PETROLEUM DISTILLATE FRACTIONS (PDF)
(This method was fully evaluated with Stoddard solvent. It can also be used to determine V.M.&P. naphtha and mineral spirits.)

Method no.:	48
Matrix:	Air
Target concentration:	2900 mg/m^3 Stoddard solvent (OSHA PEL)
Procedure:	Samples are collected by drawing a known volume of air through charcoal tubes. Samples are desorbed with carbon disulfide (CS_2) and analyzed by gas chromatography (GC) using a flame ionization detector (FID).
Recommended air volume and sampling rate:	3 L at 0.2 L/min
Reliable quantitation limit:	0.77 mg/sample (260 mg/m^3)
Precision: (1.96 SD): (Section 4.3.2)	17.8%
Status of method:	Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

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1. General Discussion

1.1 Background

1.1.1 History

Three refined petroleum mixtures are routinely analyzed at this laboratory. They are Stoddard solvent (boiling range 160-210°C), mineral spirits (boiling range 150-200°C), and petroleum distillates (V.M.&P. naphtha; boiling range 95-160°C). These mixtures will collectively be termed petroleum distillate fractions (PDF) throughout this method. All of these PDFs contain aliphatic and to a lesser extent aromatic hydrocarbons. (Ref. 5.1)

The procedures for collection (charcoal tubes) and analysis (GC/FID) of PDFs described in this evaluation are basically those used in NIOSH methods S380 and S382. (Ref. 5.2) For preparation of analytical standards, these NIOSH methods require a sample of the bulk material presumed to be the source of the air contamination (this bulk material will be referred to as the "source PDF" throughout this method). The shipment of source PDFs, which are often flammable, is inconvenient and the materials sometime require distillation before use in standards. For these reasons and because similar responses to different hydrocarbons are observed using a FID (Ref. 5.3), the use of analytical standards prepared from a PDF which is not the source PDF was investigated. In order to determine analytical conditions, it was assumed that this substitute PDF ("non-source PDF") should be of the same type, i.e. Stoddard solvent, mineral spirits, or petroleum distillates, as that used at the sampling site.

Internal standards (Istd) are routinely used in solvent analyses at this laboratory. Since the actual constituents of PDFs are unknown, the presence of an internal standard may cause an interference with the PDF or unduly lengthen the analysis time. For these reasons, the possibility of using an external standard (Estd) procedure was examined.

Also, in preliminary work it became apparent that the manner in which the baseline was set was a concern. If the data system was allowed to automatically set the baseline, inconsistencies in the positions to which the baseline was drawn were noticed (Figures 4.8.1 and 4.8.2). This produced calibration errors at lower concentrations of PDFs. To overcome this problem, an evaluation of certain "integrate functions" available in the data system software which control the baseline was done (Section 4.8.4).

In order to evaluate the parameters of baseline, Estd, and material used to prepare analytical standards, a study was done utilizing eight different PDFs consisting of five Stoddard solvents, two V.M.&P. naphthas and one mineral spirits. These were used to spike 8 sets of 12 charcoal tubes. Each 12-tube set was quantitated using analytical standards prepared from both source and non-source PDF. There were no restrictions on the analytical conditions or GC column used for these analyses, in order to avoid having data which would apply to only certain analytical conditions. (Section 4.8)

The results of this study indicate several things; there is no significant difference in results obtained by using either the source or non-source PDF (Section 4.8.2), an internal standard is not needed when consistent injection size can be maintained (Section 4.8.2), and consistent setting of the baseline may be obtained by using "integrate functions". (Section 4.8.4).

Other tests performed for this evaluation were break through, storage stability, desorption efficiencies, precision of the analytical procedure, sensitivity and reliable quantitation limit. The breakthrough tests were performed with both a Stoddard solvent (Section 4.4.1) and a V.M.&P. naphtha (Section 4.4.2) to ensure the collection procedure would work for the more volatile constituents of a V.M.&P. naphtha. All of the other tests were performed using a Stoddard solvent but the collection and analytical procedure should also be applicable to petroleum distillates and mineral spirits.

