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CHEMICAL METHODS FOR THE MEASUREMENT OF NONREGULATED DIESEL EMISSIONS

***Foreword*—**This Document has not changed other than to put it into the new SAE Technical Standards Board format.

***1. Scope*—**This SAE Recommended Practice encompasses analytical procedures for measuring nonregulated diesel exhaust emissions. Methods are recommended for the measurement of aldehydes and carbonyl compounds, sulfates, and the characterization of diesel exhaust particulates. Informational methods are presented for the measurement of polycyclic aromatic hydrocarbons (PAH) in diesel exhaust particulate samples.

The procedures are based on current proven chemical and engineering practices. However, it should be noted that the procedures are subject to change to keep pace with established experience and technology.

1.1 Purpose—The procedures are intended for use in the collection, analysis, and characterization of emissions from diesel engines. They are to be used as a guide in standardizing practices so that the results from various sources can be compared with some degree of accuracy.

The specific purpose of each chemical method is presented at the beginning of each method section.

2. References

2.1 Applicable Publications—The following publications form a part of this specification to the extent specified herein.

1. Coordinating Research Council, Inc., "Informational Report on the Measurement of Diesel Particulate Emissions," CRC Report No. 522, June 1982.
2. "Methylene Chloride Facing Regulation," Chemical and Engineering News, p. 17, March 17, 1986.
3. Perez, J.M., Lipari, F., and Seizinger, D.E., "Cooperative Development of Analytical Methods for Diesel Emissions and Particulates," SAE Paper No. 840413, Detroit, MI, March 1984.
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5. Wall, J.C. and Hoekman, S.K., "Fuel Composition Effects on Heavy-Duty Diesel Particulate Emissions," SAE Paper No. 841364, Baltimore, MD, October 1984.
6. Coordinating Research Council, Inc., "Chemical Methods for the Measurement of Unregulated Diesel Emissions," CRC Report No. 551, August 1987.

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15. U.S. EPA Standard for Emission of Particulate Regulation for Light-Duty Vehicles and Light-Duty Trucks, Federal Register, Vol. 45, No. 45, Wed. March 5, 1980.
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17. MacDonald, J.S., Barsic, N.J., Gross, G.P., Shahed, S.M., and Johnson, J.H., "Status of Diesel Particulate Measurement Methods," SAE Paper No. 840345, Detroit, MI, March 1984.
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19. MacDonald, J.S., Plee, S.L., D'Arcy, J.B., and Schrek, R.M., "Experimental Measurements of the Independent Effects of Dilution Ratio and Filter Temperature on Diesel Exhaust Particulate Samples," SAE Paper No. 800185, Detroit, MI, February 1980.
20. SAE Recommended Practices, Society of Automotive Engineers, 400 Commonwealth Drive, Warrendale, PA 15096-0001.
21. Williams, R.L., Perez, J.M., and Griffing, M.E., "A Review of Sampling Condition Effects on Polynuclear Aromatic Hydrocarbons (PNA) from Heavy-Duty Diesel Engines," SAE Paper No. 852081, Tulsa, OK, October 1985.
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31. Standard Materials, Priority Pollutant PAH, SRM #1647, National Bureau of Standards, Washington, DC.

32. Menzies, K.T., et al., Development of a Routine Technique for Analysis of a Nitro-PAH in Diesel Particulate Extract," Final Report by A.D. Little, Inc. to CRC-APRAC CAPE-30-81 Project Group, Coordinating Research Council, Inc., Atlanta, GA, February 1985.
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35. Warner, I., Karlesky, D., and Skilly, D.C., "Reactivation of an Amino Bonded Phase Liquid Chromatographic Column," Anal. Chem., 53:2146, 1981.
36. Perez, J.M., "Measurement of Unregulated Emissions: Some Heavy Duty Diesel Engine Results," Environ. International, Vol. 5, pp. 217–228, 1981, Permagon Press Ltd., Oxford, England.
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3. *Definitions*

3.1 Carbonyl Compounds—Chemical compounds containing the C=0 functional group. The compounds can be either aldehydes or ketones. In this procedure, the term refers to compounds containing one of eight carbon atoms, specifically the compounds shown in Table 1.

TABLE 1—PHYSICAL PROPERTIES OF CARBONYL COMPOUNDS

Aldehyde or Ketone	IUC Name	Chemical Formula	Molecular Weight	Melting Pt., °C	DNPH Derivative Mol. Wt.	DNPH Derivative Melting Pt., °C	DNPH Derivative Density	DNPH Derivative Rel Ret Time
Formaldehyde	Methanal	CH_2O	30.03	–92	210.15	167	0.815	0.453
Acetaldehyde	Ethanal	CH_3CHO	44.05	–121	224.18	167	0.783	0.574
Acetone	2-Propanone	CH_3COCH_3	58.08	–95	238.21	128	0.792	0.714
Propionaldehyde	Propanal	CH_3CH_2CHO	58.08	–81	238.21	156	0.807	0.795
Acrolein	Propanal	CH_2:CHCHO	56.07	–87.7	236.20	165	0.841	0.699
n-Butyraldehyde	Butanal	$CH_3(CH_2)_2CHO$	72.10	–99	252.23	122	0.817	—
Isobutyraldehyde	2-Methylpropanal	$CH_3CH(CH_3)CHO$	72.11	–65.9	252.23	182	0.794	0.911
Methylethylketone	2-Butanone	$CH_3COCH_2CH_3$	72.11	–84	252.23	—	0.805	—
Crotanaldehyde	trans-2-Butenal	CH_3CH:CHCHO	70.09	–74	250.21	190	0.858	0.870
n-Valeraldehyde	Pentanal	$CH_3(CH)_3CHO$	86.13	–92	266.26	106	0.820	—
Iso-Valeraldehyde	3-Methylbutanal	$(CH_3)_2CHCH_2CHO$	86.13	–51	266.26	—	0.805	—
Caproaldehyde	Hexanal	$CH_3(CH_2)_4CHO$	100.16	–56	279.28	104	0.833	1.23
Enanthaldehyde	Heptanal	$CH_3(CH_2)_5CHO$	114.18	–45	294.31	—	0.850	—
Benzaldehyde	Benzenecarbonal	C_6H_5CHO	106.13	–26	286.25	237	1.05	1.00
p-Tolualdehyde	4-Methylbenzene-Carbonal	$CH_3C_6H_4CHO$	120.14	—	300.27	194	1.02	—

3.2 Sulfates—Chemical compounds containing the sulfate anion (SO_4).

3.3 PAH—Chemical compounds containing three or more fused aromatic rings.

3.4 Diesel Particulate—The material collected from diesel exhaust on a PTFE-coated glass fiber filter at 50 °C + 2/–5 °C. The systems used for the collection of particulate may vary from direct sampling of the exhaust to use of full dilution tunnels (see Reference 1). Various fractions are contained in the total particulate mass (TPM) as collected on the filter:

3.4.1 TOTAL PARTICULATE MASS (TPM)—Includes all the material collected on the filter as prescribed by the sampling test procedure used.

3.4.2 SOLVENT EXTRACTABLE FRACTION (SEF)—This fraction contains the material that can be extracted from the TPM by various solvents and contains both organic and inorganic solvent extracts.

3.4.3 SOLUBLE ORGANIC FRACTION (SOF)—The SEF of the TPM that is removed by soxhlet extraction with dichloromethane ($MeCl_2$). (See Note in 3.4.7.)

3.4.4 TOTAL ORGANIC EXTRACT FRACTION (TOE)—The fraction of the TPM that is removed by soxhlet extraction using a binary mixture of 32/68 wt/wt of toluene:ethanol, b.p. 76.7 °C.

3.4.5 SULFATES (SO_4)—WATER SOLUBLE SULFATES—The major extractable inorganic fraction in the particulate sample. The sulfates are removed by agitation of the particulate sample in a water solution and analyzed directly by ion chromatography. The water solution contains 60/40 vol/vol of H_2O/isopropyl alcohol, or newer ion chromatograph procedures use only the ion chromatographic eluant for the solution.

3.4.6 COMBINED WATER (H_2O)—Water that is chemically combined with sulfuric acid and any hydrophilic metallic sulfates that may be present in the TPM.

It amounts to about 1.3 times the mass of the measured sulfate (see References 3, 4, 5) when the TPM is equilibrated at 50% relative humidity at room temperature (20 °C).

3.4.7 RESIDUAL CARBON PARTICULATE (RCP)—This fraction is the calculated particulate mass remaining after the removal of the total organic fraction, the sulfate fraction, and the combined water fraction Equation 1:

$$RCP = TPM - TOE - Sulfates - Water \quad \text{(Eq. 1)}$$

The RCP fraction may contain small quantities of sulfur and trace quantities of metals.

NOTE—Methylene chloride should only be used with adequate ventilation (see Reference 2).

4. Organization of Procedures—This document defines procedures developed cooperatively by the Chemical Characterization Panel (CCP) of the Coordinating Research Council, Inc. (see Reference 6). The methods are the result of cooperative testing and are considered to be based on sound engineering practices. Two of the methods, the PAH and the NO_2PAH methods, are still under evaluation and are presented for informational purposes. The methods are discussed separately in this document as follows:

Section 5 — Carbonyl Compounds
5.1 — DNPH Solvent Extraction Method
5.2 — DNPH Cartridge Method

Section 6 — Diesel Particulate Characterization
6.2 — Total Particulate Mass (TPM)
6.3 — Solvent Extractable Fraction (SEF)
6.3.2 — Soluble Organic Fraction (SOF)
6.3.3 — Total Organic Extract Fraction (TOE)
6.3.4 — Sulfates (SO_4)
6.3.5 — Water Fraction (H_2O)

Section 7 — Nitrated Polycyclic Aromatic Hydrocarbons (NO_2PAH)

Section 8 — Polycyclic Aromatic Hydrocarbons (PAH)
8.1.4 — PAH Method 1 (Quantitative for 12 compounds)
8.1.5 — PAH Method 2 (Qualitative screening of samples)

5. Carbonyl Compounds

5.1 DNPH Solvent Extraction Method—High performance liquid chromatographic (HPLC) dinitrophenylhydrazine (DNPH) method.

5.1.1 SCOPE—This procedure incorporates an improved 2,4-DNPH method in which C1 to C8 carbonyl compounds are collected by bubbling diesel exhaust or diluted diesel exhaust through an acetonitrile (ACN) solution of DNPH reagent and analyzed by HPLC using UV detection at 365 nm. Using an ACN solution for sample extraction allows direct injection of the sample into the HPLC, eliminating many of the recovery steps associated with previous DNPH methods, and reducing the man-hours required for sample preparation. The method results in quantitative sample recoveries, improved accuracy and provides for a simple, rapid, and low cost method for "aldehyde" analyses.

