Designation: D 5830 – 95 (Reapproved 2001)

Standard Test Method for Solvents Analysis in Hazardous Waste Using Gas Chromatography[1]

This standard is issued under the fixed designation D 5830; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method is used to determine qualitatively and quantitatively the presence of the following compounds in waste samples using gas chromatography. This test method is designed for use as a screening method with a typical reporting level of 0.1 %.

Dichodifluoromethane	Tetrahydrofuran
Trichlorofluoromethane	Acetone
1,1,2-Trichloro-1,2,2-trifluoroethane	Methyl Ethyl Ketone
	MIBK
Methanol	Cyclohexanone
Ethanol	Ethyl Acetate
Isopropanol	Propyl Acetate
n-Propanol	Butyl Acetate
Isobutanol	Benzene
n-Butanol	Toluene
tert-Butanol	Ethylbenzene
Methylene Chloride	Xylenes
Chloroform	Styrene
Carbon Tetrachloride	Chlorobenzene
1,1-Dichloroethane	Dichlorobenzenes
1,2-Dichloroethane	Nitrobenzene
1,2-Dichloropropane	Fluorobenzene
1,1-Dichloroethylene	*n*-Propyl Benzene
1,2-Dichloroethene	Isopropyl Benzene
1,1,1-Trichloroethane	Isobutyl Benzene
Tetrachloroethylene	*n*-Butyl Benzene
Trichloroethylene	2-Ethoxyethanol
Tetrachloroethane	2-Butoxyethanol
Cyclopentane	2-Ethoxyethanol Acetate
Pentane	2-Methoxyethanol
Hexane	Bromoform
Heptane	Carbitol
Cyclohexane	Ethyl Ether
*Iso*octane	1,4-Dioxane
Nitropropane	Diacetone Alcohol
Ethanolamine	Acetonitrile
Nitromethane	Pyridine
Ethylene Chloride	Toluidine
Benzyl Chloride	Ethylene Glycol
	Propylene Glycol

1.1.1 This compound list is a compilation of hazardous solvents and other constituents that are routinely seen in hazardous waste samples.

1.2 The scope of this test method may be expanded to include other volatile and semivolatile organic constituents.

1.2.1 Hydrocarbon mixtures such as kerosene and mineral spirits.

1.2.2 High-boiling organics, defined here as compounds which boil above *n*-Hexadecane.

1.2.3 Other organics that the analyst is able to identify, either through retention time data or gas chromatography/mass spectrometric (GC/MS) analysis.

1.3 Gas chromatographic methods are recommended for use only by, or under close supervision of, an experienced analyst.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

2.2 *EPA Document:*

Gas Chromatography/Mass Spectrometry Method 8260, Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW-846, Third Edition, Final Update 1, July 1992[3]

3. Summary of Test Method

3.1 Waste samples are analyzed by direct injection, or by carbon disulfide, *M*-Pyrol, or other suitable solvent extraction and injection of the extract into a gas chromatograph. Detection is achieved using a detector which is specific for the needed application, for example, flame ionization detector (FID), electron capture detector (ECD), thermal conductivity detector (TCD), photoionization detector (PID), or mass selective detector (MSD). This test method may be expanded to utilize other detector types not previously mentioned.

[1] This test method is under the jurisdiction of ASTM Committee D34 on Waste Management and is the direct responsibility of Subcommittee D34.01.06 on Analytical Methods.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

