-1. Several of the jet fuel components have been discussed in detail in their individual ATSDR toxicological profiles (e.g., benzene and polycyclic aromatic hydrocarbons), which should be consulted for more information on analytical methods (ATSDR 1991a, 1991b).

Analytical methods for detecting JP-4 and jet fuel (petroleum naphtha and kerosene vapors) in air include IR spectroscopy and GC/FID (IARC 1989; NIOSH 1984; Thomas and Richardson 1981). The total hydrocarbon content of JP-4 in air can be determined by IR spectroscopy. The IR technique is best adapted to pure hydrocarbon exposures, such as exposure to JP-4. For both methods, samples are collected with either charcoal tubes or vapor monitor badges. Poor recovery (<75%) was obtained with the IR method using only Freon®113 as a desorbent. Recovery was improved (86-88%) using a mixture of Freon®113 and perchloroethylene. For the IR method, precision was excellent, ranging from 0.006% to 0.020% coefficient of variation (CV). Recoveries with the GCLFID method were excellent (97-101%) (NIOSH 1984; Thomas and Richardson 1981). For the GC/FID method, precision was also excellent (0.052% relative standard deviation [RSD]) (NIOSH 1984). Sensitivity for both methods is in the ppm range (IARC 1989; NIOSH 1984; Thomas and Richardson 1981).

GC/FID, HRGCLFID, and IR spectroscopy have been used to measure JP-4 in water (Puyear et al. 1981; Roberts and Thomas 1986). GCLFID was used to measure the major water-soluble hydrocarbons, the aliphatics and alkylbenzenes, of JP-4 (Puyear et al. 1981). The average recovery of all hydrocarbons tested (aliphatics and alkylbenzenes) was 43-72%; however, the recovery of the aliphatics only was 90-94% (Puyear et al. 1981). Overall recovery was improved from 43% to 72% with the use of ethyl acetate as an extraction solvent for JP-4. Under the chromatographic conditions used, the individual aliphatics were not well resolved. However, the alkylbenzenes were well separated and quantitation of each component was possible (Puyear et al. 1981). Sensitivity and precision were not reported (Puyear et al. 1981). The total hydrocarbon content of JP-4 in water can also be determined by IR spectroscopy (EPA 1978; Roberts and Thomas 1986) and fluorescence spectroscopy (ASTM 1982). Since JP-4 has a distinctive gas chromatographic profile, it is possible to distinguish JP-4 from other fuels present in environmental samples by examining selected peak areas or peak ratios for certain hydrocarbons (Roberts and Thomas 1986).

TABLE 6-1. Analytical Methods for Determining JP-4 and JP-7 in Environmental Samples

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Air (JP-4)	Collect air samples on charcoal tubes or vapor monitor badges; desorb hydrocarbons with Freon®113/perchloroethylene (for IR method); desorb with carbon disulfide (for GC/FID method)	IR	0.4 mg/m <sup>3</sup>	86-88	Thomas and Richardson 1981
		GC/FID	NR	≥98	NIOSH 1984
Air (petroleum naphtha and kerosene vapors)	Collect air sample on charcoal tube; desorb with carbon disulfide; inject aliquot	GC/FID	5 mg/m <sup>3</sup>	97	IARC 1989; NIOSH 1984
Water (JP-4)	Concentrate water-soluble hydrocarbon components of JP-4 on Sep-Pak®; elute with ethyl acetate	GC/FID	NR	72	Puyear et al. 1981
Water (Total petroleum hydrocarbon)	Sample acidified to pH <2 extracted with Freon®113, extract passed through silica gel absorbent (EPA Method 418.1)	IR	<1 mg/L	NR	EPA 1978
Water (total petroleum hydrocarbon)	Extract with cyclohexane (ASTM D3650)	Fluorescence spectroscopy	NR	NR	ASTM 1982
Groundwater (JP-4)	Extract water sample with Freon®113; analyze by IR	IR	NR	NR	Roberts and Thomas 1986
		HRGC/FID	NR	NR	Roberts and Thomas 1986
Soil (JP-4)	Extract sample with methylene chloride in ultrasonic bath; clean up on microcolumn	GC/FID; GC/MS	NR	83.9	Vandegrift and Kampbell 1988

FID = flame ionization detector; GC = gas chromatography; HRGC = high-resolution gas chromatography; IR = infrared spectroscopy; JP-4 = jet propellant-4; JP-7 = jet propellant-7; MS = mass spectrometry; NR = not reported.

