

## 6. ANALYTICAL METHODS

### 6.2 ENVIRONMENTAL SAMPLES

As with biological materials, detection of Stoddard solvent in environmental samples is based on the detection of component hydrocarbons. See Table 6-2 for a summary of the analytical methods used to determine Stoddard solvent hydrocarbons in environmental samples.

The primary method for detecting volatile components of Stoddard solvent in air is GC using a flame ionization detector (FID) (NIOSH 1984; Otson et al. 1983). Stoddard solvent in air may be determined by absorption to an appropriate column such as charcoal, desorption in a solvent (carbon disulfide is recommended), and subsequent quantification. Although the precision of this method is good (greater than 10% relative standard deviation when the recovery is greater than 80%), in general, recovery tends to be rather poor (18-80%) because of the slow volatilization of Stoddard solvent (Otson et al. 1983).

No analytical methods specific for Stoddard solvent in water or soil samples were located; however, determination of Stoddard solvent may be assumed to be similar to the detection of comparable hydrocarbon mixtures. Detection of Stoddard solvent in water is dependent on the identification and quantification of the specific hydrocarbon components of the solvent. The primary method, GC either alone or in combination with MS, may be used for the identification of the major hydrocarbon components, i.e., *n*-alkanes, branched alkanes, cycloalkanes, and alkylbenzenes. Separation of the aliphatic and aromatic fractions may be achieved by liquid-solid column chromatography followed by dilution of the eluates with carbon disulfide. Aqueous samples may be extracted with trichlorotrifluoroethane, while solid samples may be extracted by Soxhlet extraction or sonication methods (Air Force 1989). Purgeable (volatile) aromatics may be determined with a purge-and-trap apparatus. This method requires a trap with a Tenax/Chromosorb absorbent and the use of GC with a photoionization detector (PID) (EPA 1991c), an ion trap detector (ITD), or FID (Thomas and Delfino 1991). A modification of the purge-and-trap method uses ambient temperature, has the advantage of being applicable to a variety of waters, requires virtually no sample preparation (no solvents are required for desorbing the hydrocarbons), and has an analysis time of approximately 30 minutes (Bianchi et al. 1991). While this method may be used for determining the presence of industrial solvent mixtures in water, it cannot distinguish between various sources of this contamination, e.g., gasoline, kerosene, Stoddard solvent.

**TABLE 6-2. Analytical Methods for Determining Stoddard Solvent in Environmental Samples**

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Air	Adsorb to solid sorbent tube (e.g., charcoal); desorb in CS <sub>2</sub> ; equilibrate; inject aliquot to GC	GC/FID	0.1 mg/5–10-mL sample	96–106	NIOSH 1984
Air	Adsorb to charcoal tube; extract with CS <sub>2</sub> ; inject extract to GC	GC/FID	<50 µg/L	78–91; 106	Otson et al. 1983
Water	Strip sample in sparger with helium; adsorb effluent gas to adsorption tube; thermally desorb to GC	GC/FID/MS	10 µg/L	89.7–95.7	Bianchi et al. 1991
Water (purgeable aromatics)	Purge sample with inert gas; adsorb vapor in trap; heat trap; backflush to GC	GC/PID	0.2 µg/L	92–96	EPA 1991c
Soil (other solid materials)	Extract sample with CCl <sub>4</sub> ; inject extract	GLC	NR	NR	Midkiff and Washington 1972

**TABLE 6-2. Analytical Methods for Determining Stoddard Solvent in Environmental Samples (*continued*)**

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Soil	Extract sample with $\text{CCl}_4$ ; centrifuge; remove water and humic materials with $\text{Na}_2\text{SO}_4$ and $\text{Al}_2\text{O}_3$ ; inject extract	GC/FID	NR	NR	Galín et al. 1990a
Sediment	Add internal sample to sample; extract with KOH in methanol; partition into petroleum ether; concentrate; purify and isolate hydrocarbon fractions using TLC or column chromatography	GLC/FID	NR	NR	Gearing et al. 1980