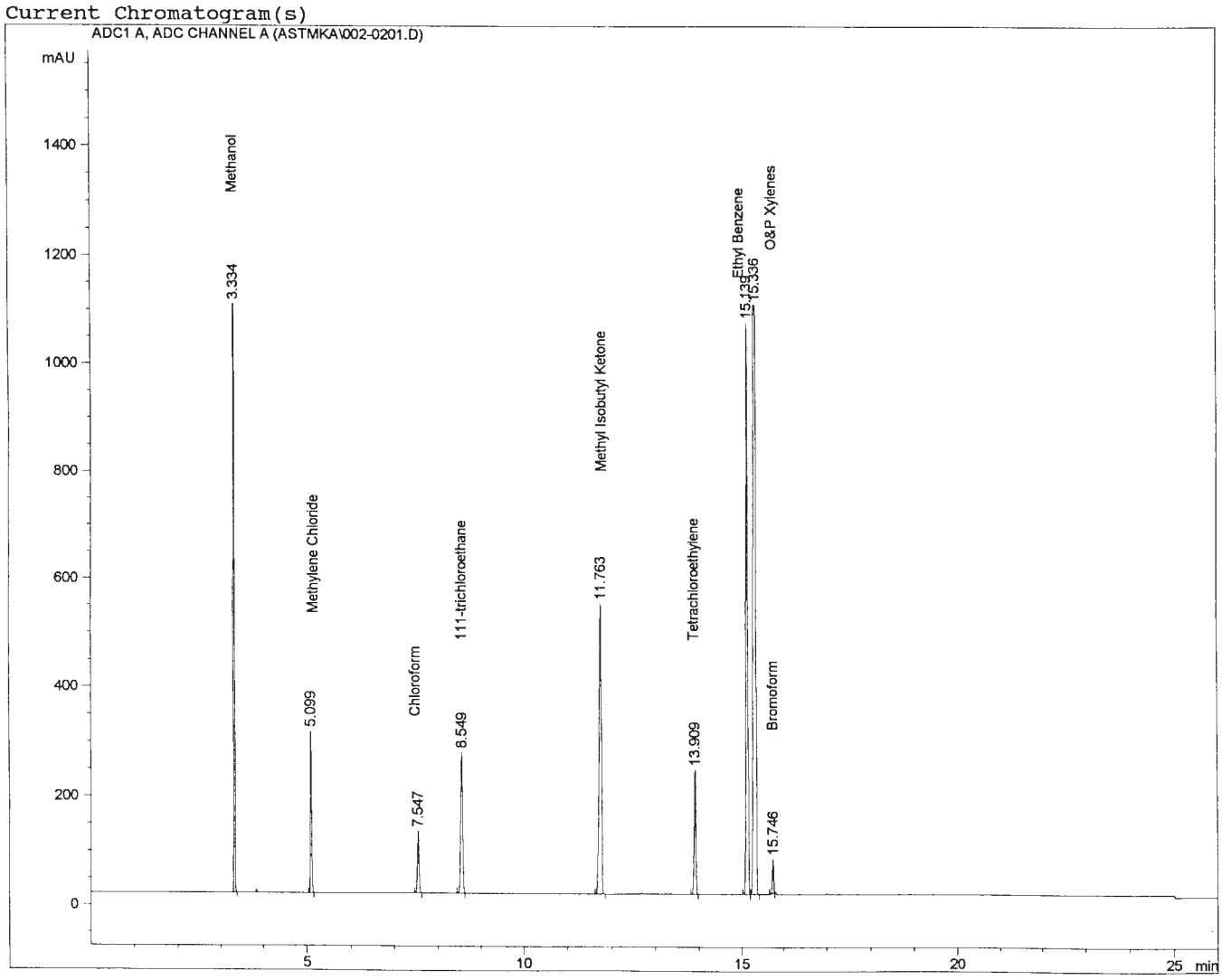

FIG. 1 Daily QC Standard FID/DB-1701

4. Significance and Use

4.1 This test method is useful in identifying the major solvent constituents in hazardous waste samples. This test method is designed to support field or site assessments, recycling operations, plant operations, or pollution control programs.

5. Interferences

5.1 Interferences may be encountered from any number of organic compounds that respond in the detector. Also, closely eluting components may complicate identification based solely on retention time. When these types of interferences are encountered, the analyst must rely on other sources of information for positive identification, such as:

5.1.1 Gas chromatography/mass spectrometric (GC/MS) confirmation, see EPA Method 8260, direct injection technique;

5.1.2 Use of confirmation column, or confirmatory detector;

5.1.3 Use of varying temperature programs or standard comparison, or both;

5.1.4 Sample history, for example, any information available from the waste generator; and,

5.1.5 Physical characteristics, for example, flammability, specific gravity, or miscibility with water.

5.2 Interferences may also be encountered from syringe carryover. Immediately following each injection, the syringe should be thoroughly rinsed with carbon disulfide, or *M*-Pyrol. Other solvents such as methanol may be used as rinse solvents if sample types necessitate their use, but be aware that carryover and possible interferences may occur if the rinse solvent is not completely cleaned from the syringe before reuse. Before each injection the syringe must be thoroughly rinsed with the sample to be injected, where the first two pumps are flushed into a separate waste receptacle.

5.3 When carbon disulfide (CS_2) is used to extract solids or sludges that contain significant amounts of water, low recovery of the water miscible solvents may result.

5.4 Some grades of CS_2 may contain trace amounts of benzene.

5.5 *M*-Pyrol seems to degrade slowly with time. The low-level degradation products interfere with some late eluting compounds on some columns (approximately five small peaks).

5.6 Interference from the CS_2 solvent peak may occur if using a TCD.

5.7 When using a TCD, be aware that water, as well as oxygenated compounds, for example, MEK, MIBK, may suppress detector response.

5.8 If an electrolytic conductivity detector (ECD) must be used, be aware that CS_2, *M*-Pyrol, and high concentrations of halogenated compounds may overload and possibly damage the detector. It is recommended that the ECD be used only when very low detection levels of halogenated compounds are expected and direct injection of the sample is possible.

6. Apparatus

6.1 *Gas Chromatograph System*—Equipped with capillary or packed column injection ports, or both, detector, and data system.

6.2 *Recommended Chromatographic Columns*:

6.2.1 *Capillary; Microbore or Megabore*.

6.2.1.1 DB-1701, 30M × 0.25-mm inside diameter, 0.25-µm film thickness.

6.2.1.2 DB-624, 30M × 0.3-mm inside diameter, 1.8-µm film thickness.

6.2.2 *Packed: Stainless Steel or Glass*.

6.2.2.1 1 % SP-1000, 60/80 Carbopak B, 8-ft by ⅛-in. inside diameter.

6.2.2.2 10 % SP-2100, 100/120 Chromosorb WHP, 2M × 2 mm ID.

NOTE 1—These columns are recommended and have shown to give good results. Operating conditions for each is listed in Section 10. Equivalent or alternative columns, or both, may be used depending on application.