5.1.2 DEFINITION OF "ALDEHYDES" OR CARBONYL COMPOUNDS—These terms refer to compounds containing the C=0 functional group. Specifically, this procedure refers to C1 to C8 compounds shown in Table 1. The method may also be applicable to higher molecular weight compounds.

5.1.3 DESCRIPTION OF METHOD

5.1.3.1 Experimental

5.1.3.1.1 Reagents—Reagents used in this procedure should be HPLC grade, distilled in glass, or equivalent grade solvents as indicated:

ACN—Burdick and Jackson Labs, Inc., Fisher Scientific Co., J.T. Baker Chemical Co. or equivalent quality

2,4-DNPH—Aldrich Chemical Co. or J.T. Baker, recrystallized twice from HPLC grade methanol (MeOH) or ACN

Distilled, deionized water (HPLC) grade

Hydrochloric acid solution (2N) prepared from best source HCl

Ethanol—best source

Perchloric acid—best source

Aldehyde standards—individual aldehyde compounds for the preparation of standards (reference compounds) should be the best available grade

2,4-DNPH derivatives—preparation will be discussed in 5.1.3.1.3

5.1.3.1.2 Equipment—The equipment required for this method includes:

A HPLC with UV detection capability at 365 nm wavelength

5 µ zorbax ODS 4.6 x 25.0 cm HPLC column

Midget impingers (light-duty diesel) or 100 mL glass impingers (heavy-duty diesels)

Flowmeter, pump, and meter—required for sample collection system Figure 1

LC syringes as required

Melting point apparatus

5.1.3.1.3 Pretest Preparations:

a. Aldehyde-DNPH Derivatives—The 2,4-DNPH derivates are prepared by the reaction of the individual aldehydes with a saturated DNPH solution in 2N HCl. The derivatives are filtered, washed with 2N HCl and H_2O, air dried, and stored in sealed vials. The purity of the derivatives is checked by melting point determinations Table 1. Purity can be improved by recrystallization from absolute ethanol or MeOH, if required. Individual derivatives or a mixture of the standards should also be checked for purity.

b. Preparation of Solutions and Standards—A 6.25 μ mole/mL of the 2,4-DNPH stock solution is prepared by addition of 100 mL of ACN to 120 mg of purified DNPH crystals. Dilution of the stock solution with ACN is used to prepare a 1.6 μ mole/mL DNPH absorbing solution in the bubblers. Five drops of 1N $HCl0_4$ catalyst is added per each 20 mL of absorbing solution. The acid is added just prior to use.

Standard solutions of the aldehydes are prepared by injecting 5.0 μL of the aldehyde into a septum sealed vial containing 5.0 mL of ACN. The concentrations of the stock solutions are calculated from the density of the aldehydes. The formaldehyde concentration is determined from the concentration of formalin solution by titration. Standard derivative solutions are prepared by injecting 2.0 to 20 μL of the aldehyde solution into a septum sealed vial containing the derivatizing reagent. Weighing the solid DNPH hydrazones and dissolving them in ACN can also be used to prepare the standard derivatives.

The derivatives may be purchased commercially but the purity should be checked by measuring the melting points, or by gas chromatography. If the results do not agree with the data in Table 1, recrystallize as per 5.1.3.1.3a.

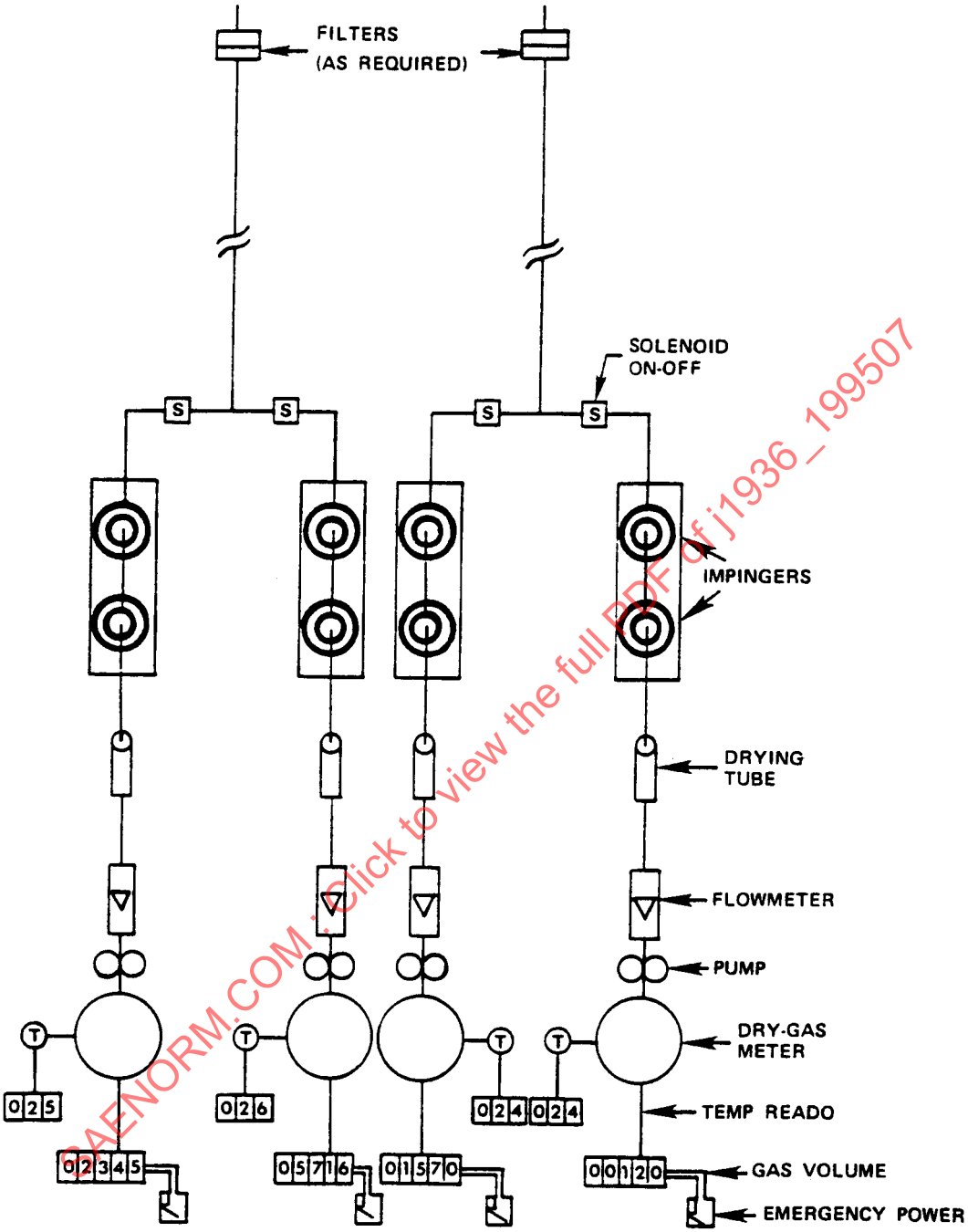


FIGURE 1—SAMPLING CHART (SCHEMATIC DIAGRAM)

5.1.3.2 Sample Collection

5.1.3.2.1 Sampling System—The sampling system used can vary depending on the source of the aldehydes. One system, shown in Figure 1 (see References 7, 8), was designed to sample diluted exhaust from various size dilution tunnels or heated PTFE bags containing diluted exhaust gases. For sampling directly from undiluted exhaust streams a short (approximately 2 m x 0.635 cm OD) stainless steel line should be added to allow some cooling of the exhaust prior to entering the PTFE coated heated line.

5.1.3.2.2 Sampling—A 1.6 μ mole/mL DNPH solution is used for emission testing. This is obtained by diluting the stock solution as indicated in 5.1.3.1.3 or the solution required can be prepared by dissolving about 31 mg of purified DNPH in 100 mL of ACN.

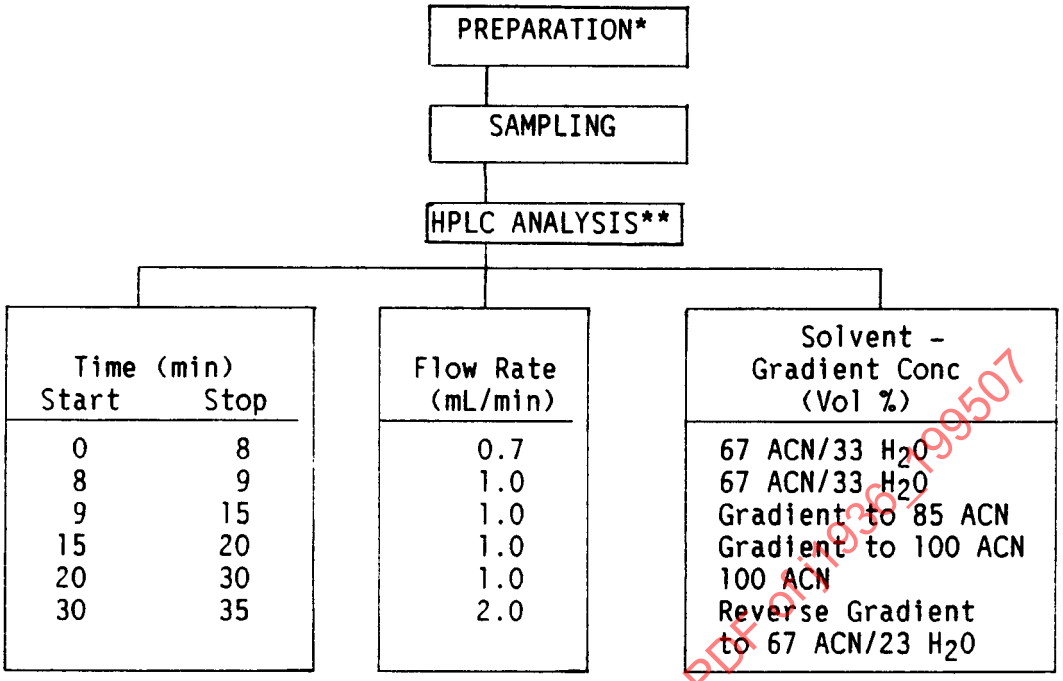
For each light-duty diesel (LDD) sample taken, the impingers are prepared by adding 10 mL of the DNPH solution and two drops (approximately 100 μL) of the 1N $HCl0_4$ to each impinger. Two samplers are connected in series and placed in the ice bath. For sampling heavy-duty diesels (HDD), 20 mL of the DNPH solution and four drops of the 1N $HCl0_4$ are added to each impinger or bubbler. Sample flow through the bubblers is maintained at 1/2 L/min for LDD and 2 to 4 L/min for HDD sampling. Normally 10 to 30 L of exhaust (100 to 300 L at 9:1 dilution ratio) is adequate to obtain sufficient sample for a reliable analysis. The amount sampled depends on the source. The lower the source concentration, the more sample that is required for good quantitative results.