There are two OSHA PELs that pertain to petroleum distil late fractions. The PELs are 2900 mg/m^3 for Stoddard solvent and 2000 mg/m^3 for petroleum distillates (naphtha). Due to numerous synonyms and the overlapping boiling range fractions that are available, there is much confusion as to which standard is applicable in many instances. Mineral spirits, which is almost identical to Stoddard solvent in boiling range, should be compared to the Stoddard solvent PEL; while the lower boiling range petroleum distillate fractions should be compared to the petroleum distillate (naphtha) PEL.

This evaluation shows that PDFs can be collected using charcoal with a 3-L air volume, analyzed by GC/FID and a non-source PDF may be used to prepare analytical standards.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy).

"Short-term Exposure: Overexposure to Stoddard solvent causes irritation of the eyes, nose, and throat and may cause dizziness. Very high air concentrations may cause unconsciousness and death. Long-term Exposure: Prolonged overexposure to the liquid may cause skin irritation." (Ref. 5.4)

"Short-term Exposure: Overexposure to petroleum distillates may cause dizziness, drowsiness, headache, and nausea. They may also cause irritation of the eyes, throat, and skin. Long-term Exposure: Prolonged exposure may cause drying and cracking of the skin." (Ref. 5.5)

Men were exposed to mineral spirits concentrations of 2500 to 5000 mg/m^3 for an unspecified time period. Both concentrations produced nausea and vertigo in the subjects. In another study at 4000 mg/m^3 there was a prolongation of reaction time. (Ref. 5.1)

1.1.3 Potential workplace exposure

NIOSH estimates that about 600,000 workers in the United States are potentially exposed to all "specialized naphthas" (Ref. 5.1).

Petroleum distillates (V.M.&P. naphtha) is used as a quick evaporating paint thinner. Stoddard solvent is used in the dry cleaning industry. Mineral spirits is a general purpose thinner, a dry cleaning agent, and a solvent for paint and varnish industries. (Ref. 5.1)

1.1.4 Physical properties (Ref. 5.1 unless otherwise stated)

Petroleum distillates	
molecular weight:	approximately 87-114
odor:	pleasant aromatic odor
boiling range:	95 - 160°C
specific gravity:	0.7275 - 0.7603
color:	clear, water white to yellow
vapor pressure:	2 - 20 mm Hg at 20°C
flashpoint:	-6.7 to 12.8°C (closed cup)
synonyms:	benzine, naphtha 76, ligroin, high boiling petroleum ether
molecular species:	C_7-C_{11}

Stoddard solvent	
molecular weight:	approximately 135 - 145
odor:	kerosene-like
boiling range:	160 - 210°C
specific gravity:	0.75 - 0.80
color:	colorless
vapor pressure:	4 - 4.5 mm Hg at 25°C
flashpoint:	37.8°C (closed cup)
synonyms:	140 flash solvent, odorless solvent and low end point solvent
molecular species:	C_9-C_{11}

Mineral spirits	
molecular weight:	approximately 144 - 169
odor:	pleasant sweet odor
boiling range:	150 - 200°C
specific gravity:	0.77 - 0.81
color:	clear, water white
vapor pressure:	0.8 mm (Hg) at 20°C
flashpoint:	30.2 - 40.5°C (closed cup)
synonyms:	white spirits, petroleum spirits, and light petrol
molecular species:	C_9-C_{12}

1.2 Limit defining parameters (Air concentrations are based on the recommended air volume (3 L) and a desorption volume of 1 mL.)

1.2.1 Detection limits

Since PDF consist of numerous and varying components, the determination of meaningful detection limits was not considered feasible.

1.2.2 Reliable quantitation limit

The reliable quantitation limit is 0.77 mg/sample (260 mg/m^3) This concentration was arrived at by taking all the results for calibration methods #4 and #5 from Tables 4.8.1 through 4.8.8 that were near certain concentrations, i.e., 0.3 mg/mL and 0.7 mg/mL, and finding the average recoveries, the average concentrations, and standard deviations (SD) near those concentrations. The results for samples near 0.77 mg/mL met both the requirements of 75% recovery and a precision (1.96 SD) of ±25% or better. (Section 4.2)

1.2.3 Sensitivity

The sensitivity of the analytical procedure over a range representing 0.5 to 2 times the target concentration based on the recommended air volume is 300954 area units per mg/mL. This is determined by the slope of the calibration curve. (Section 4.3.3.)