6.3 *Glass Screw-Cap Vials or Equivalent*—To collect samples and store standards. Polytetrafluoroethylene or other inert material should be used for the cap liner.

6.4 *Microsyringes*, 1.0, 10, and 100 µL.

6.5 *Analytical Balance*, accurate to 0.0001 g.

6.6 *Pipettes*, glass, disposable, or volumetric micropipettor or equivalent.

6.7 *Microdisk Filters*, 0.45, 1.0, or 5.0 µm, optional.

6.8 *Centrifuge*, optional.

6.9 *Vortex-Type Mixer*.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*— Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

7.3 *Nitrogen or Helium (High Purity)*—For carrier and makeup gases. Air and hydrogen (high purity) for fuel gases. Gases may be obtained from a gas generator if available, through purification of a lower grade, or from a high-purity tank supply.

7.4 *Carbon Disulfide, CS_2*—Chromatography grade.

7.5 *M-Pyrol, C_oH_oNO*—Available through several chemical suppliers and sources as 1-methyl-2-pyrrolidone.

7.6 *Individual Standards for Each Component of Interest*—99 % purity available from many vendors.

8. Standard Preparation

8.1 *Stock Standard Solutions*—Stock standards are prepared from pure standard materials. It is recommended that the standards be prepared so that each component is 5 to 10 % by weight. The stock standards must be prepared by directly weighing each component. For extremely volatile components, such as ether and freons, it is recommended that a new stock standard be prepared daily or as needed. If a dilution solvent is needed when preparing the stock standards, use the same solvent used for sample extraction or dilution in Section 7.

NOTE 2—Due to the incompatibility of some standard compounds, that is, some compounds are not miscible with each other, and also because of the number of compounds typically looked for in a single chromatographic run, it is advisable to prepare 3 or 4 standard solutions each composed of 10 to 15 compounds. A set of standard chromatograms and a retention timetable should be available for reference.

8.2 *Secondary Working Standards*—These are prepared from stock standard solutions using the appropriate solvent. Secondary standards should encompass the linear range of the GC system.

NOTE 3—Linear response and range must be established with all detectors and chromatography systems used for quantitation. All calibration and sample analysis must be done within the established linear range.

8.3 *Calibration Check Standard*—A calibration check standard should be prepared. The standard mixture should provide a good overall check of the GC/detector system. The compounds should cover the major compound types, for example, alcohols, aromatics, aliphatics, ketones, and halogenates. A typical calibration check standard flame ionization detector (FID) chromatogram is shown in Fig. 1.

9. Sample Collection, Preservation, and Handling

9.1 Sample collection should be in accordance with appropriate sampling protocols.

[4] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

9.2 Samples should be collected in glass containers, that have tightly sealing caps. If very volatile organics are of particular interest, the headspace in the container should be kept to a minimum.

9.3 *Sample Transfer Implements*—Implements are required to transfer portions of waste samples from the sample containers to the laboratory containers. Liquid samples may be transferred using disposable pipets. Solids and semisolids may be transferred using a conventional laboratory spatula.

9.4 Samples shall be handled maintaining safe laboratory practices. Any samples with special hazards must be appropriately labeled.

9.5 Unused sample material, laboratory dilutions, and waste from the samples may be regulated. Consult your specialist or the regulations, or both, for guidance in the proper handling and disposal of laboratory wastes.

10. Procedure

10.1 *Sample Preparation*:

10.1.1 Analyze liquid matrices with relatively low viscosity using direct injection into the GC, either as received or after dilution with CS_2, *M*-Pyrol, or other suitable solvent.

10.1.2 Analyze solid or semisolid samples as follows:

10.1.2.1 For carbon disulfide or *M*-Pyrol preparation, weigh 3 g of the waste sample in a 15-mL glass vial. Add 3 g of carbon disulfide or *M*-Pyrol to the vial and the mixture is vortexed vigorously. After allowing the solids to settle, inject the CS_2 or *M*-Pyrol extract into the GC.

10.1.2.2 Use alternate sample sizes and extraction solvent weights if necessary. Actual sample size and solvent weight must be recorded in the appropriate sample preparation log book. It is essential for accurate waste sample analysis that sample size be sufficient to ensure a representative sample. If alternate sample size or extraction solvent volumes, or both, are used, this must be reflected in the calculations under the dilution factor in Section 11.

10.1.3 Multiple phases or layers are typically present in hazardous waste samples. Depending on treatment or process requirements, it may be necessary to analyze each phase or layer individually.

10.2 *Recommended GC Operating Conditions*:

10.2.1 For Capillary DB-1701 with FID

Column flow rate	1–1.5 mL/min
Make-up gas flow rate	30–60 mL/min
Split flow	60 cm^3/min
Injector temperature	250°C
Detector temperature	250°C
Airflow (FID)	Approximately 300 mL/min
Hydrogen flow (FID)	Approximately 30 mL/min
Initial oven temperature	35°C
Initial time	6 min
Level 1 rate	6°C/min
Level 1 final value	180°C
Level 2 rate	10°C/min
Level 2 final value	230°C
Run time	40 min
Threshold	4 units
Peak width	0.04 min

NOTE 4—Typical chromatograms are shown in Figs. 2-5.