Samples should be analyzed immediately or refrigerated until used.

5.1.3.3 Sample Analysis

5.1.3.3.1 Analysis Procedure—Samples should be analyzed as soon as possible, preferably within a few hours, to minimize the losses of certain species. The procedure for analysis is shown in Figure 2. Following an acceptable HPLC blank, the calibration standards are run. An example of an HPLC trace for the standards is shown in Figure 3. It should be emphasized that the appearance may vary depending on the HPLC system utilized. However, the relative retention times of the peaks should closely agree with those shown in Table 1. If not, retention times should be redetermined using a set of standards. The time required from injection to the appearance of the internal standard, benzaldehyde, is considered to be 1.0. The times for all other peaks to elute are normalized to it. If an automated system is utilized, the samples can be sequenced, running a standard check at the end of the series or every four to six samples depending on the number of samples to be analyzed.

5.1.3.3.2 Sample Stability—The stability of samples indicates that losses of individual aldehydes, with the exception of acrolein, are only about 10% in 24 h. Experimental determined losses for formaldehyde, acrolein, and the total aldehydes have been reported (see References 3, 4). The acrolein losses were shown to be concentration dependent. Higher concentrations of acrolein (80 to 100 μg/sample) exhibited about 35% loss in 24 h. Fortunately, this species is a minor constituent of the total aldehydes found in diesel exhaust. Typically, sampling and analysis are completed within 24 h. Storage stability results beyond 24 h are shown in Table 2. The data show losses in total aldehydes over an eight-week period were less than 5%. This is primarily due to the degradation of acrolein and crotonaldehyde in the samples.



*DNPH Solutions Standards

**HPLC - 4.6 mm x 25 cm column - 5 μ Zorbax ODS; 600 PSI (initial); UV 365 nm; sensitivity 0.2 AUFS

FIGURE 2—CARBONYL ANALYSIS METHOD

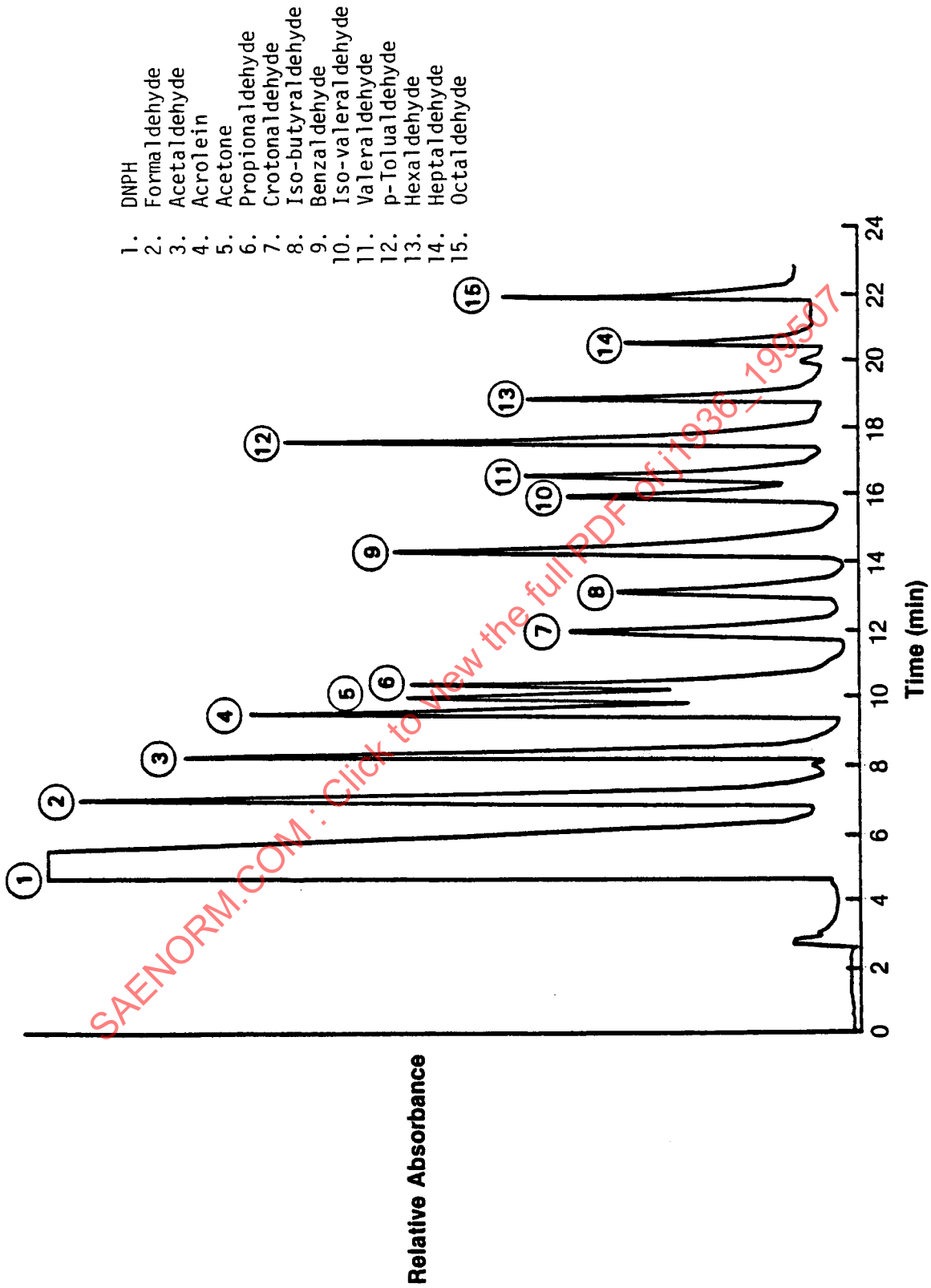


FIGURE 3—CHROMOTOGRAM OF THE STANDARD DNPH—ALDEHYDE MIXTURE

TABLE 2—STORAGE STABILITY (NG/ML)

Sample No.	1 Orig.	1 A	1 B	2 Orig.	2 A	2 B	3 Orig.	3 A	3 B	4 Orig.	4 A	4 B
Formaldehyde	23.0	22.0	22.7	23.6	22.0	22.3	14.1	13.5	13.8	14.1	13.3	13.5
Acetaldehyde	3.98	3.82	3.97	4.16	3.86	3.81	2.30	2.08	2.06	2.24	2.01	1.96
Acrolein	1.03	0.16	0.21	0.94	0.17	0.20	0.77	0.11	0.14	0.67	0.12	0.09
Acetone	0.85	0.83	0.89	0.90	0.89	0.87	0.56	0.56	0.57	0.54	0.53	0.52
Propionald.	0.86	0.82	0.85	0.91	0.83	0.84	0.47	0.43	0.47	0.47	0.44	0.46
Crotonald.	0.52	0.42	0.47	0.52	0.32	0.30	0.42	0.14	0.12	0.30	0.14	0.12
Isobutryald.	0.58	0.58	0.58	0.61	0.85	0.74	0.34	0.42	0.35	0.32	0.33	0.42
Benzald.	0.31	0.29	0.31	0.32	0.27	0.30	0.09	ND	ND	ND	ND	ND
Hexanal	0.19	0.14	0.10	0.15	0.12	0.10	0.07	ND	ND	ND	ND	ND

A = 6 weeks B = 2 months ND = Not Detected

5.1.3.4 Precision and Accuracy

5.1.3.4.1 The method precision and accuracy were determined in the cooperative round-robin conducted by the CCP of the CRC-APRAC CAPI 1–64 Inhouse Group (see Reference 3). The concentration levels of aldehydes in the study are considered to be a worst case situation involving low levels of aldehydes. Reproducibility, that is, the agreement within a laboratory, was better than 20% relative standard deviation (rsd). Repeatability, that is, the agreement between laboratories, was as high as 35% rsd. The precision and accuracy improved as the concentration of aldehydes in the samples increased. The concentration levels in the CRC study were of the order of 0.02 μ mole/mL and should be considered minimum levels required for an analysis to obtain 20% rsd reproducibility. With experience and analysis of samples within 24 h after collection, a precision and accuracy of 10% rsd or better was demonstrated by some participants.

5.1.3.4.2 Two participants developed an alternative cartridge aldehyde method that is described in 5.2. Improved precision and accuracy were reported (see References 9, 10).

5.2 DNPH Cartridge Method—A sample collection modification of the HPLC DNPH method.

5.2.1 SCOPE—This procedure utilizes silica-gel cartridges coated with 2,4-DNPH for the collection of carbonyl compounds. The coated cartridge is ideal for long-term sampling of carbonyls at low parts per million levels in ambient air or for short-term sampling of carbonyls at low ppb to ppm levels in diluted diesel exhaust.