1.2.4 Recovery

The recovery of samples used in a 15-day storage test remained above 94% (Section 4.6). The recovery of the analyte from the collection medium during storage must be 75% or greater.

1.2.5 Precision of the analytical procedure

The pooled coefficient of variation obtained from replicate determinations of analytical standards at 0.5, 1, and 2 times the target concentration is 0.019 (Section 4.3.1).

1.2.6 Precision of the overall procedure

The precision of the overall procedure at the 95% confidence level is ±17.8% (Section 4.3.2). This includes an additional 5% for sampling error. The overall procedure must provide results that are ±25% or better at the 95% confidence level.

1.2.7 Reproducibility

Six samples spiked by liquid injection and a draft copy of this procedure were given to a chemist unassociated with this evaluation. The samples were analyzed after 2 days of storage at 22°C. The average recovery was 97.7% with a SD of ±3.53%. (Section 4.7)

1.3 Advantages

1.3.1 The collection procedure is convenient.

1.3.2 The analytical procedure is rapid and precise.

1.4 Disadvantages

None

2. Sampling Procedure

2.1 Apparatus

2.1.1 A personal sampling pump which can be calibrated within ±5% of the recommended flow rate is needed.

2.1.2 Coconut shell charcoal tubes which consist of glass tubes 7 cm long, 6-mm o.d., and 4-mm i.d., containing a 100-mg section and a 50-mg section of charcoal separated with a urethane foam plug are used. The glass tube is flame sealed at both ends. For this evaluation, SKC, Inc. charcoal tubes, lot 120, were used.

2.2 Reagents

None required

2.3 Technique

2.3.1 Immediately before sampling, break open the ends of the charcoal tube. All tubes should be from the same lot of charcoal.

2.3.2 Connect the charcoal tube to the pump with a short piece of flexible tubing. The 50-mg portion of the charcoal tube is used as the backup section; therefore, air should flow through the 100-mg portion first.

2.3.3 Position the tube vertically to avoid channeling through the charcoal.

2.3.4 Air being sampled should not pass through any hose or tubing before entering the charcoal tube.

2.3.5 Record the temperature and relative humidity of the atmosphere being sampled.

2.3.6 Immediately after sampling, seal the ends of the tubes with the plastic caps.

2.3.7 With each set of samples, submit at least one blank charcoal tube from the same lot as the sample tubes. The blank tube should be treated in the same manner as the samples (break ends, seal, transport) except no air is drawn through it.

2.3.8 Transport the samples and corresponding paperwork to the laboratory for analysis.

2.3.9 Submit source PDF whenever possible. Place the material in glass bottles with Teflon-lined caps, and transport to laboratory separately from air samples.

2.4 Breakthrough

Studies to determine the 5% breakthrough value were done near the PEL for Stoddard solvent, using a dynamically generated atmosphere with approximately 75% relative humidity at 22°C and a sampling rate of 0.203 L/min. These studies were performed using only the 100 mg portion of a charcoal tube. The average breakthrough for Stoddard solvent was 6.9 L and average capacity was 20 mg. (Section 4.4.1). Breakthrough studies were performed with a petroleum distillate (V.M.&P.) naphtha since this type of PDF boils at a lower temperature. The average breakthrough volume for this V.M.&P. naphtha was 9.4 L and the average capacity was 20.3 mg. (Section 4.4.2)

2.5 Desorption efficiency

Desorption efficiencies were determined at several different loadings of Stoddard solvent. These loadings corresponded to the mass of Stoddard solvent which would be collected on a charcoal tube when sampling 3 L of an atmosphere containing 0.1, 0.5, 1, and 2 times the PEL. The tubes were prepared by liquid injection of the Stoddard solvent and stored in a refrigerator for 24 h before analysis. The average desorption efficiency was 100%. (Section 4.5)

2.6 Recommended air volume and sampling rate.

The recommended air volume is 3 L at 0.2 L/min.

2.7 Interferences

2.7.1 Since charcoal will collect vapors from many organic compounds all organics being used in significant amounts near the sampling area could decrease the capacity of the charcoal for PDF.