10.2.2 For Capillary DB-624 with FID

Column flow rate	3.5 mL/min
Make-up gas flow	29 mL/min
Airflow (FID)	Approximately 300 mL/min
Hydrogen flow (FID)	Approximately 30 mL/min
Injector temperature	275°C
Detector temperature	275°C
Initial oven temperature	35°C
Initial time	5 min
Level 1 rate	5°C/min
Level 1 final value	150°C
Level 1 hold time	4 min
Level 2 rate	20°C/min
Level 2 final value	225°C
Run time	45 min

10.2.3 For Packed SP-1000 with FID

Column flow rate	40 mL/min
Air pressure (FID)	300 kPa
Hydrogen pressure (FID)	130 kPa
Injector temperature	250°C
Detector temperature	250°C
Initial oven temperature	90°C
Initial time	6 min
Level 1 rate	3°C/min
Level 1 final value	120°C
Level 2 rate	5°C/min
Level 2 final value	180°C
Level 3 rate	10°C/min
Level 3 final value	230°C
Run time	46 min

10.2.4 For packed SP-2100 with FID

Carrier gas flow	30 mL/min
Injector temperatuare	250°C
Detector temperature	300°C
Airflow (FID)	Approximately 300 mL/min
Hydrogen flow (FID)	Approximately 30 mL/min
Initial oven temperature	45°C
Initial hold time	3 min
Level 1 rate	15°C/min
Level 1 final value	90°C
Level 2 rate	10°C/min
Level 2 final value	195°C
Run time	16.5 min

10.3 *Linear Range Determination*—The linearity and linear range for each compound must be established on any GC system used for quantitation. This must be done on an annual basis or after any major maintenance or alteration of the system configuration, for example, detector replacement. Final quantitation for each compound must be done within the linear range of that compound.

10.4 *Calibration (External Standard Procedure)*:

10.4.1 A single-point initial calibration of all compounds must be performed monthly. Inject 0.5 to 2.0 µL of the working standards that were prepared in 8.2. Tabulate peak area against concentration and express response factors (RF) for each component. This calculation is shown in 11.1. It is recommended for ease of calculation that the response factors be expressed as area counts per 1 % by weight.

10.4.2 The response factors must be verified daily or after every 20 samples, whichever is more frequent, by injecting 0.5 to 2.0 µL of the calibration check standard. This must be done for every column used for quantitation. If the predicted response varies by ±20 % from the initial calibration, corrective action must be taken, for example, septum, liner, or column maintenance, or a combination thereof. If the variance cannot be solved using the corrective action techniques, a new initial calibration must be performed.

