

TECHNICAL NOTE

John J. Lentini,¹ B.A. and Andrew T. Armstrong,² Ph.D.

Comparison of the Eluting Efficiency of Carbon Disulfide with Diethyl Ether: The Case for Laboratory Safety

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ABSTRACT: Carbon disulfide is the solvent of choice for eluting adsorption packages prior to analysis by GC/FID. In laboratories which utilize mass selective detectors instead of flame ionization detectors, diethyl ether, a much friendlier solvent, can be used in place of the CS₂. No loss of sensitivity occurs, and there is a salutary impact on bench workers' health as well as on the aroma of the fire debris laboratory.

KEYWORDS: forensic science, fire debris analysis, carbon disulfide, diethyl ether, adsorption/elution, laboratory safety

Carbon disulfide (CS₂) has long been the "solvent of choice" for the elution of adsorption packages used in fire debris analysis. The selection of CS₂ stems from its selection by the industrial hygiene community because of its efficiency at displacing materials adsorbed on charcoal, and because of its minimal response with flame ionization detection (1). The application of activated charcoal for the adsorption of organic vapors and desorption of carbon disulfide was described as early as 1964 by Otterson and Guy (2). When adsorption/elution techniques developed by the Bureau of Alcohol Tobacco and Firearms were first applied to fire debris analysis, carbon disulfide was the solvent of choice. Early articles describing this application have been widely promulgated through the ATF's Arson Accelerant Detection Course (3,4).

Other solvents have been used during the development of adsorption/elution technology, particularly when the adsorbing medium is something other than charcoal. Diethyl ether has been described as a suitable desorption solvent for silica gel, activated alumina, porous polymers, and GC packings, as well as for activated charcoal (5).

Although carbon disulfide does an adequate job of elution, its primary advantage is the small signal which it produces when passing through a flame ionization detector. Hydrocarbon solvents tend to produce very large peaks, which obscure the early region of the chromatogram.

Carbon disulfide, however, is one of the most dangerous liquids

used in forensic laboratories today. It has a wide flammable range, and an auto-ignition temperature of 90°C, and is easily capable of being ignited by contact with heated surfaces, such as injection ports, or with hot water. Additionally, chronic exposure to carbon disulfide vapors can lead to an impressive array of diseases affecting the brain, heart, kidney, liver, and eyes. The strong unpleasant odor of carbon disulfide, often described as similar to rotten brocoli, is actually a benefit, in that laboratory workers can be alerted to the fact that the solvent has gotten loose in their environment, but it would seem that if it is possible to avoid the use of this solvent, steps should be taken in that direction.

Many forensic laboratories now routinely use mass selective detectors (MSD) for the analysis of fire debris samples. The MSD is turned off while the solvent is eluting, and therefore, any solvent which does an adequate job of displacing the analyte from the sorbent will provide acceptable result. The desorption efficiency of a particular solvent has been described as one of the first indicators of potential utility in a suggested method of adsorption/elution, and one parameter which is relatively easy to determine experimentally (5).

This study was undertaken to explore the use of diethyl ether as an eluting solvent prior to analysis by GC/MS. Diethyl ether, although it has a reputation for forming explosive peroxides when left unattended for long periods of time, has been found to be an effective substitute which poses far fewer hazards to laboratory workers. Although both the vapor density and the flammability ranges of ether and carbon disulfide are nearly equal, and both present significant fire hazards, the lower ignition temperature of carbon disulfide makes it more dangerous with respect to flammability as well as to health. Figures 1 and 2 show the flammability, exposure limits, and chronic inhalation warnings from The Fisher Scientific material safety data sheets (MSDS) for carbon disulfide and diethyl ether. Exposure limits for diethyl ether are generally about 40 times higher than those for carbon disulfide. Certainly, both solvents can be used safely, but in the event of a spill or a breakdown of ventilation equipment, the health risks posed by diethyl ether are significantly less than those posed by CS₂.

Methods and Materials

Six Protek® (Albrayco Labs, Cromwell, CT) charcoal strips, which had been punched into 0.3 cm² disks were suspended above a piece of filter paper onto which 10 µL of a test mixture had been added. The test mixture consisted of roughly equal quantities

¹Manager, Fire Investigations, Applied Technical Services, Inc., Marietta, GA 30066.

²Vice president, Armstrong Forensic Laboratories, Arlington, TX 76012.

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Carbon Disulfide Hazards

FIRE AND EXPLOSION HAZARD:

Dangerous fire hazard when exposed to heat or flame.

Dangerous explosion hazard when exposed to heat or flame.

Vapors are heavier than air and may travel a considerable distance to a source of ignition and flash back.