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GC/FID has been used to quantify JP-4 in soil samples, while GC/MS has been used to identify the principal components in JP-4 (Vandegrift and Kampbell 1988). Sample preparation for GC/FID included extracting the fuel from soil with methylene chloride in an ultrasonic bath. Recovery was good (83.9%). Precision was adequate (12.6% CV). Sensitivity was in the low-ppm range (Vandegrift and Kampbell 1988).

Other methods reported for the analysis of the aromatic components in aircraft fuels, including JP-4, include HRGC combined with an ultraviolet detector (UVD), photoionization detector (PID), and GC combined with a nitrogen specific alkali-flame detector (AFD) (Air Force 1982a). Sample preparation includes fractionation of the fuel into an aromatic fraction and a nonaromatic fraction. The fractionation is accomplished by using adsorption column chromatography with silica gel, alumina, or Florisil. The aromatic fraction is then eluted using moderately polar solvents such as methylene chloride, benzene, or ethyl ether. The UV detector is specific for aromatic compounds. The estimated detection limits for benzenes and naphthalenes were 10 µg/mL and 2 µg/mL, respectively. Precision ranged from 5% to 10%. The photoionization detector is about 10 times as sensitive as a UVD or FID for the detection of aromatic hydrocarbons, although it does not provide the selectivity obtainable with the UVD. Nitrogen-containing compounds in fuels are detected using a nitrogen-specific AFD. A gas chromatographic method involving the simultaneous use of a UVD, FID, and AFD was recommended as a rapid, inexpensive, and selective method for the analysis of aircraft fuels (Air Force 1982a).

### 6.3 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 JP-4 and JP-7 is available. Where adequate information is not available, ATSDR, in conjunction with 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 JP-4 and JP-7.

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 or eliminate the uncertainties of human health assessment. This definition should not be

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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 may be proposed.

### 6.3.1 Identification of Data Needs

**Methods for Determining Biomarkers of Exposure and Effect.** No biomarkers of exposure were identified for JP-4 or JP-7. No standard procedures exist for identifying or quantifying exposure to JP-4 or JP-7 in biological media. Therefore, it is not possible to state whether existing methods are sensitive to measure background levels in the population or levels at which health effects occur. Biomonitoring studies are needed to adequately assess exposure to JP-4 and JP-7.

No biomarkers of effect were found for JP-7. Potential biomarkers for neurological effects of JP-4 are mild muscular weakness, staggering gait, and decreased sensitivity to painful stimuli (Davies 1964). No standard procedures exist for identifying and quantifying these biomarkers of effect for JP-4.

### Methods for Determining Parent Compounds and Degradation Products in

**Environmental Media.** Methods exist for measuring the hydrocarbon components of jet fuels, specifically JP-4, in air, water, and soil (IARC 1989; NIOSH 1984; Puyear et al. 1981; Roberts and Thomas 1986; Thomas and Richardson 1981; Vandegrift and Kampbell 1988). Although no methods were located specifically for analyzing JP-7 in environmental samples, the methods used to measure the hydrocarbon components of JP-4 can be used for measuring the hydrocarbon components of JP-7. These methods are relatively sensitive, selective, and reliable and can be used to detect the levels of jet fuel components found in the environment and levels at which health effects occur. Sensitivity and precision data are needed for measuring the components in water. These data will aid in comparison of sensitivity and precision between methods and indicate where improvements in sensitivity are needed. This information will be useful in monitoring contamination in the environment,

### 6.3.2 Ongoing Studies

The Environmental Health Laboratory Sciences Division of the Center for Environmental Health and Injury Control, Centers for Disease Control and Prevention, is developing methods for the analysis of certain components of JP-4 and JP-7 and other volatile organic compounds in blood. These methods

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use purge and trap methodology and magnetic sector mass spectrometry which gives detection limits in the low parts per trillion range.

No other ongoing studies were located for JP-4 or JP-7.