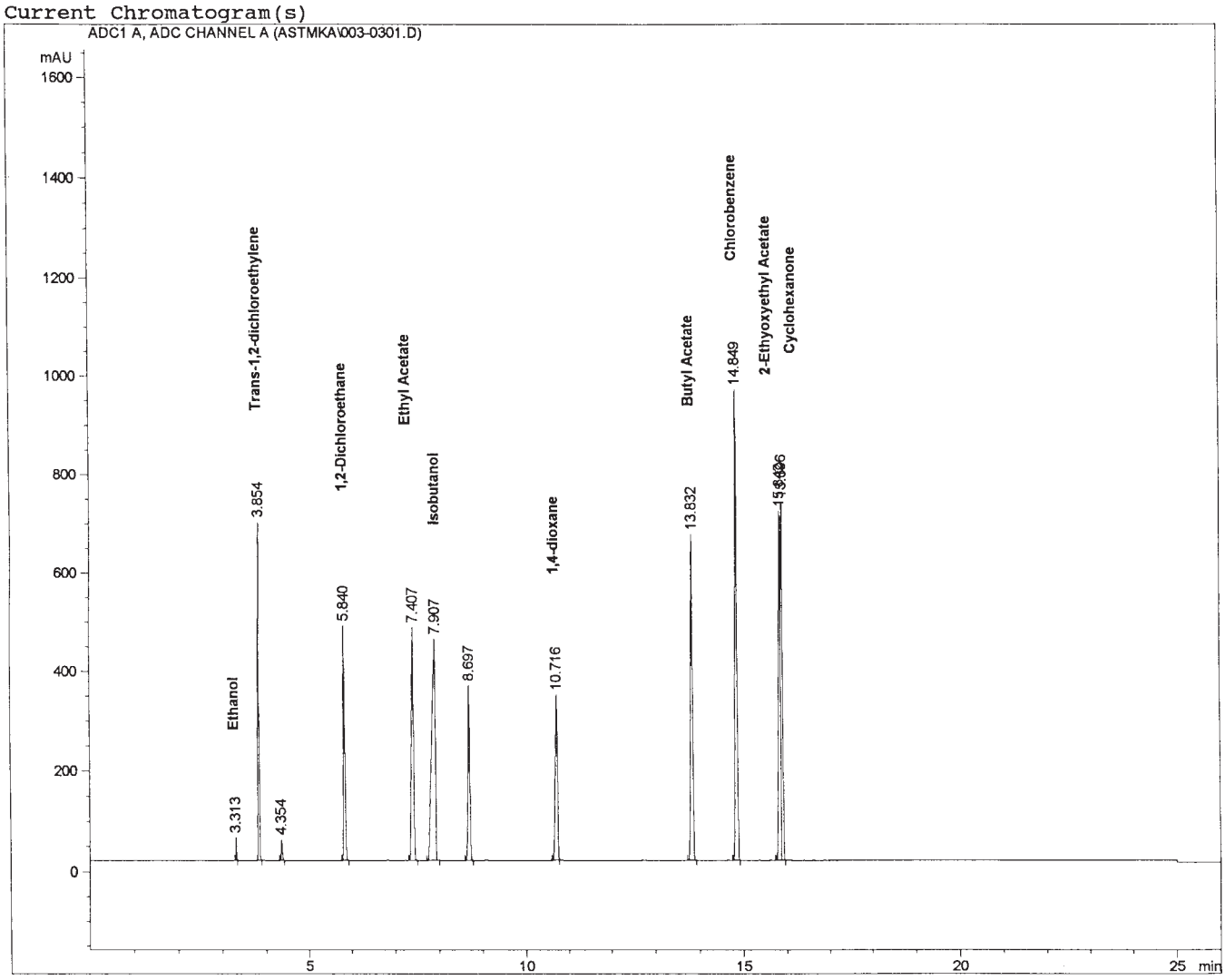

FIG. 2 Solvent Standard #1 FID/DB-1701

10.5 *Gas Chromatographic Analysis*:

10.5.1 Liquid samples are introduced into the gas chromatograph by direct injection of 0.5 to 2.0 µL of sample. This may be done as received or after dilution or extraction with the appropriate solvent.

10.5.2 Solid and semisolids should be prepared in accordance with 10.1.2, followed by injection of 0.5 to 2.0 µL of the extract.

NOTE 5—Because of the number of different types of compounds typically present in hazardous waste samples or looked for in a single chromatographic run, interferences from coelution may complicate identification based solely on retention time. The analyst should use the tools listed in 5.1 and any other available knowledge to correctly identify the compound.

11. Calculation

11.1 The compound concentration is determined by the following calculations:

$$Csamp = (Asamp/RF) \times D \quad (1)$$

where:

Csamp = concentration of compound in sample (wt %),
Asamp = peak area of compound in sample,
RF = response factor, and
D = dilution factor.

$$RF = Astd/Cstd \quad (2)$$

where:

Astd = peak area of compound in standard, and
Cstd = concentration of compound in standard (wt %).

This calculation assumes a reproducible injection volume. A dilution factor must be applied if additional sample or solvent amounts are used for extraction. For example, when using CS_2, if 6 g of CS_2 instead of the normal 3 g is used for extraction, a dilution factor of two must be applied to Csamp since the compounds in the 3 g of the original sample are now diluted in