Vapor-air mixtures are explosive.

Due to low electroconductivity of the substance, flow or agitation may generate electrostatic charges resulting in sparks with possible ignition.

FLASH POINT: -22 F (-30 C) (CC)

UPPER EXPLOSIVE LIMIT: 50.0%

LOWER EXPLOSIVE LIMIT: 1.0%

AUTOIGNITION TEMP.: 194 F (90 C)

EXPOSURE LIMITS:

4 ppm (12 mg/m³) OSHA TWA (skin); 12 ppm (36 mg/m³) OSHA STEL

10 ppm (30 mg/m³) ACGIH TWA (skin)

1 ppm (3 mg/m³) NIOSH recommended 10 hour TWA (skin)

10 ppm (30 mg/m³) NIOSH recommended STEL

10 ppm (30 mg/m³) DFG MAK TWA (skin);

20 ppm (60 mg/m³) DFG MAK 30 minute peak, average value, 4 times/shift

500 ppm Immediately Dangerous to Life or Health.

CHRONIC INHALATION EXPOSURE:

Prolonged or repeated exposure may cause neurologic effects including headache, apprehension, lethargy, sleepiness, hearing and position sense loss, paresthesias, muscle pain, tremors, ataxia, staggering gait, weakness, loss of lower extremity reflexes, and paralysis. Retrobulbar neuritis may occur and be characterized by central scotoma, decreased visual acuity, impaired recognition of red and green, optic nerve atrophy, nystagmus diplopia, and disturbed pupillary reaction to light. A decrease in corneal reflex may be an early indication of chronic intoxication. Concentrations as low as 20 ppm have been shown to produce neurologic damage.

Women may be more sensitive to the neurotoxic effects than men. Psychiatric symptoms may include memory loss, bad dreams leading to insomnia, mental deterioration, acoustic and visual hallucinations, and rapid mood changes ranging from irritability to manic-depressive psychoses, especially maniacal. Suicidal tendencies have also been reported. Functional modifications in muscular and nervous systems have been reported following exposure to 1-10 ppm/9 months. Liver damage may be indicated by palpable, tender liver and minor derangements of liver function. Interference with trace minerals and inhibition of enzyme systems may result from long-term exposures. Cholesterol and lipid substances may accumulate in vessel walls and stimulate atherosclerosis, which may affect the brain, kidney, heart, and retinal vessels. Signs of atherosclerosis with hypertension have been reported to occur at 7-20 ppm, and diabetogenic changes at 20 ppm. Vascular encephalopathy has been reported to occur at 10-482 ppm. Secondary neurologic and neuropsychologic effects may occur due to the encephalopathy. Chronic renal dysfunction may occur from long-term exposure to concentrations that are not intense enough to induce neurologic deficiencies. Angina pectoris, hypertension, arrhythmias, and ECG changes consisted with ischemia have been reported in workers, as well as an increased mortality from coronary heart disease. Gastric or duodenal ulcers may also be evident. Periodontic changes have been reported to occur at 6-22 ppm. Pathologic findings include degeneration of the gray matter in the brain and cerebellum, changes in the pons and spinal cord, degenerative changes in peripheral nerves and sheaths, and atrophy, hypertrophy and hyaline degeneration of muscle fibers. Disturbances of sexual dynamics including loss of libido and impotence, and effects on sperm have been reported in workers exposed to 13-26 ppm with peaks up to 250 ppm. Exposure to 3 ppm has produced menstrual and ovarian functional disorders in women, and an increased risk of spontaneous abortion around 9 ppm. The occurrence of irregular menses increased with the length of exposure. Reproductive effects have also been reported in animals.

FIG. 1—Flammability, exposure limits, and inhalation toxicity warnings from the Fisher Material Safety Data Sheets for carbon disulfide.

of the normal alkanes from C₆ through C₂₀, toluene, para-xylene, meta-ethyltoluene, ortho-ethyltoluene, and 1,2,4-trimethylbenzene (pseudocumene). A second can, containing an accelerant mixture consisting of 5 μ L each of 50% evaporated gasoline and 50% evaporated diesel fuel, was run side-by-side with the test mixture.

Sample cans were heated to 80°C for a period of 16 h, at which time, the disks were removed and eluted. Three of the disks were eluted with 0.50 mL of carbon disulfide (Fisher Spectranalyzed®)

and three were eluted with 0.50 mL of diethyl ether (Sigma-Aldrich HPLC Grade). Both of the eluting solvents had been spiked with tetrachloroethylene (EM Science, 98%, stabilized), which was used as an internal standard. 0.05% v/v was added to the solvents used for eluting the test mixture, and 0.01% v/v was added to the solvent used for eluting the gasoline/diesel fuel mixture. Samples were allowed to equilibrate for 30 min before being placed in the autosampler.