2.7.2 Water vapor also may decrease the capacity of charcoal.

2.8 Safety precautions

2.8.1 Wear eye protection when breaking the ends of the charcoal tubes.

2.8.2 Place the sampling pump on the employee in a manner so it will not interfere with the work being done.

2.8.3 Place the charcoal tube in a holder so the broken ends are not exposed.

2.8.4 Obey all safety regulations of the workplace.

3. Analytical Procedure

3.1 Apparatus

3.1.1 A gas chromatograph (GC) equipped with a flame ionization detector (FID) is used for analysis. A Hewlett-Packard 5710 GC was primarily used in this evaluation.

3.1.2 A GC column capable of separating carbon disulfide (CS_2) and the internal standard, if any, from the constituents of the PDF. For this evaluation, a 20 ft by 1/8 in. stainless steel column packed with 10% SP-1000 on 80/100 Supelcoport was used.

3.1.3 An integrator for determining peak area is needed. A Hewlett-Packard 3357 data system was used.

3.1.4 Small vials with Teflon-lined caps for desorption of charcoal: Two-milliliter vials are preferable.

3.1.5 Microliter syringes such as 10-µL for preparing standards and 1-µL for sample injection are needed.

3.1.6 Pipettes for dispensing the desorbing solution may be used. A 1-mL reagent dispenser is convenient.

3.1.7 Volumetric flasks are used for standard preparation.

3.1.8 An analytical balance is used to prepare standards.

3.1.9 A distillation apparatus may be needed.

3.2 Reagents

3.2.1 Carbon disulfide, reagent grade.

3.2.2 Source PDF, when possible, from the operation where sampling was done.

3.2.3 Internal standard compound such as hexylbenzene, reagent grade (optional).

3.2.4 GC grade hydrogen, air and nitrogen.

3.2.5 Desorbing solvent: CS_2 or 1 µL internal standard/mL CS_2.

3.3 Standard preparation

3.3.1 Analytical standards are prepared in the desorbing solvent.

3.3.2 Source PDF received from the sampling site may be used as the analytical standard if it appears clear and colorless, and has a density in the range of 0.74-0.79 g/mL. If the bulk is colored or has a density greater than 0.79 g/mL, it needs to be distilled to separate the volatile solvents from the pigments or heavier oils before it can be used as an analytical standard.

3.3.3 If source PDF is not submitted or is unusable, a nonsource PDF from the laboratory should be used.

3.3.4 Standards must be prepared at four different concentrations so proper integration of the peaks may be confirmed (Section 3.5.3). A useful range for standard concentrations is approximately 1 µL/mL to 10 µL/mL.

3.4 Sample preparation

3.4.1 The 100-mg portion of the charcoal tube is placed in a vial and the 50-mg portion is placed in a separate vial. The glass wool and urethane plugs are discarded.

3.4.2 One milliliter of desorbing solvent is added to each vial.

3.4.3 The vials are immediately capped and shaken periodically for 30 min before analysis.

3.5 Analysis

3.5.1 GC conditions

oven:	initial temperature 100°C for 4 min programmed to 180°C at 8°/min
injector:	200°C
detector:	225°C
nitrogen (carrier):	22 mL/min
hydrogen:	30 mL/min
air:	250 mL/min
injection size:	1 µL
chromatogram:	Figure 3.5.1

3.5.2 The data system used in this evaluation was a Hewlett-Packard 3357 which contains several "integrate functions." The integrate function termed "hold the baseline" should be used for the analyses. This function should be started before the constituents of the petroleum distillate fraction begin to elute from the column and it should be canceled after the PDF constituents have eluted or when column bleed becomes significant whichever occurs first.

3.5.3 The areas of the peaks due to PDF constituents are added together (area summation) in the analysis of the standards and samples. The summed areas and the concentration of the analytical standards are used to determine a linear least squares fit equation. The concentration of the samples is determined by entering their summed areas into the least squares equation.

3.5.4 If the peaks present in the samples do not elute in approximately the same time range as the standards, a comparison of the constituents in the samples and standard should be done by GC/MS to confirm that the samples do contain PDF type compounds and of what type for reporting purposes. If distinct analytes are confirmed by GC/MS, their identity and approximate concentration should be reported.