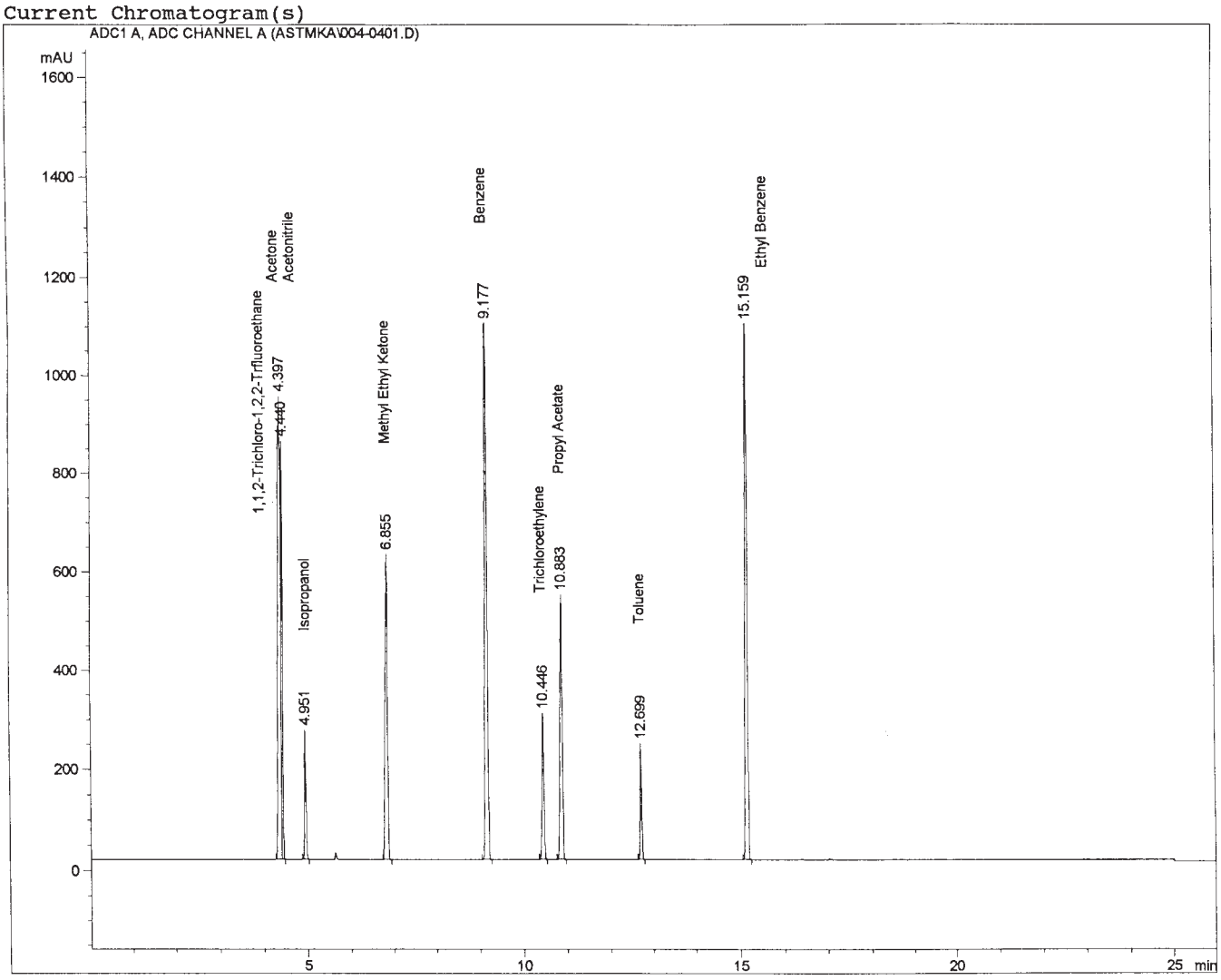

FIG. 3 Solvent Standard #2 FID/DB-1701

6-g CS_2. This is also true if any dilutions are made prior to direct injection of the sample.

NOTE 6—If solids or semisolids are soluble in CS_2 or *M*-Pyrol, use an additional dilution factor for calculation. This is mainly true for oils and sludges.

11.2 Calculated results should be reported to one significant figure for values of 1 % or less, and to two significant figures for values greater than 1 %.

12. Quality Control

12.1 Each laboratory using this test method will operate a formal quality control program. The minimum requirements of this program must consist of an initial demonstration of laboratory capability and the ongoing analysis of method blanks, duplicate and spiked samples to evaluate, and document quality data.

12.2 Before processing any samples, the analyst must demonstrate through the analysis of a method blank, that the interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is prepared or there is a change in reagents, a method blank must be processed as a safeguard against chronic laboratory contamination. The method blank must be carried through all stages of sample preparation and measurement.

12.3 On an ongoing basis, the laboratory must analyze a replicate sample and a matrix spike or a matrix spike and a replicate matrix spike. This will allow the laboratory to assess precision and bias.

12.4 On a monthly basis, each laboratory must demonstrate the ability to identify each compound at the reporting levels. For a signal to be considered a valid peak it must have a signal-to-noise ratio greater than ten.

13. Precision and Bias

13.1 With the exception of commercial paint, the following mixtures were synthesized by weight. Carbon disulfide was the predominant solvent used for extraction and dilution in obtaining Tables 1-4.

NOTE 7—*Theo* % represents the theoretical value of the compound in the mixture as prepared by the round-robin technician. *Avg.* represents the average value reported from all the laboratories. *% RSD* represents the percent relative standard deviation between laboratories based on reported