Diethyl Ether Hazards

FIRE AND EXPLOSION HAZARD:

Dangerous fire and explosion hazard when exposed to heat or flame.

May accumulate static electric charges that result in ignition of its vapors.

Vapor-air mixtures are explosive.

May form explosive peroxides if exposed to air or light for long periods of time.

Vapors are heavier than air and may travel a considerable distance to source of ignition and flashback.

FLASH POINT: -49 F (-45 C) (CC) UPPER EXPLOSIVE LIMIT: 48.0%

LOWER EXPLOSIVE LIMIT: 1.9% AUTOIGNITION TEMP.: 356 F (180 C)

EXPOSURE LIMITS:

400 ppm (1210 mg/m³) OSHA TWA; 500 ppm (1520 mg/m³) OSHA STEL

400 ppm (1210 mg/m³) ACGIH TWA; 500 ppm (1520 mg/m³) ACGIH STEL

400 ppm (1210 mg/m³) DFG MAK TWA;

800 ppm (2420 mg/m³) DFG MAK 30 minute peak, average value, 4 times/shift

19,000 ppm Immediately Dangerous to Life or Health.

CHRONIC INHALATION EXPOSURE:

Repeated or prolonged exposure may cause anorexia, exhaustion, headache, drowsiness, dizziness, excitation, and psychic disturbances. Damage to the liver and kidney may occur. Tolerance may be acquired through repeated exposures.

FIG. 2—Flammability, exposure limits, and inhalation toxicity warnings from the Fisher Material Safety Data Sheets for diethyl ether.

TABLE 1—Chromatographic parameters.

Parameters	
Instrument	Hewlett-Packard Model 5890 Series II gas chromatograph Hewlett-Packard Model 5971A mass selective detector Hewlett-Packard Model 7673 automatic liquid sampler (Hewlett-Packard, Avondale, PA)
Column	HP 1 nonpolar capillary, 25 m by 0.2 mm ID, 0.5 μm film thickness.
Carrier	Helium at 100 kPa.
Injection	1 mL, splitless.
Temperature Program	
Initial Temperature	60°C
Initial Hold	6 min.
Ramp Rate	20°C/min
Final Temperature	280°C
Final Hold	4 min
Total Run Time	21 min
Mass Spectrometer	
Solvent Off Time	0.3–1.5 min
Ions Scanned (Scan Mode)	33–300 amμ
Ions Scanned (SIM Mode)	31, 45, 55, 57, 71, 78, 83, 91, 105, 117, 119, 128, 131, 142, 156, 168
Dwell Time per Ion Ionization	50 msec Electron Impact

TABLE 2—Recoveries using ether versus CS₂.

Analyte	% Recovery (CS ₂ = 100)*
Aliphatics (average)	95
n-Hexane	83
n-Heptane	86
n-Octane	105
n-Nonane	116
n-Decane	120
n-Undecane	118
n-Dodecane	118
n-Tridecane	109
n-Tetradecane	97
n-Pentadecane	89
n-Hexadecane	90
n-Heptadecane	87
n-Octadecane	84
n-Nonadecane	82
n-Eicosane	93
Aromatics (average)	100
Toluene (91)	82
p-Xylene (91)	101
m-Ethyltoluene (105)	110
o-Ethyltoluene (105)	104
1,2,4-Trimethylbenzene (105)	103

*Average of three samples, normalized to the 168 ion of the internal standard, 0.05% v/v tetrachloroethylene.

Samples were analyzed using a Hewlett-Packard 5890 Series II gas chromatograph with a 25 m HP1 column, connected to a Hewlett-Packard Model 5971A mass selective detector, operating in the SIM mode. Chromatographic parameters are shown in Table 1.

Data Analysis

For the normal alkanes, peak areas were collected using Ion 57, and normalizing those areas to the area of the peak of Ion 168, generated by the tetrachloroethylene internal standard. For the aromatics, Ions 91 and 105 were collected, and again, the areas