3.5.5 Any sample above the PEL should be confirmed by GC/MS or another suitable technique.

3.6 Interferences

3.6.1 Since PDF are mixtures of aliphatic and aromatic hydrocarbons and elute from a GC in a peak cluster, it may be difficult to eliminate interfering compounds. If a large interfering peak appears in an air sample, identification by GC/MS may be necessary.

3.6.2 It may be difficult to separate a single analyte which is requested for analysis from the PDF constituents. Changing columns such as from a polar to a non-polar (SP-1000 to an SP-2100) may help separate the analyte.

3.7 Calculations

3.7.1 PDF should be reported as mg/m^3 since any ppm value would require the use of an approximate molecular weight.

3.7.2 The air concentration in mg/m^3 is determined from the mass of analyte in the sample as in the following example:

Upon analysis, 3.5 mg was found for a sample with a 3-L air volume.

mg/m^3 = (mg/desorption efficiency)/air vol.
mg/m^3 = (3.5 mg/1.00)/(0.003 m^3)
mg/m^3 = 1167 mg/m^3

3.8 Safety precautions

3.8.1 Work in a hood when using solvents during sample and standard preparation.

3.8.2 Keep solvents away from sources of high temperatures such as detectors and injectors.

3.8.3 Avoid skin contact with solvents.

3.8.4 Wear safety glasses at all times.

4. Backup data

4.1 Detection limits of the analytical and overall procedure

The determination of detection limit values is not practical in the context of a rigid definition such as a peak with a height of 5 times the baseline noise. Since PDFs may have similar constituents which have unsimilar concentrations, there is no one representative peak that can be used to determine detection limits for all PDFs.

4.2 Reliable quantitation limit

The amount of 0.77 mg/sample (260 mg/m^3) is determined to be the approximate amount reliably quantitated for any applicable petroleum distillate fraction within the requirements of at least 75% recovery and a precision (1.96 SD) of ±25% or better. The injection size recommended in the analytical procedure (1 µL) was used in the determination of the reliable quantitation limit.

Table 4.2
Reliable Quantitation Limit Data

sample number	calibration method*	lstd	mass (mg) spiked	mass (mg) recovered	% recovered
1	4	yes	0.789	0.873	111
		no		0.823	104
	5	yes		0.773	98
		no		0.762	96
8	4	yes	0.789	0.847	107
		no		0.806	102
	5	yes		0.751	95
		no		0.746	95
14	4	yes	0.777	0.812	104
		no		0.779	100
	5	yes		0.930	120
		no		0.863	111
21	4	yes	0.777	0.753	97
		no		0.778	100
	5	yes		0.845	109
		no		0.845	109
31	4	yes	0.753	0.643	85
		no		0.663	88
	5	yes		0.703	93
		no		0.689	92
35	4	yes	0.753	0.684	91
		no		0.696	92
	5	yes		0.748	99
		no		0.723	96
39	4	yes	0.754	0.658	87
		no		0.552	73
	5	yes		0.602	80
		no		0.529	70
47	4	yes	0.754	0.655	87
		no		0.715	95
	5	yes		0.609	81
		no		0.685	91
51	4	yes	0.779	0.828	106
		no		0.823	106
	5	yes		0.825	106
		no		0.821	105
60	4	yes	0.779	0.820	105
		no		0.810	104
	5	yes		0.818	105
		no		0.809	104

Table 4.2
Reliable Quantitation Limit Data

sample number	calibration method*	lstd	mass (mg) spiked	mass (mg) recovered	% recovered
65	4	yes	0.761	0.793	104
		no		0.778	102
	5	yes		0.816	107
		no		0.788	102
70	4	yes	0.761	0.824	108
		no		0.793	104
	5	yes		0.831	109
		no		0.819	108
76	4	yes	0.776	0.900	116
		no		0.949	122
	5	yes		0.838	108
		no		0.845	109
83	4	yes	0.776	0.851	110
		no		0.912	117
	5	yes		0.792	102
		no		0.815	105
				$\overline{X}$	100.7%
				SD	10.76
				1.96SD	21.09%

* Explanation of calibration methods under Table 4.8.2

4.3 Precision and Sensitivity

4.3.1 The precision of the analytical method was determined by replicate injections of analytical standards prepared at 0.5, 1, and 2 times the target concentration. The pooled coefficient of variation is 0.019.