5.2.2 BACKGROUND—The use of solid sorbents for the sampling of aldehydes has been used with varying success (see References 9 to 13). The methods described use a variety of absorbants. Tejada has utilized silica-gel coated cartridges for sampling diesel exhaust and reported the method to the CCP (see Reference 14). The method has been utilized by panel members. The method basically involves purification of DNPH, preparation of DNPH-coated silica cartridges, sampling, recovery of sample, and HPLC analysis. In addition to apparent improved stability of some of the aldehydes, the tentative identification of a compound suspected as the decomposition product of acrolein was reported. The method as described is essentially the one developed by Tejada at EPA-Research Triangle Park. Cooperative testing has been limited and the method is described for informational purposes.

5.2.3 DESCRIPTION OF METHOD

5.2.3.1 Experimental

5.2.3.1.1 Reagents and Chemicals—All solvents used in this procedure should be distilled in glass, HPLC grade solvents, or equivalent grade solvents.

5.2.3.1.1.1 2,4-DNPH—The DNPH should be recrystallized in HPLC grade ACN. Recrystallization is accomplished at 40 to 60 °C by slow evaporation of the solvent to maximize crystal size. Large crystals facilitate the removal of surface impurities and minimize the loss of the purified material during rinsing. Following final removal of impurities, the DNPH is stored in a glass tube (4 cm ID x 15 cm long) fitted with a high porosity glass filter frit and a three-way stopcock at one end and a standard stoppered connection at the other end. A glass stopper, with a vented connection to a DNPH-coated silica cartridge, minimizes exposure of the purified material to carbonyl contaminants from the surroundings. About 50 mL of ACN is maintained above the purified crystals at all times as the source of saturated DNPH stock solution. The stock solution is checked periodically by HPLC for impurities. The concentration of the stock solution prepared in this procedure is about 11 mg DNPH/mL at room temperature.

5.2.3.1.1.2 Solution Checks—Formaldehyde, acetaldehyde, and acetone were usually observed in the blanks and absorbing solutions at levels typically less than 0.01 µg/mL, measured as hydrazones.

5.2.3.1.1.3 Standards—The hydrazone derivatives used as gravimetric standards are prepared by the reaction of individual carbonyl compounds with saturated DNPH solution in 2N HCl. Purity is determined by melting point measurement and HPLC analysis. Calibration standards are prepared by dissolving known quantities of the hydrazone derivatives in ACN.

5.2.3.1.2 Preparation of DNPH-coated Silica Cartridges—Prepacked silica cartridges are obtained for coating. The units contain about 0.7 g of silica gel (approximately 100 mesh) compactly sealed in a plastic tube (1 cm x 2 cm) by plastic filter frits. The cartridges can be connected to a standard male luer type syringe port.

The cartridge is washed by gravity feed elution of 10 mL of ACN from a syringe reservoir. The ACN wash is immediately followed by 7 mL of acidified DNPH coating solution. The DNPH coating is prepared by diluting 25 mL of the saturated stock solution to 1 L with ACN and adding 1 mL of concentrated HCl. Excess solvent is removed by blowing aldehyde-free nitrogen (passed through a DNPH coating cartridge) at 0.3 to 0.4 L/min for 15 min. The cartridges are stored in a refrigerator in an all-glass capped container. Coated cartridges can be prepared in lots of 50 to 100. To produce a consistent lot of cartridges, positive displacement repetitive pipet dispensers can be used for mass cleaning and coating of the cartridges.

Typical concentrations of impurities in cartridges should not exceed those shown in Table 3. These are determined by eluting each of several randomly selected cartridges from each lot with 5 mL of ACN.

TABLE 3—TYPICAL LEVELS OF DNPH CARTRIDGE IMPURITIES (µG PER 5 ML OF ACN WASH)

Formaldehyde	0.2 – 0.7 µg/mL
Acetaldehyde	0.01 – 0.02 µg/mL
Acetone	0.02 – 0.06 mg/mL

5.2.3.2 *Sampling*—The cartridges are used to sample diluted exhaust from diesel engines running either at steady-state or transient operating conditions. The sampling probe and the sampling lines should be heated to about 100 °C to prevent condensation in the sampling system. Exhaust samples are collected via parallel cartridge samples utilizing a heated glass manifold with at least four sampling ports. The flow rate through the cartridges should be between 0.25 and 1.0 L/m. The cartridges are used either singly or with two in series. The latter case would be for sampling conditions where concentration levels are unknown or suspected to be high enough to saturate the cartridge. Short pieces of PTFE FEP tubing that were heat flared on the ends may be used to connect the cartridges. Flow may be controlled with either needle valves or mass flow controllers and monitored using flow meters. A stainless steel metal bellows pump can be used to pump the exhaust through the cartridges. The pump, flow measuring, and controls should be located after the cartridges.

The manifold should have shutoff valves or stopcocks to allow sampling of two tubes in parallel while setting up the next two sampling tubes for a subsequent sampling run.

5.2.3.3 *Sample Recovery and Analysis*—The cartridge samples are recovered by elution with 6 mL of ACN. The elution is in the reverse flow direction by gravity feed. The eluate is collected in a 5 mL volumetric flask and ACN is added to make a 5 mL sample. The sample is analyzed by HPLC using the same procedure as the solvent extraction method found in 5.1.3.3.

Very good recovery and correlation between the two methods was reported by Tejada (see Reference 9). Percent rsd is within 10% for both methods. Both short-term (1 h) and long-term (12 h) samplings were studied as was storage stability with and without refrigeration. Cartridges stored for two weeks without refrigeration and for over one month with refrigeration were not compromised on sample integrity.

6. Diesel Particulate Characterization—The methods of collection of particulate sample from LDD vehicles and HDD engines for certification purposes are specified by USEPA procedures (see References 15, 16). These documents go beyond the certification procedures and are intended for use in the collection and characterization of particulate emissions from diesel engines and vehicles. They are aimed at obtaining a better understanding of engine emissions. It should be kept in mind that the procedures that follow may be subject to change to keep pace with experience and technical advances. The procedures cover the following:

a. TPM
b. SEFs
c. Sulfates and combined water
d. NO_2PAH
e. PAH

6.1 Description of Methods

6.1.1 METHODS OVERVIEW—In the procedures described, the particulates are collected on preweighed, PTFE coated, glass fiber filters. The TPM is determined by weighing the filters before and after use. The filters are extracted with $MeCl_2$ in a soxhlet unit, dried and weighed again to obtain the mass of the soluble fraction. The filter is next extracted with a water solution by agitation and the sulfate is determined by ion exchange chromatography. The mass of solid material in the particulate is determined by subtracting the mass of sulfate and SOF from the total particulate matter. PAH and NO_2PAH analyses are conducted on the SOF. Variations of these procedures are in use depending on the objectives of the tests (see References 17, 18, 19).

The NO_2PAH procedure is found in Section 7. The PAH method is found in Section 8 along with a short PAH analysis version that is useful for the screening of samples. A vacuum sublimation method useful in measuring residual carbonaceous particulate simultaneously on large numbers of samples is described in 6.3.2.1i. The mass rate of each component is calculated by dividing the mass of the component collected by the cubic meters of exhaust sampled, the kW·h of work done, the distance traveled, or on a specific fuel consumption basis. The particulate emission results can be expressed in mass units of g/m^3 of exhaust, g/kW·h, g/mile, or g/kg of fuel consumed.

6.1.2 EXPERIMENTAL

6.1.2.1 Reagents-solvents should be high purity, distilled in glass quality, or equivalent:

a. $MeCl_2$ (methylene chloride)

NOTE—Should only be used in a laboratory hood with adequate ventilation (see Reference 19)

b. Toluene
c. Ethanol
d. Distilled, deionized water

6.1.2.2 Equipment—Best Source Available

a. Filters—Pallflex TX40HI20WW or equivalent
b. Filter holder [1]
c. Pump and metering system[1]
d. Timer[1]
e. Millipore filter cassettes or petri dishes
f. Soxhlet extractor with boiling flask and reflux condenser
g. Microbalance capable of reading to ±0.01 mg
h. Constant temperature and humidity chamber or room
i. Rotary evaporator
j. Kuderna-Danish (KD) evaporator
k. Yellow lighting for room (no wavelengths below 500 nm)
l. Filter forceps
m. Ultrasonic bath

6.2 TPM

6.2.1 PURPOSE—This section describes the particulate sample collection and measuring procedures recommended to obtain the TPM emitted from diesel engines.

6.2.2 PROCEDURES

6.2.2.1 Operation of the Engine—Diesel particulate can be collected in a variety of tests. For steady-state particulate collection with or without a dilution tunnel, the engine operating procedures as described in SAE J1003 (see Reference 20) are guidelines for engine operation. For transient tests, the USEPA (see Reference 15, 16) procedures can be used as a guideline.

6.2.2.2 Dilution Ratio—The dilution ratio used to collect particulate is normally about 10-20:1, air to exhaust. In practice, the actual dilution ratio is usually determined by the incoming exhaust temperature and the amount of air required to achieve a 52 °C (125 °F) or lower filter temperature. The time to collect a desired mass of particulate is also a factor in selecting the dilution ratio. References 6 and 7 discuss these

1. Components of particulate collection system which may vary with respect to individual system design.

interactions. Normally, the CO_2 levels of the raw exhaust and the diluted exhaust, corrected for the CO_2 in the incoming air, are used to calculate dilution ratio in steady-state tests. Mass flow measurements are used in transient tests to determine the dilution.

6.2.2.3 *Tunnel Background*—Tunnel background emission levels and the tunnel conditioning methods can affect the levels of some specific hydrocarbon species such as the PAH. The tunnel background is normally not a major factor in total particulate and SOF measurements if some simple precautions are taken. Tunnel blanks should be periodically run by drawing dilution air through the filter for an equivalent period of time as that used for sampling. Background levels should be well under 1% of the total mass expected to be collected. On start-up of a test, engine exhaust conditions, for example, temperatures and FID emissions, should be established before introducing the exhaust into the tunnel. Only air should be run through the tunnel during engine warm-up (see References 21, 22).