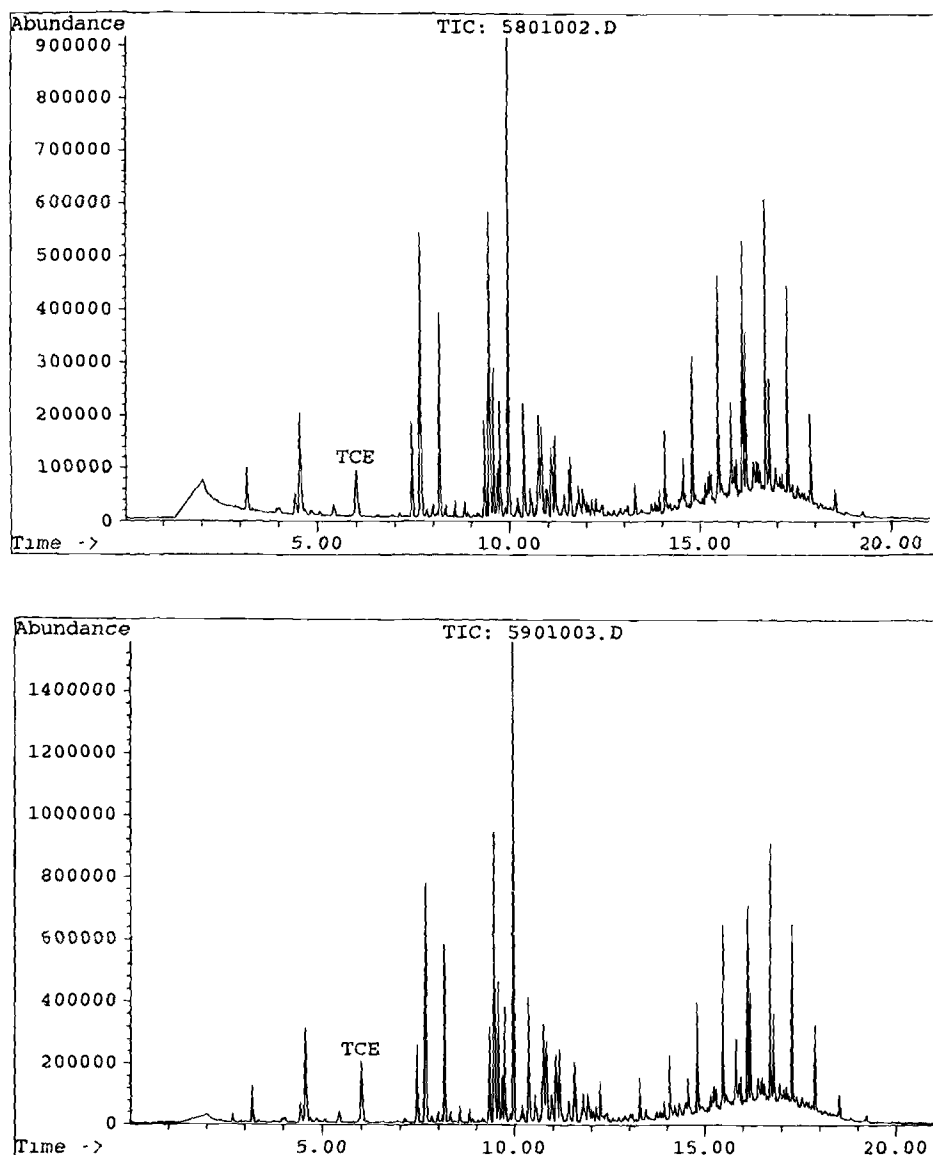


FIG. 3—Total ion chromatograms for 10 μ L of a mixture of 50% weathered gasoline and 50% weathered diesel fuel, adsorbed according to ASTM E 1412 and eluted with CS_2 (top) and diethyl ether (bottom).

of those peaks were normalized to the area of the Ion 168 peak produced by the tetrachloroethylene. Relative recoveries are reported in Table 2.

Results

The relative areas of the alkane peaks produced by the ether solution ranged from 82 to 120% of the areas of the peaks from the carbon disulfide solutions. On average, the 15 normal alkanes in the ether solution gave a signal 95% as strong as the peaks within the carbon disulfide solution.

The range of ratios was 82 to 110% for the aromatics, but on average, the aromatics in the ether solution gave peaks equal in size to the aromatics in the carbon disulfide solution. No significant differences were detected in the abilities of carbon disulfide and ether to elute the test mixture successfully. Equilibration time beyond 30 min had no apparent effect on the recovery rate. (The first 30 min of any batch run is usually taken up by running a blank sample.) No significant differences were noted in the size

or appearance of the profile of peaks from the ignitable liquid mixture. The two chromatograms are shown in Fig. 3.

Discussion

Although the use of any flammable solvent requires that proper laboratory safety practices be followed, for fire debris laboratories using mass selective detectors instead of flame ionization detectors, diethyl ether may be a better choice than carbon disulfide in that it has equal powers to elute compounds of interest from adsorption packages, and poses a much smaller health risk to laboratory personnel.

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Additional information and reprint requests:
John J. Lentini
Applied Technical Services, Inc.
1190 Atlanta Industrial Drive
Marietta, GA 30066