Table 4.3.1
Precision of Analytical Method

× target concn	0.5×	1.0×	2.0×
area counts	1322304	2761497	5482172
	1272435	2731651	3394150
	1328744	2757576	5505614
	1350244	2735224	5451850
	1377105	2731653	5466193
	1381708	2693328	5413149
$\overline{X}$	1338756	2735155	5452188
SD	40538	24375	42052
CV	0.030	0.0089	0.0077
$\overline{CV}$	0.019		

4.3.2 The precision of the overall procedure was calculated by taking the average of the SDs for methods #4 and #5 (both Istd and Estd) from Table 4.8.1 and multiplying by 1.96. This number includes ±5% for sampling error. The usual value on the cover page is the standard error of estimate from the storage test but in this evaluation this value would not have included variability for using different PDFs for analytical standards.

4.3.3 Sensitivity is defined as the slope of the calibration curve for analytical standards from 0.5 to 2 times the target concentration. (Table 4.3.1, Figure 4.3.2) The sensitivity is 300954 area counts/(mg/mL). The sensitivity will change depending on the detector and method of integration.

4.4 Breakthrough

4.4.1 Breakthrough was determined by sampling a dynamically generated test atmosphere of Stoddard solvent (about 2900 mg/m^3 with 76% RH at 23°C), using a charcoal tube containing only the 100-mg portion of charcoal and monitoring the concentration of Stoddard solvent in the air which had passed through the charcoal. Five-percent breakthrough is defined as the point during this sampling when the air exiting the charcoal tube has a concentration of Stoddard solvent that is 5% of the test atmosphere. Two tests were performed, with 5% breakthrough air volumes of 6.5 L and 7.3 L and capacities of 19.1 mg and 21.5 mg being obtained respectively. The average 5% breakthrough air volume was 6.9 L and capacity was 20.3 mg. (Fig. 4.4)

4.4.2 Breakthrough tests were also performed using a petroleum distillate bulk since its boiling range is lower than Stoddard solvent and it contains more volatile constituents. The test atmospheres were about 2000 mg/m^3 with 74% RH at 23°C. Three tests were performed, with 5% breakthrough air volumes of 9.6, 9.1 and 9.5 L and capacities of 20.82, 19.73 and 19.95 mg being obtained respectively. The average capacity was 20.3 mg and the average 5% breakthrough air volume was 9.4 L.

4.5 Desorption efficiencies

Desorption efficiencies were determined by injecting known amounts of Stoddard solvent onto the 100-mg portion of six charcoal tubes, allowing them to sit overnight and analyzing the tubes on the next day. The average desorption efficiency over the range of 0.08 to 2 times the target concentration is 100%.

Table 4.5
Desorption Efficiencies

× target concn	0.08×	0.5×	1×	2×
µg/sample	0.76	4.55	9.1	18.6
desorption	103	100	100	99
efficiency, %	102	101	100	99
	99	102	100	98
	102	102	101	95
	100	101	101	96
	103	101	101	94
$\bar{X}$	102	101	101	97

4.6 Storage data

Thirty-six samples were collected from a dynamically generated atmosphere of Stoddard solvent. The atmosphere was approximately 2900 mg/m^3 and 75% RH at 22°C. Of these 36 samples, six were analyzed immediately, while the remaining 30 were stored; 15 at ambient temperature and 15 at -5°C. Approximately every third day, 3 samples from each of the storage sets were analyzed. The average recovery was 96% for ambient storage and 97% for refrigerated storage. The data of Table 4.6 are shown graphically in Figures 4.6.1 and 4.6.2.