A minimum of 20 min at the desired dilution ratio should be allowed for tunnel equilibration before starting to collect samples. If the sampling point follows a high hydrocarbon emission point, for example, low idle or some light load conditions, a 15 min burnout of the exhaust system may be desirable prior to setting the engine test condition.

6.2.2.4 *Particulate Collection*—Particulate collection methodology for the transient tests is defined in the USEPA procedures (see References 15, 16). For steady-state measurements, the methodology can be considerably different depending on the type of dilution tunnel used (see References 1, 17). The procedures used are usually those that have been developed by the researcher. The particulate characterization methods discussed in the following do not depend on how the sample was collected. However, several precautionary items that will improve the reproducibility in a laboratory are as follows:

a. Utilize Pallflex TX40HI20WW filters. (Filter sizes ranging from 47 to 102 mm are commonly used.)
b. Handle the filter at all times using tweezers or forceps. Avoid using fingers on the filters or any device that may tear particles from the filter.
c. Condition the filter by allowing it to equilibrate in a constant temperature and humidity environment for 16 to 24 h prior to collection of the sample. After sampling, the filters should be conditioned in the same environment prior to weighing. Room temperature should not vary more than 20 °C ± 3 °C during conditioning. The humidity, during conditioning, should be between 30 and 70% and be controlled to a range of ±10%.
d. The filter shall be weighed to the nearest 0.01 mg just prior to use.
e. Monitor the delta P across the filter during sampling. A pressure drop greater than 13 cm Hg is excessive and the termination of the test should be considered. In no case should the pressure drop across the filter exceed 25 cm Hg.
f. It is preferable to collect as large a sample in as short a time as possible. Sample times of 20 to 40 min are common. Table 4 shows the minimum mass collected per filter. At light particulate loads, longer collection times may be required to obtain sufficient sample.
g. Filter face velocities of 10 to 20 cm/s are suggested.
h. Two or three blank filters from each lot of filters should be chosen at random and then subjected to the same process as filters used for the SOF and sulfate analyses described in 6.3. Normally the values for SOF on these blanks will be less than 0.1 mg and sulfates should be below detection limits.
i. Two blank filters from each lot of filters should be selected at random and stored in the constant temperature and humidity chamber or room. Each day the filters can be weighed and recorded. The weight can be compared to the previous day's values and can serve as an indicator of the performance of the environmental chamber.
   Additional filters loaded with standard particulate (see Reference 23) or with sulfuric acid may be more sensitive to changes.

TABLE 4—MINIMUM MASS COLLECTED PER FILTER

Filter Size, mm	Minimum Mass, mg
47	1
70	2
90	3.5
102	5

6.2.3 MEASUREMENT OF TOTAL PARTICULATE

6.2.3.1 After the sample is obtained as per 6.2.2.4, place the filter in the constant temperature and humidity chamber or room and allow the sample to equilibrate in the dark or under yellow light for 16 to 24 h. As an option, see Section 6.2.3.2.

6.2.3.2 Place the filter in a vacuum desiccator saturated with NH_4OH for 1 h. An alternative is to evacuate the desiccator with a water aspirator or vacuum pump to approximately 20 mm Hg vacuum and allow ammonia gas to leak into the desiccator until it is at atmospheric pressure. Let the filter sit in the ammonia atmosphere for 15 min then displace the ammonia atmosphere with clean air. Place the filter in the constant humidity chamber for 16 to 24 h.

If the NH_4OH procedure is used, the combined water correction in 6.3.5 does not apply. This method is useful in handling samples containing high sulfate levels. It stabilizes the weight at about one mole of water per mole of sulfate (see Reference 24).

6.2.3.3 Remove the filters from their containers with forceps and weigh to the nearest 0.01 mg. Record the weight.

6.2.3.4 The difference in weight between the first weighing of the filter and the weighing after step 6.2.3.3 is the TPM, if ammoniation is not used. If the ammoniation is used, the weight added by the addition of two mole equivalent weights of NH_4 for each mole of sulfate must be subtracted from the TPM mass.

6.2.3.5 For long-term storage, the filter is returned to the cassette or petri dish, wrapped with aluminum foil, and stored in a cooler at −20 °C. When the filter is removed from storage, it should be re-equilibrated for 24 h and reweighed to see if any losses in TPM occurred during storage. If losses are equal to, or greater than, 10% wt of the TPM or 20% wt of the SOF, discard the sample.

6.3 SEF

6.3.1 PURPOSE—The methods of collection of a particulate sample from light-duty diesel vehicles and heavy-duty diesel engines are specified by USEPA procedures (see Reference 1). These samples are collected directly from diesel exhaust or from dilution tunnels using specific engine operating and sampling procedures and are composed of various subfractions described in the next section. These fractions are of interest in evaluating health effects issues and effects of engineering or technology changes in the engine systems. Particulate samples can be obtained at transient or steady-state conditions depending on the purpose of the test.

SEF fractions discussed include the SOF, TOE, sulfate fraction, and the combined water.

6.3.2 EXTRACTION OF SOF—This fraction is obtained by extraction of the TPM with $MeCl_2$ (see Note in 3.4.7).

6.3.2.1 *Procedure*—This procedure is based on the results obtained through the cooperative studies of the CCP of CRC-APRAC CAPI 1–64 (see References 3, 4, 25, 26).

a. Carry out all operations under "yellow light" and minimize sample exposure to sunlight. Keep the samples stored in the dark when not being used.
b. Fold the filter in half, quarters, and eighths with the particulate on the inside. Carefully bend over the top of the filter before the final fold. Use the filter forceps, wear gloves, and avoid tearing fibers from the filter. Carry out the filter folding on a clean plate glass surface. Place the filter in the soxhlet extractor with the point of the folded filter toward the base of the extractor. If done correctly, negligible loss of particulate through carryover occurs.
c. Assemble the soxhlet apparatus. For the 47 mm filters, a microsoxhlet unit equipped with a 30 mL flat bottomed flask is used. Put 20 mL of $MeCl_2$ in the flask. Wrap the flask and the extractor unit in aluminum foil if not under yellow light. Start the water flowing through the condenser.
Larger flasks and extractor units are required for larger filters (see Reference 4).
d. Start hot plate or place soxhlet units in a constant temperature bath and allow the solvent to begin cycling through the apparatus. Adjust the temperature so that the solvent cycles through the extraction cell about every 5 to 10 min. Extract for at least 4 h.
Cycle time of the extractors may vary. A total of 40 cycles should be used as a guideline.
e. Turn off the heat, or remove the extractors from the bath and allow the solvent to stop boiling. Examine the solvent in the flask for particulate. If the folding of the filter in 6.3.2.1b was not done properly, some particulate may be carried over into the solvent reservoir. If this occurs, filter the solvent through a tared filter paper, allow to dry, and weigh the residue. Add the particulate weight to that in 6.3.2.1g.
f. Disassemble the soxhlet apparatus and carefully remove the filter with filter forceps. Avoid tearing any fibers from the filter. Place the filter on a clean watch glass or petri dish and allow the $MeCl_2$ to evaporate in a fume hood. After 30 min at room temperature, place the filter back into the cassette and return it to the constant temperature and humidity chamber. Remove the cover and let the filter equilibrate for 16 to 24 h.
g. The filter is then removed from its container and reweighed on the microbalance to the nearest 0.01 mg.
h. The loss in weight after this extraction is the SOF.
i. Vacuum sublimation is a possible alternative to this method if the SOF is not required for further analyses. The filters are held in a vacuum oven at 200 °C, 15 to 20 in of Hg pressure or less. After 16 h, carefully release the vacuum and remove the filters. The filters are then allowed to cool and are placed in the weighing room at constant temperature and humidity to equilibrate for 16 to 24 h. Data to support vacuum sublimation have been reported (see Reference 27). Data found in Table 5 indicate shorter times can be used. Additional study of the sublimation method was recommended by the CCP. The disadvantage of the vacuum sublimation technique is that the fraction volatilized is lost and cannot be further analyzed.

TABLE 5—COMPARISON OF SOF AND VACUUM REMOVAL OF ORGANIC FRACTION

Sample Size, mg	SOF wt %	Vacuum Temperature[1], °C 93 wt Loss, %	Vacuum Temperature[1], °C 135 wt Loss, %	Vacuum Temperature[1], °C 177 wt Loss, %
9.90	36.4	38.6	41.4	44.0
10.2	43.4	—	48.2	49.2
7.77	—	22.0	39.5	—
7.77	46.1	48.6	—	51.0

1. All samples were under vacuum (Δ15 in Hg) for 6 h.

6.3.3 EXTRACTION OF TOE—This fraction contains the more polar organics and is extracted using a toluene:ethanol binary solvent (32:68 wt/wt, BP = 76.7 °C). The fraction contains material that is not removed by $MeCl_2$ and is equal to the SOF plus the additional polar compounds extracted. Depending on the purpose of the extraction, the entire fraction can be removed in one step, bypassing the SOF extraction.

NOTE—The TOE extraction solvent may also remove some of the sulfates. Therefore, sulfate analysis should not be conducted on filters after a TOE extraction.

6.3.4 DETERMINATION OF SULFATE—The filter from the SOF determination may be used to determine sulfates or a separated particulate filter may be used. If enough TPM was collected for an accurate analysis, sufficient sulfate will have been collected if current No. 2 diesel fuels were used. Basically, the procedure involves the extraction of the water soluble sulfates and analysis by ion chromatography. Instrument operating procedures are supplied by the manufacturer (see Reference 28).

6.3.4.1 Procedure

a. Place the filter in a 4 oz PTFE capped bottle and add 20 mL of an aqueous solution that is 0.003 molar in $NaHCO_3$ and 0.0024 molar in Na_2CO_3. Distilled, deionized water should be used. Some units using older column technology may use 60/40 isopropyl alcohol/water solution for the extraction.
b. Shake the bottles vigorously or place the bottles in a sonication bath with a 1 in level of water in the bath. Shake or sonicate the samples for 10 min or until the filter breaks up.
c. Filter the sample through a 0.45 µm filter on a luer fitted syringe filter.
d. Calibrate the ion chromatograph with a standard potassium sulfate solution to obtain a calibration curve.
e. Inject 5 mL of the filtered sample directly into the ion chromatograph or dilute with the eluent if sulfate concentrations are too high.
f. Compare the response from the filter sample to the calibration curve.
g. Calculate the mg of sulfate on the filter and relate the results to the volume of exhaust sampled.