$\text{Al}_2\text{O}_3$  = aluminum oxide;  $\text{CCl}_4$  = carbon tetrachloride;  $\text{CS}_2$  = carbon disulfide; FID = flame ionization detector; GC = gas chromatograph(y); GLC = gas liquid chromatography; KOH = potassium hydroxide; MS = mass spectrometry;  $\text{Na}_2\text{SO}_4$  = sodium sulfate; NR = not reported; PID = photoionization detector; TLC = thin-layer chromatography

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Although no analytical methods were identified for determining the presence of Stoddard solvent in soil samples, methods do exist for detecting other hydrocarbon mixtures, such as kerosene, and these may be applicable to Stoddard solvent. Two methods that have been used for petroleum distillates include GC/FID (Galín et al. 1990) and gas liquid chromatography (GLC) with FID (Midkiff and Washington 1972). Soil samples are extracted with carbon tetrachloride. Recovery, sensitivity, and levels of detection data were not reported. Quantification of oils and grease, by gross weight only, in soils and sludges may be accomplished by extraction with a Soxhlet apparatus using either trichlorotrifluoroethane (APHA 1985) or methylene chloride (Martin et al. 1991) as the solvent, although this method is qualitative, not quantitative, and cannot be used to identify the type of oil or grease bound to the soil.

While no analytical methods were located that are specific for detecting Stoddard solvent in sediment, as with water and soil, methods that detect other hydrocarbon mixtures may be applicable. For example, quantification of fuel oil hydrocarbons from sediments is a relatively involved process. Following extraction, the saturated and olefinic hydrocarbon fraction is separated from the aromatic hydrocarbon fraction using thin-layer chromatography or column chromatography. Fractions are subsequently analyzed by GLC (Gearing et al. 1980).

### 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 Stoddard solvent 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 Stoddard solvent.

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 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.

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### 6.3.1 Identification of Data Needs

**Methods for Determining Biomarkers of Exposure and Effect.** There are no known methods for determining biomarkers of exposure or effect that are specific to Stoddard solvent. Components of white spirit have been identified in human blood, fat, and alveolar air using GC-MS. Further information of this type, including the possible identification of a trace compound(s) for Stoddard solvent as well as information on its metabolites in humans, would be useful for determining whether an individual has been exposed to Stoddard solvent. It has been suggested that elevated levels of dimethylbenzoic acid or dimethylhippuric acid, metabolites of trimethylbenzene, in the urine may be indicative to exposure to Stoddard solvent (Fukaya et al. 1994; Pfaffli et al. 1985). Metabolites of t-butylcyclohexane, another component of white spirits, were found in rat urine (Henningesen et al. 1987). Further studies concerning the use of these compounds as biomarkers of exposure are needed.

**Methods for Determining Parent Compounds and Degradation Products in Environmental Media.** Although no specific methods were located for measuring Stoddard solvent in soil or water, methods do exist for measuring particular hydrocarbon components of Stoddard solvent, such as 2,6-dimethyloctane, based on analysis with GC. In addition, it may be possible to identify Stoddard solvent based on characteristic ratios of hydrocarbon components, but such ratios have not been established. An analytical method does exist for determining Stoddard solvent in air using GC/FID (NIOSH 1984; Otson et al. 1983). The precision of the method is good, but recovery is poor. Some methods for detecting hydrocarbon fractions for other hydrocarbon mixtures (e.g., gasoline, fuel oils) in environmental media may be applicable to Stoddard solvent (Bianchi et al. 1991; Gearing et al. 1980; Midkiff and Washington 1972) but should be subjected to further analysis to determine their precision, recovery, and selectivity when used for Stoddard solvent. In addition, methods should be developed to distinguish between contamination from Stoddard solvent versus other petroleum distillates. At present, knowledge on the exact hydrocarbon components and their ratios in various hydrocarbon mixtures (e.g., kerosene, Stoddard solvent, and paint thinners) is scarce, and more precise numbers would facilitate the determination of the exact hydrocarbon mixture present in environmental samples. This would be particularly useful for determining hydrocarbon wastes and contamination at hazardous waste sites where several such mixtures may be present.

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### 6.3.2 On-going Studies

No on-going studies were located for Stoddard solvent.