Table 4.6
Storage Tests

time	percent recovery (ambient)			percent recovery (refrigerated)		
(days)						
0	97	99	100	99	99	99
3	95	96	96	96	97	96
7	95	96	97	96	97	97
11	95	96	97	97	96	96
13	95	96	96	96	96	96
19	98	96	96	97	99	97

4.7 Reproducibility data

Six samples, spiked by liquid injection, and a draft copy of this procedure were given to a chemist unassociated with this evaluation. The samples were analyzed after 3 days of storage at 22°C. The average recovery was 97.7% with a standard deviation of ±3.53%.

Table 4.7
Reproducibility Results

µg spiked	µg recovered	percent recovered
7756	7432	95.8
7756	7510	96.8
7756	7443	95.8
7756	7493	96.6
7756	7466	96.3
7756	8136	104.9
	$\bar{X}$	97.7
	SD	3.53

4.8 Quantitation factors

4.8.1 A total of 96 samples were used to evaluate differences between source and non-source PDF, automatic baseline set and controlled baseline set, and internal and external standard procedures. They were prepared by liquid injection of each of 8 PDFs on 12 charcoal tubes. These 8 sets were prepared at different times. Each set and an aliquot of the source PDF were given to the branch of this laboratory which routinely analyzes samples for PDF. The samples were desorbed with a CS_2/Istd solution and analytical standards were prepared in the same solution from the source PDF and a non-source PDF chosen by the analyst. The data for these standards and samples was quantitated with nine different calibration methods. Explanations of these calibration methods are given at the bottom of Table 4.8.2. Both internal and external standard procedures were used for calibration methods #1-5. For the external standard procedure, the peak from the internal standard was ignored in all the calculations. The results from these 8 sets of PDF samples are presented in Tables 4.8.2-4.8.9, each table represents the data from one PDF. Table 4.8.1 summarizes the data as average percent recoveries for all PDFs analyzed with each calibration method using internal and external standard procedures. For all calibration methods except #3 the summation of the peak areas for the constituents of the PDF was used to determine the response factors. Method #3 used the peak area of the largest peak in the PDF for determination of the response factors.

4.8.2 The six analytical standards were analyzed at the same time as the samples. A linear least squares fit for each set of standards was used in all of the calibration methods except methods #3, #8 and #9. In these cases only one standard was used for calibration. Source PDF was used with calibration methods #1, #4, #6 and #8. By comparing the average results and the standard deviations obtained for method #1 to #2, #4 to #5, #6 to #7, and #8 to #9 in Table 4.8.1., it can be seen that there is no significant difference in the results; therefore, source or non-source PDF may be used to prepare analytical standards.

4.8.3 An internal standard was present in all of the samples used but results were calculated both with the internal standard correction and without it for calibration methods #1 through #5. (Tables 4.8.1 to 4.8.9). For all of the analyses, automatic liquid sampling devices were used with a single injection of each sample. At the bottom of Table 4.8.1 are the average results for all the PDFs using all the calibration methods calculated with both the internal standard (Istd) and external standard (Estd) procedures. From this data there appears to be no real difference between the results using the Istd correction and not (Estd). The use of an internal standard is left to the judgment of the analyst since the lengthening of the analysis and possible interferences caused by an internal standard compound will be different for each set of samples.

4.8.4 Three different techniques of setting the baseline during analysis were investigated. One technique was to allow the data system (Hewlett-Packard 3357) to calculate the baseline and set it automatically. The other techniques require the analyst to control the baseline by using either a basic program to set the baseline and integrate the area under the chromatogram or an "integrate function" built into the data system to set the baseline.

a) At lower concentrations of PDFs, the technique of allowing the data system to automatically set the baseline produced inconsistent results. (Figure 4.8.1 and 4.8.2) This may be due to a parameter in the data system termed "slope sensitivity", but since single analytes are often requested in addition to PDF, setting the slope sensitivity for PDF may not be accurate for the single analytes. Calibration methods #6, #7, #8 and #9 used this technique (Tables 4.8.1 - 4.8.9). The results in Table 4.8.1 are the

average recoveries for each calibration technique with the 8 different PDFs. As can be seen in this table, the percent recoveries for each separate PDF using calibration methods #6, #7, #8 and #9 ranged from 28-143%. The average results listed at the bottom of the table for all PDFs using these four calibration methods ranged from 74-103%. Methods #6 and #7 used a linear least squares fit for calibration while methods #8 and #9 used a one point calibration. The linear least squares fit does provide results (103 and 96%) closer to the expected value but the standard deviation is larger than for methods #1-#5 in which the baseline is controlled. Therefore, controlling the baseline is recommended.