6.3.5 COMBINED WATER—The combined water is the amount of water that has associated with the sulfates in the particulate sample.

6.3.5.1 The preferred method is to equilibrate the particulate samples in the weighing room at 50% humidity and subtract 1.3 times the weight of the sulfate from the TPM. Correction factors for other humidity levels can be determined from Figure 4.

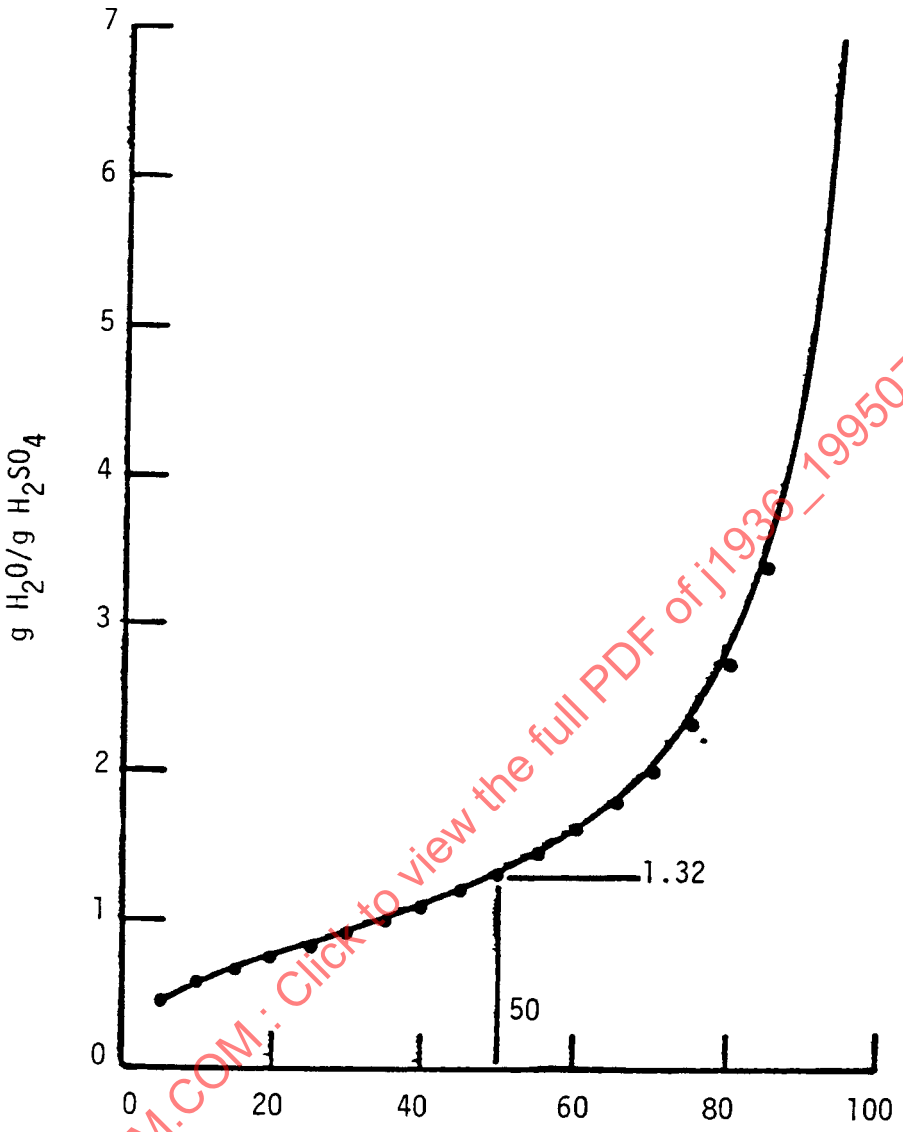


FIGURE 4—MASS OF BOUND H_2O PER GRAM H_2SO_4 IN AN AQUEOUS SOLUTION VERSUS RELATIVE HUMIDITY (25 °C)

Alternate methods are listed as follows:

a. An option is to place the filter, in its container with the top removed, into a desiccator containing Drierite for 16 to 24 h. Then remove the filter and rapidly weigh it. Subtract this weight plus a one mole weight equivalent to the number of moles of sulfate from the gross weight obtained for the TPM.
b. If the ammoniation method (6.2.3.2) is used, subtract a weight equal to 0.2 the weight of the sulfate from the TPM to correct for the added ammonia. (The stoichiometer suggests two moles of NH_3 per mole of sulfate. However, experimental data indicate only about 2% wt increase.)

6.3.6 REPEATABILITY—The precision of the measurement of TPM, SOF, TOE, and sulfate depend on the total mass of each component collected with higher masses producing better precision. A CRC-APRAC round-robin interlaboratory program established a rsd of ±15% for SOF and TOE when using a minimum particulate sample size of 1 mg. For particulate samples of 10 mg or larger, precision within a laboratory should be better than ±10%. The round-robin test results have been reported (see Reference 25).

Precision of the sulfate measurement has not been established but is expected to be ±5% or better.

7. Nitrated PAH

7.1 Scope—This procedure defines the system and analytical method for the measurement of NO_2PAH in diesel particulate samples by their conversion to amines and detection by fluorescence. Due to limited round-robin testing, the procedure is only informational at this time and is not a recommended practice at this time.

7.1.1 BACKGROUND—The determination of NO_2PAH compounds described in this procedure is based on an analytical method developed by Tejada at the US EPA-RTP laboratories (see Reference 29). The method was initially developed for the analysis of 1-nitropyrene (1-NOP) and is currently undergoing cooperative round-robin testing. The method is an HPLC method and uses a Pt/Rh catalyst, at 80 °C, to convert the NO_2PAH to amines on the column. The amines are then analyzed using fluorescence detection.

7.1.2 DEFINITIONS AND ABBREVIATIONS

NO_2PAH = Nitrated Polycyclic Aromatic Hydrocarbons
1-NOP = 1-Nitropyrene
HPLC = High Performance Liquid Chromatography
Pt/Rh = Platinum/Rhodium
ID = Internal Diameter
MeOH = Methanol
$MeCl_2$ = Dichloromethane

7.1.3 EXPERIMENTAL

7.1.3.1 Equipment—HPLC—Various units available

Columns

a. Pt/Rh catalyst coated on 5 µm Superisorb 5AY Alumina or equivalent (see Caution). Two columns (typically 5 cm x 4.6 mm) are required.
   CAUTION—MeOH must be flushed from the column with water every time an end fitting is removed. (The catalyst has been observed to flame spontaneously when allowed to dry in air after use of a MeOH-rich aqueous solution.)
b. Zorbax ODS (25 cm x 4.6 mm ID) or equivalent.
c. Zorbax ODS (15 cm x 4.6 mm ID) or equivalent.
d. Fluorescence detector—various types available. Requires a minimum of 360 nm excitation and 430 nm emission.

A schematic of the system is shown in Figure 5.

7.1.3.2 Solvents

7.1.3.2.1 MeOH—Use distilled in glass quality or equivalent.

7.1.3.2.2 $MeCl_2$—Use distilled in glass quality or equivalent (see Note in 3.4.7).

7.1.3.2.3 Water—Distilled, deionized water.

7.1.3.3 *Procedure*—The NO_2PAH do not fluoresce but can be converted on the column in the HPLC to amines that do fluoresce. This method is currently one of two being evaluated by the CCP. The method was recently utilized in the CRC-APRAC CAPE-33-80 Research Project conducted by an independent contractor (see Reference 30):

a. The system utilizes two short reduction catalyst columns. The first one removes oxygen containing compounds from the solvent. The second catalyst converts the NO_2PAH to fluorescent NH_2PAH. The HPLC oven is set at 80 °C for the columns.
b. Two 5 µm Zorbax ODS analytical columns, or equivalent, are also used. The first column separates any NH_2PAH present in the extract from the NO_2PAH before they enter the reduction catalyst. The second analytical column further separates the reduced NO_2PAH from other interfering compounds in the extract.
c. The appropriate extract of SEF fraction is dissolved in a 50:50 mixture of $MeCl_2$ and MeOH. The actual volume of solvent used depends on the NO_2PAH levels expected. Initially, use 1 mL of each solvent and dilute as appropriate.
d. The flow rate of the mobile phase is set at 1 mL/min with the first solvent (77% MeOH/23% H_2O).
e. Following the elution of the desired reduced NO_2PAH, that is, 1-NOP elutes at about 30 min after the injection, the solvent flow is changed to pump No. 2 and 100% MeOH is used to clean the columns. After about 20 min, the column flow is switched back to pump No. 1 and the columns are equilibrated for 20 min prior to injection of the next sample (see Caution in 7.1.3).
f. Samples are quantified against standards obtained from the National Institute of Standards and Technology (NIST) (see Reference 31).