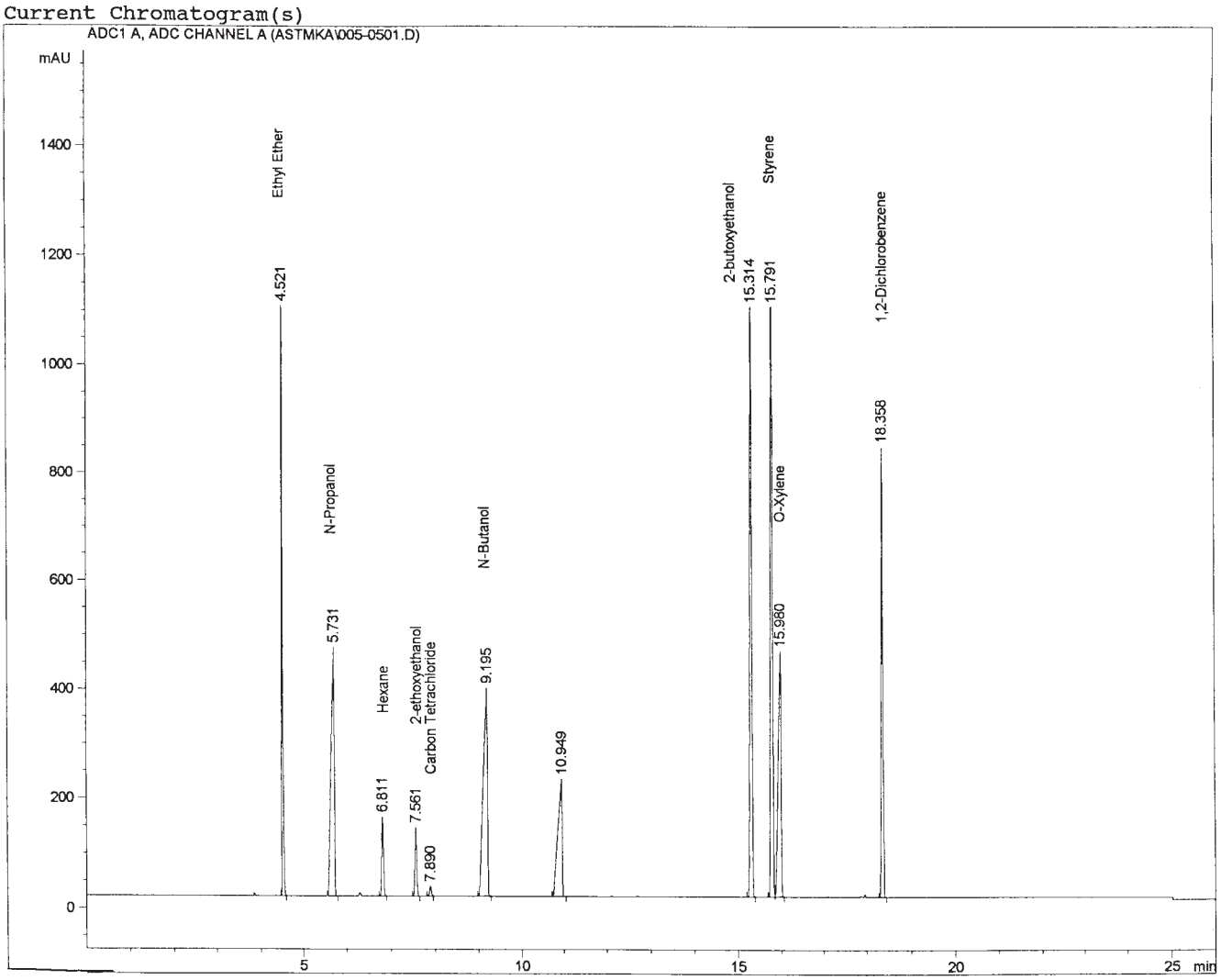

FIG. 4 Solvent Standard #3 FID/DB-1701

values. *Avg. Rec.* represents the average recovery based on the reported values and the theoretical values. Average recovery data is not reported for solvents in commercial paints because theoretical values are given only as ranges.

NOTE 8—All precision and bias data are based on multilaboratory round-robin analyses.

Compound Key:
ChlBz = Chlorobenzene
CCl4 = Carbon Tetrachloride
EB = Ethylbenzene
MeCl2 = Methylene Chloride
MEK = Methylethyl Ketone
TCA = 1,1,1-Trichloroethane
TCE = Trichloroethylene
TOL = Toluene
PERC = Perchloroethylene
XYL = Xylene

14. Keywords

14.1 flame ionization; gas chromatography; hazardous waste; solvents; thermal conductivity detector