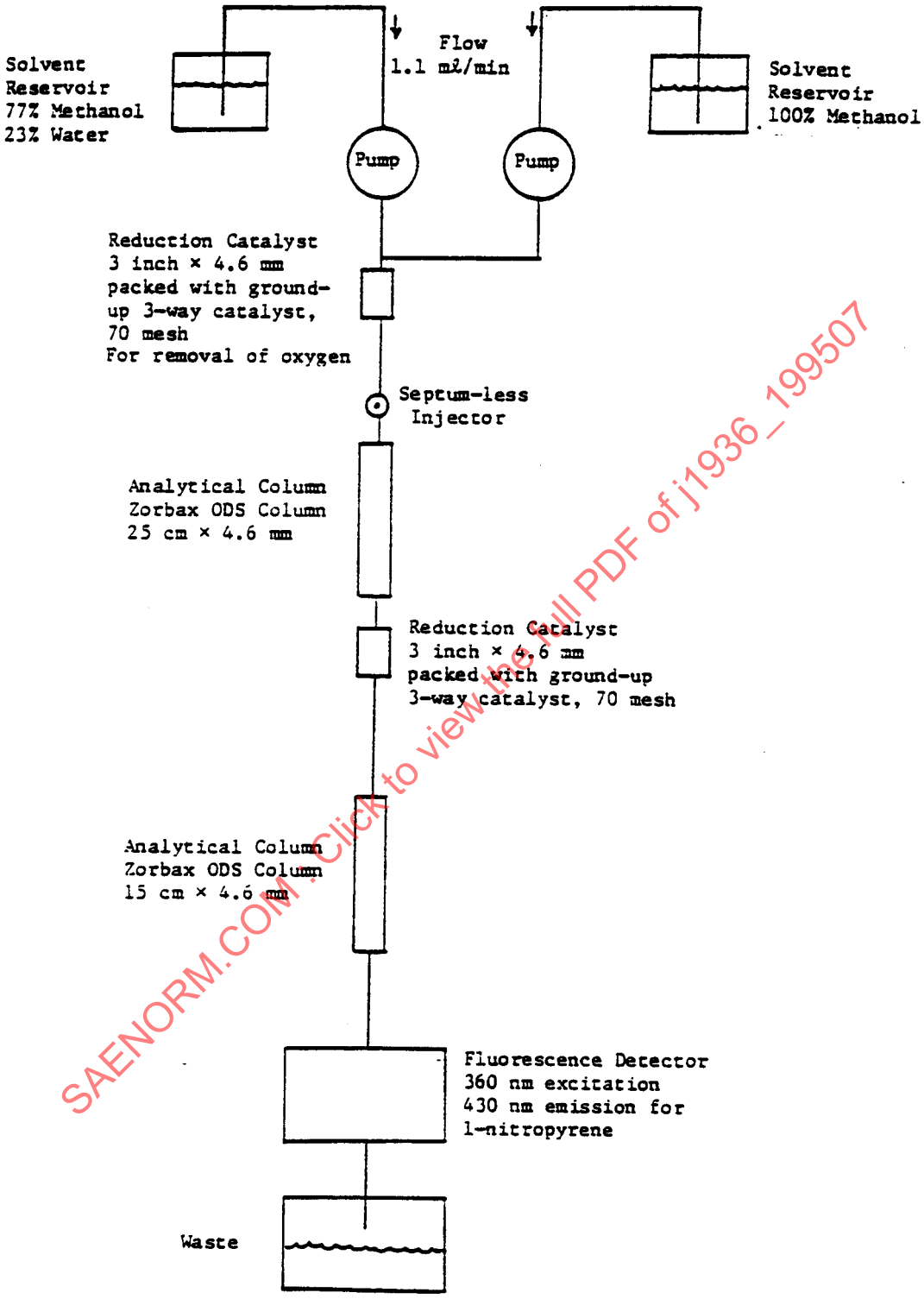


FIGURE 5—SCHEMATIC OF NITROPYRENE ANALYSIS SYSTEM

7.1.3.4 *Precision and Accuracy*—The precision and accuracy of the method have not been determined. A round-robin is currently in progress and should add limits to this area.

Lab test repeatability is estimated to be ±20% or better.

7.1.3.5 *Alternate Column Configuration*—If interference or peak separation problems do occur, the column system can be modified as described by Tejada (see Reference 29). Tejada's column system is more complicated but does eliminate the overlap of some peaks.

7.1.4 ALTERNATE METHOD—A gas chromatographic method utilizing an electron capture detector (ECD) was developed by A.D. Little, Inc., under contract for the CRC-APRAC CAPE-30 Project Group. The method is reported in the literature (see Reference 32). The method has been used by members of the CCP. However, they did replace the splitless injection of the sample with on-column injection of the sample to obtain better results.

8. PAH

8.1 Scope—This procedure defines the system and analytical method for the measurement of PAH in diesel particulate samples by HPLC. This procedure should only be considered informational at this time. An international round-robin study coordinated by the NIST is in progress and may dictate a final procedure.

8.1.1 BACKGROUND—The analysis of PAH compounds and NO_2PAH compounds in diesel exhaust has received considerable attention relative to the health issues associated with diesel particulates. Two methods are discussed in this section. The first method evolved as a result of cooperative efforts of the CCP. However, the method is manpower intensive, requiring some 10 to 12 HPLC runs to analyze each sample. The method uses a normal phase chromatographic extract cleanup followed by an analysis using reverse phase columns and fluorescence detection for quantification. The compounds analyzed are found in Table 6. The method development was conducted under a CRC contract (see References 23, 33) and a round-robin was conducted.

The second method requires only a silica gel column cleanup followed by an HPLC separation. It is adequate for routine screening of samples but is not as comprehensive as PAH Method No. 1.

TABLE 6—HPLC OF POLYCYCLIC AROMATIC HYDROCARBONS: FRACTION 1 [1]

PAH	Retention Time, min	Fluorescence Wavelength, nm Excitation	Fluorescence Wavelength, nm Emissions [2]	Detection Limit, ng [3]
Fluorene	16.50	260	370	3.67
Phenanthrene	18.85	260	370	0.93
Anthracene	20.92	260	370	0.50

1. HPLC elution conditions—4.6 mm x 25.0 cm vydac five micron reverse phase column; linear gradient, ACN/water (50/50, vol/vol) to ACN/water (70/30, vol/vol) in 30 min, then to 100% ACN in 10 min, followed by 10 min at 100% ACN. The system was returned to initial conditions using a reverse gradient of 5%/min for 10 min and equilibrated at initial conditions for 15 min; flow: 1.0 mL/min; detector range: 1.0 (minimum range: 0.01); injection volume: 15 µL.
2. A detector with a 370 nm emission cutoff filter was used.
3. The detection limit was defined as the on-column amount of compound that would give a peak that was five times the baseline noise under these instrumental conditions.

8.1.2 DEFINITIONS AND ABBREVIATIONS—

ACN = Acetonitrile
CCP = Chemical Characterization Panel, CRC-APRAC CAPI 1-64 Inhouse Project Group
HPLC = High Performance Liquid Chromatography
NO_2PAH = Nitrated Polycyclic Aromatic Hydrocarbons
PAH = Polycyclic Aromatic Hydrocarbons
SOF = Soluble Organic Fraction
TOE = Total Organic Extract Fraction
VOC = Vapor Phase Organic Compounds
vol/vol = volume/volume

PAH Compounds

Fl = Fluorene
Ph = Phenanthrene
Anth = Anthracene
Fluor = Fluoranthene
Py = Pyrene
BaA = Benz(a)anthracene
Ch = Chrysene
BbF = Benzo(b)fluoranthene
BkF = Benzo(k)fluoranthene
BaP = Benz(a)pyrene
B(g,h,i) = Benzo(g,h,i)perylene
BeP = Benz(e)pyrene

8.1.3 EXPERIMENTAL

8.1.3.1 *Equipment*—HPLC = High performance liquid chromatograph. Stop flow capability preferred but is not required. Various instruments are available on the market.

UV Detector = Requires 254 nm wavelength. This is used for fractionation of the extract in Method No. 1.

Bondapak NH_2 Column = Normal phase aminosilane semipreparative column, 7.5 mm x 30 cm.

Vydak Five Micron Column = Reverse phase analytical column, 4.6 mm x 25 cm.

Fluorescence Detector = Wavelength capability as shown in Tables 6, 7, and 8.

Evaporator = KD evaporator with a microsnyder condenser.

TABLE 7—HPLC OF POLYCYCLIC AROMATIC HYDROCARBONS: FRACTION 2 [1]

PAH	Retention Time, min	Fluorescence Wavelength, nm Excitation	Fluorescence Wavelength, nm Emissions [2]	Detection Limit, ng [3]
Fluoranthene	10.50	260	370	1.22
Pyrene	11.97	260	370	2.26
Benz(a)anthracene	17.40	280	389	0.51
Chrysene	18.72	260	370	0.59

1. HPLC elution conditions—4.6 mm x 25.0 cm vydac five micron reverse phase column; isocratic elution, ACN/water (70/30, vol/vol) for 15 min, then a linear gradient to 100% ACN in 15 min, followed by 15 min at 100% ACN. The system was returned to initial conditions using a 10 min gradient followed by an equilibration period of 15 min; flow: 1.0 mL/min; detector range: 1.0 (minimum range: 0.01); injection volume: 30 µL.
2. A detector with a 370 and 389 nm emission cutoff filter was used in these analyses.
3. The detection limit was defined as the on-column amount of compound that would give a peak that was five times the baseline noise under these instrumental conditions.

TABLE 8—HPLC OF POLYCYCLIC AROMATIC HYDROCARBONS: FRACTION 3 [1]

PAH	Retention Time, min	Fluorescence Wavelength, nm Excitation	Fluorescence Wavelength, nm Emissions [2]	Detection Limit, ng [3]
Benzo(b)fluoranthene	32.34	280	389	0.29
Benzo(b)fluoranthene	34.11	280	389	0.23
Benzo(a)pyrene	35.73	280	389	0.29
Benzo(g,h,i)perylene	40.82	280	389	1.71

1. HPLC elution conditions—4.6 mm x 25.0 cm vydac five micron reverse phase column; linear gradient, ACN/water (50/50, vol/vol) to ACN in 40 min, followed by 20 min at 100% ACN. The system was returned to initial conditions for 15 min; flow: 1.0 mL/min; detector range: 1.0 (minimum range: 0.01); injection volume: 30 µL.
2. A detector with a 389 nm emission cutoff filter was used.
3. The detection limit was defined as the on-column amount of compound that would give a peak that was five times the baseline noise under these instrumental conditions.

8.1.3.2 *Solvents*—Distilled in glass or equivalent quality:

ACN

$MeCl_2$

Hexane

Iso-octane

Tetrahydrofuran (THF)

All solvents should be degassed immediately prior to use.

8.1.4 PAH METHOD 1—The analysis of PAH compounds in diesel exhaust particulate involves an extraction to remove the organic fraction containing the PAH compounds from the particulate or collection media. The extract undergoes a separation procedure to isolate the PAH compounds. This is followed by chromatographic analysis of the PAH. The large number of compounds in diesel extracts make the precise and accurate analysis of the PAH difficult unless there is prior cleanup of the sample.

This method was developed under contract to the CRC (see Reference 22) and evaluated by the CCP (see Reference 33). The method may be further modified as a result of a second round-robin in progress but the major changes are unlikely. Figure 6 is a schematic summarizing the method. This method is applicable to SOF, TOE, and VOC samples.

8.1.4.1 Procedure

8.1.4.1.1 Step 1—Extract Preparation—Following the extraction of the SOF, TOE, or VOC, the extracts are reduced in volume to about 1 mL by evaporation of the solvent using a gentle stream of clean nitrogen in the KD evaporator at 65 °C. The solvent level is adjusted, if required, to about 1 mL just prior to making a solvent exchange to heptane. (Iso-octane can be used if extract solubility problems are observed.) In the case of TOE fractions, a solvent exchange to $MeCl_2$ must be conducted prior to the heptane exchange.

In the heptane exchange, add 2 mL of heptane and evaporate the sample under a gentle stream of nitrogen to less than 0.5 mL. Add an additional 3 mL of heptane and concentrate the sample to a final volume of exactly 1 mL. The extract in heptane (50 µL) is fractionated using the normal phase Bondapak column.

NOTE—Small extract samples, less than 4 mg, or samples containing low PAH concentrations may require further concentrating of the heptane solution to obtain adequate samples from the fractionation in the next step. This can better be evaluated after conducting Step 2.

8.1.4.1.2 Step 2—Extract Fractionation—The heptane solution (50 µL) is fractionated using normal phase HPLC on the 7.5 mm x 30 cm Bondapak aminosilane column. The eluant is hexane at a flow rate of 3 mL/min. The eluting compounds are monitored using a UV detector at a wavelength of 254 nm. Three fractions are collected as they elute from the column at approximately 0 to 11 min, 11 to 21 min, and 21 to 40 min. A typical separation is found on Figure 7. Fraction 1 contains PAH with three rings or less, Fraction 2 contains four ring compounds and Fraction 3 contains the PAH with five or more rings. The collection times may vary slightly depending on experimental factors, for example, column packing differences, sample composition, etc. It is important, therefore, to periodically run a PAH standard. The actual collection times can be determined by analyzing a standard solution containing both F1 and Ch. The collection time for Fraction 2 begins just prior to the elution of F1 and ends just after the elution of Ch. The NIST standard (see Reference 31) contains both compounds and can be used to establish the actual fraction collection times.

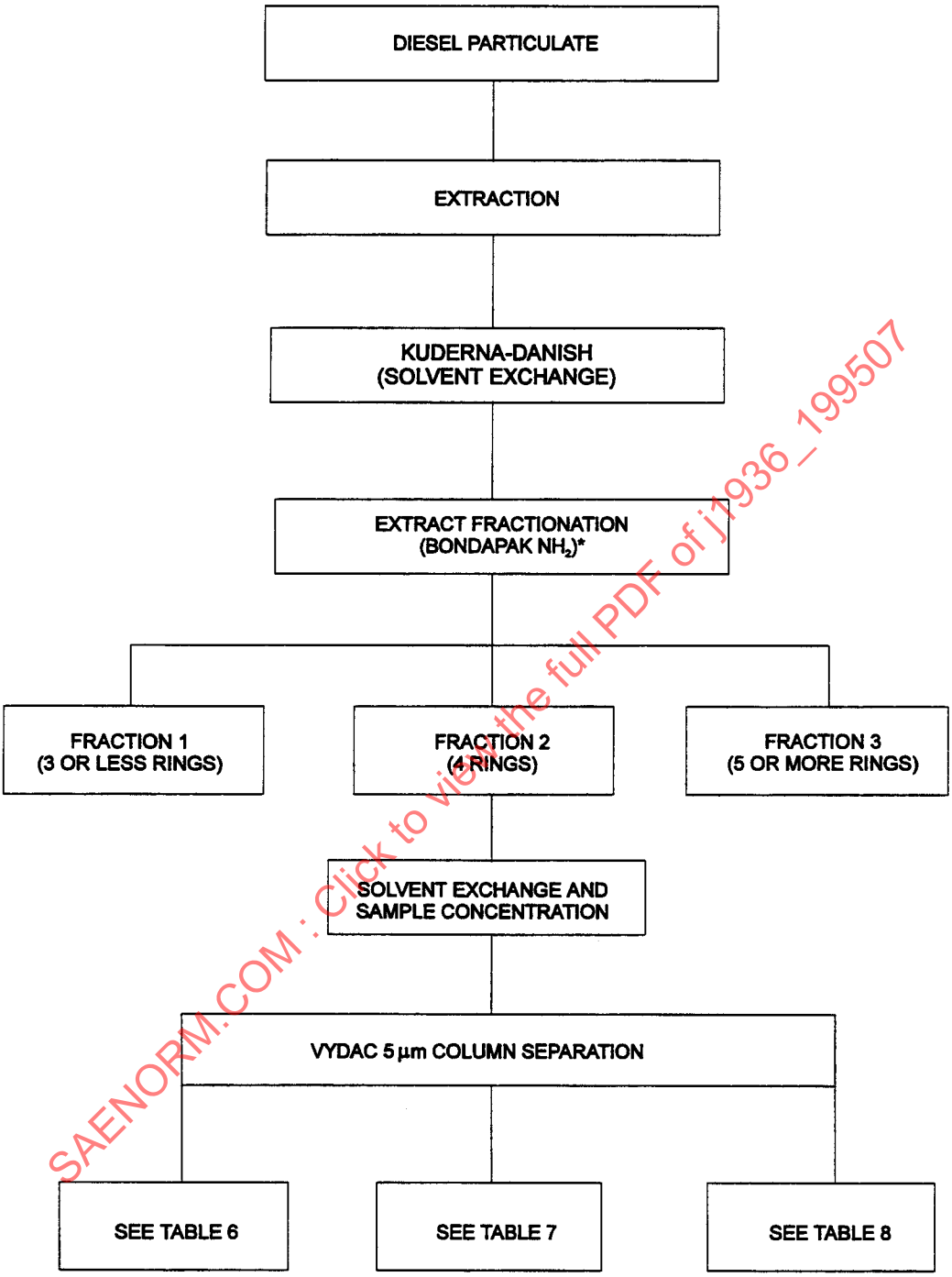


FIGURE 6—HPLC PAH METHOD NO. 1

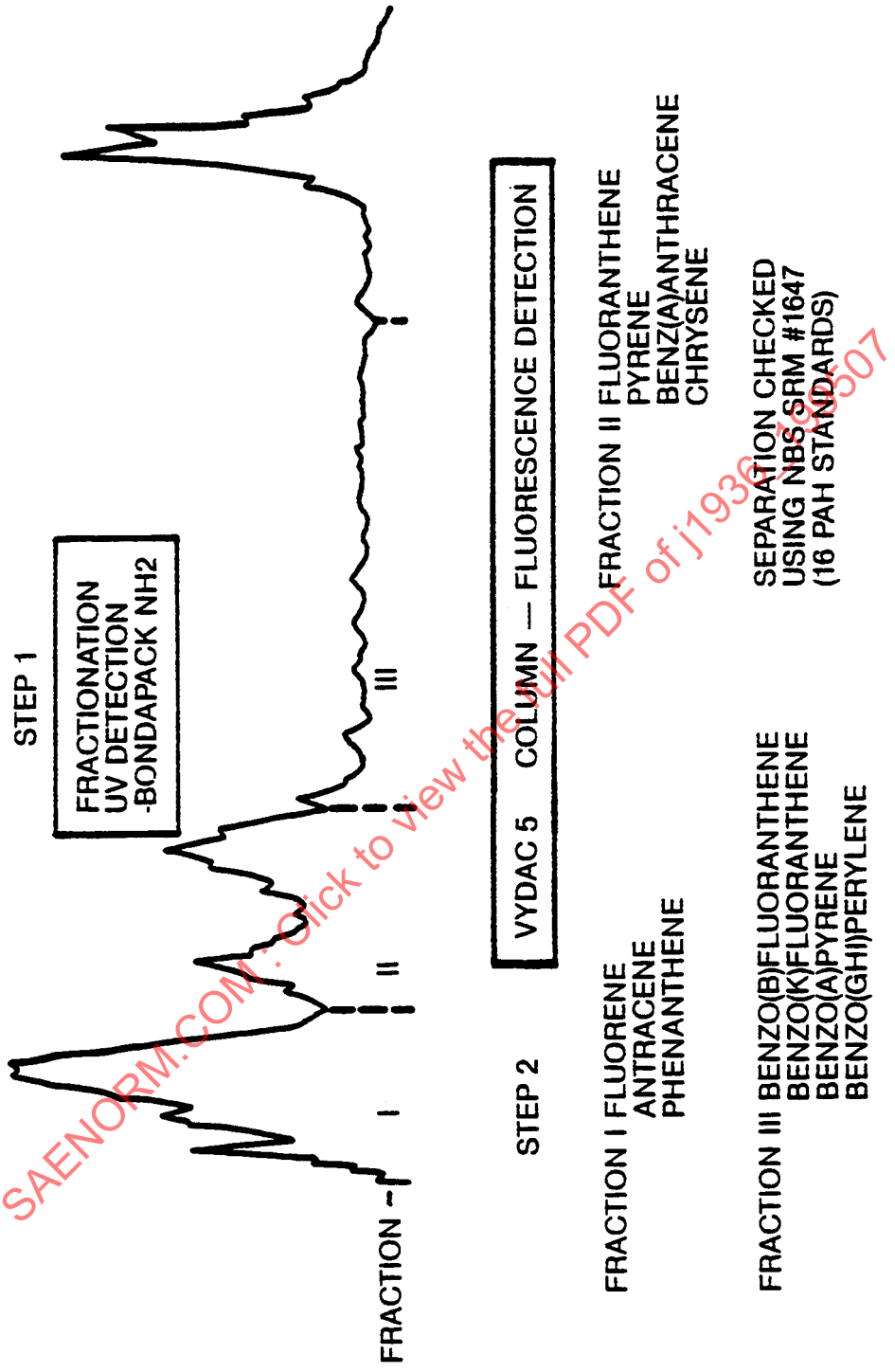


FIGURE 7—HPLC METHOD SUMMARY—FRACTIONATION OF THE DIESEL EXTRACT