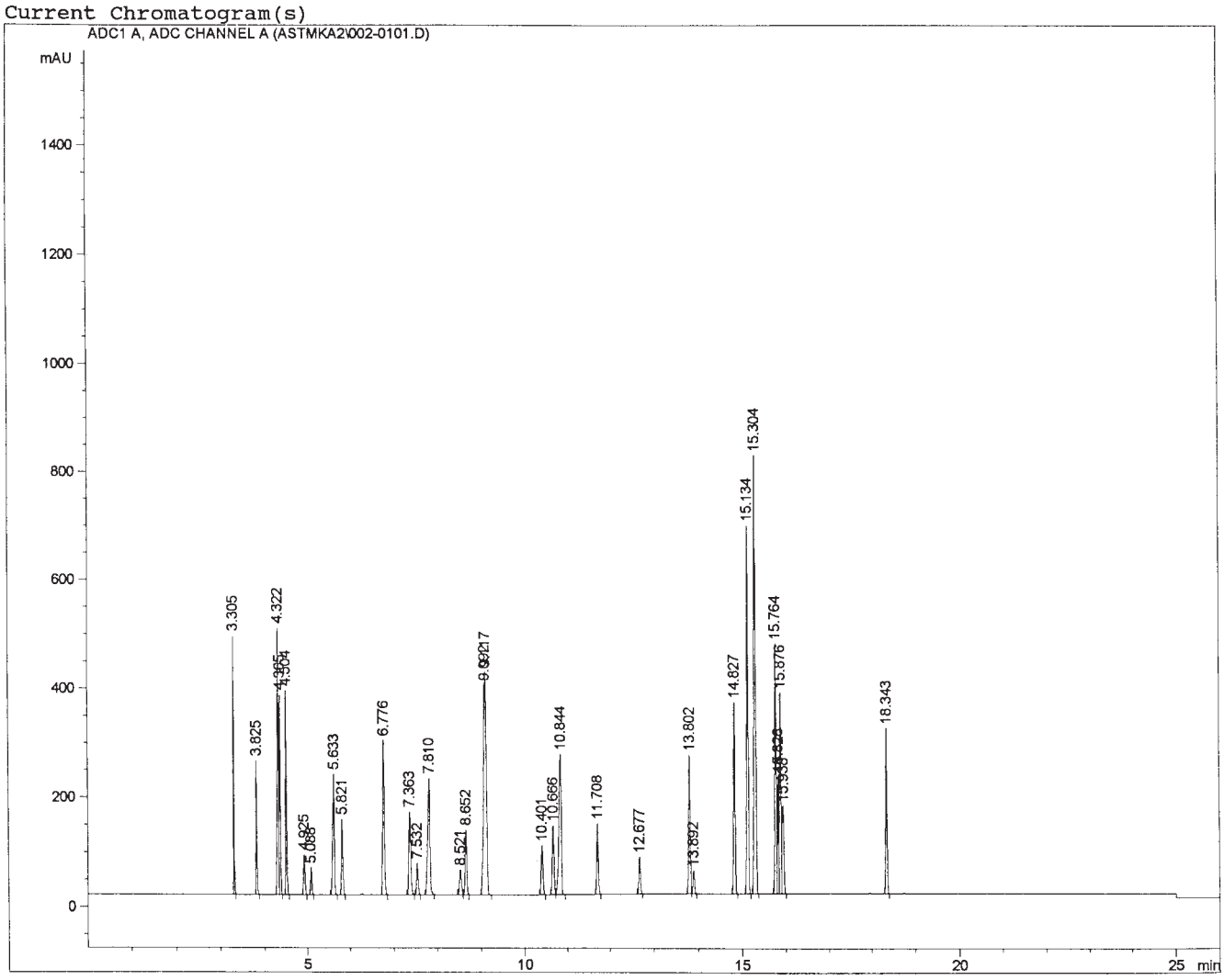

FIG. 5 Combined Solvent Standards FID/DB-1701

TABLE 1 Solvents in Motor Oil, Percent Detected

	Compound				
Laboratory No.	XYL	$MeCl_2$	PERC	TCA	TCE
1	1.1	3.7	3.2	62.5	2.7
2	1.7	3.9	...	69.5	...
3	0.5	2.0	1.4	39.4	...
4	2.1	4.2	2.7	76.5	2.4
5	1.2	3.0	2.7	59.7	...
6	1.3	4.0	3.0	71.1	2.5
7	1.4	3.9	3.2	67.7	2.4
8	1.7	5.1	4.1	59	3.2
9	...	4	3.3	65.9	2.9
10	1.1	4.2	5.2	37.1	2.7
11	1.8	3.5	...	50.6	...
12	1.4	4.1	3.3	59	2.3
13	1.2	3.6	2.7	...	...
Theo%	1.5	3.7	3.0	61.9	2.2
Avg.	1.4	3.8	3.2	59.8	2.6
%RSD	29.7	8.9	29.3	20.3	11.6
Avg. Rec.	92	103	105	97	117

TABLE 2 Solvents in Commercial Paint, Percent Detected

	Compound			
Laboratory No.	EB	MEK	TOL	XYL
1	...	3.2	13.6	25.4
2	5.8	...	11.2	15.8
3	...	4.4	9.3	27
4	5.3	4.1	15.1	...
5	...	2.2	7.5	15.5
6	3.6	...	8.7	17.8
7	2.7	2.7	6.5	14
8	5.5	4.1	12	27.4
9	6.2	4.9	16	...
10	...	4.5	18.2	...
11	3.7	3.7	10.4	22.8
12	4.7	3.2	11.4	22.8
13	2.9	...	7.3	23.1
Theo%	...	3–4	10–11	23–30
Avg.	4.5	3.7	11.3	21
%RSD	28.8	23.2	31.8	25

TABLE 3 VOCs in Methanol, Percent Detected

	Compound				
Laboratory No.	ChlBz	EB	TCA	TCE	TOL
1	...	0.36	0.35	0.39	0.4
2	0.13	0.39	0.35	0.42	0.44
3	...	...	...	0.3	0.3
4	0.08	0.26	0.24	0.27	0.3
5	...	...	0.2	0.23	0.23
6	0.13	0.4	...	...	...
7	...	0.23	...	...	...
8	0.1	0.3	0.28	0.32	0.35
9	0.09	0.33	0.26	0.31	0.37
Theo%	0.1	0.32	0.29	0.35	0.37
Avg.	0.11	0.32	0.28	0.32	0.34
%RSD	19.8	18.2	21.4	18.7	20.5
Avg. Rec.	102	100	97	92	92

TABLE 4 Solvents in Oil, Percent Detected

	Compound				
Laboratory No.	CCl_4	PERC	TCA	TCE	TOL
1	5.5	5.3	7.1	4.7	2.1
2	3.4	6.0	4.7	4.0	3.4
3	...	5.0	...	4.6	2.1
4	4.2	3.8	...	3.2	1.5
5	4.1	4.1	5.8	3.5	1.6
6	4.7	4.5	6.2	4.1	1.7
7	5.8	5.3	8.5	6.0	2.3
8	6.1	7.0	4.6	6.0	2.7
9	...	3.9	5.0	3.2	1.6
10	4.4	5.0	6.2	3.1	1.7
11	4.5	5.3	7.3	4.6	2.0
Theo%	5.1	5.1	7.2	4.6	1.9
Avg.	4.7	5.0	6.2	4.3	2.1
%RSD	18.7	18.9	21.1	24.1	27.2
Avg. Rec.	93	98	86	93	106