b) Calibration methods #1 and #2 used a basic program for baseline setting and integration. This basic program was written to be used after analyzing the standards, blanks and samples. The raw data collected during an analysis is in the form of area slices which are simply detector voltages taken and stored every 0.5 s. The analyst enters into the basic program the time span over which the PDF constituents elute. The program saves the value of the first area slice in the analytical run to be used as the baseline and when the start time of the PDF is reached the program subtracts the baseline area slice from all the area slices in the specified time span and sums the differences. This summation is used as the area of PDF constituents. This program integrated the area above the baseline but not as individual peaks. The average recoveries are presented in Table 4.8.1. Since this program did not have any peak detection routine, it would not differentiate between a rise in the baseline due to a peak and column bleed. Therefore, if the baseline was not consistent and PDF constituents were eluting from the column at these times, area may be added to the PDF area which was caused by column bleed and not PDF constituents. This technique of baseline control is not recommended.

c) The two evaluated integrate functions which control the baseline were "hold the baseline" (Figure. 4.8.2) and "valley reset" (Figure 4.8.4). The "valley reset" function resets the baseline every time the data system detects a zero slope or a switch from negative to positive slope of the detector output. This function is performed by the data system with start and stop times entered by the analyst. Calibration method #3 used this function and the area of the largest peak for calibration of a response factor. As can be seen in Table 4.8.1, the average results for all the PDFs analyzed with method #4 were 102(±2.3)% with the internal standard procedure and 102(±4.1)% with the external standard procedure. Comparing these results to those of the other calibration methods, method #4 is the most accurate. However, this method requires that the source PDF be used as analytical standards because the ratio of the area of the chosen peak to the others in the PDF must be constant.

d) The "hold the baseline" function simply records the detector voltage at a certain time during the analysis and maintains that as the baseline until the function is canceled. The time to start this function is slightly before the PDF constituents begin to elute and the time to cancel it is after the constituents have eluted or when column bleed becomes significant. Both of these times are set by the analyst. After the function is canceled, the data system is free to set the baseline and it usually does correct for baseline drift due to column bleed; therefore, excess area is not added to the PDF as it was with the basic program. Calibration methods #4 and 5 used this technique. The average results and standard deviations for all PDFs for these two methods given at the bottom of Table 4.8.1 are better than the other calibration methods except #3, although this calibration method (#3) requires the use of source PDF in preparing analytical standards. Therefore, using the integrate function of "hold the baseline" is recommended and a linear least squares fit of the standards should be used to quantitate the samples.

4.8.5 Recommendations

For analysis of petroleum distillate fractions, either the source PDF (Section 3.3.2) or a non-source PDF may be used to prepare analytical standards. It is recommended that the baseline be controlled with the "hold the baseline" integrate function during elution of the PDF constituents or until column bleed becomes significant whichever occurs first. Finally, either internal standard or external standard may be used with no loss in accuracy or precision.

Table 4.8.1
Average Percent Recoveries
Calculated from Tables 4.8.2 to 4.8.9

(see notes)		calibration methods								
table	Istd	#1	#2	#3	#4	#5	#6	#7	#8	#9
4.8.2	yes	105	96	104	107	95	97	92	100	93
	no	103	95	100	102	95				
4.8.3	yes	106	115	104	100	111	99	101	110	110
	no	108	115	104	106	109				
4.8.4	yes	109	104	99	91	99	93	113	91	93
	no	115	106	103	94	98				
4.8.5	yes	103	102	104	90	83	110	93	93	91
	no	103	105	102	87	83				
4.8.6	yes	99	97	100	104	103	98	84	75	75
	no	98	96	99	103	103				
4.8.7	yes	100	95	104	103	104	107	110	31	32
	no	99	97	100	100	102				
4.8.8	yes	85	91	100	106	99	143	100	29	28
	no	104	93	109	114	101				
4.8.9	yes	119	125	100	99	100	83	73	67	73
	no	135	135	95	95	95				
$\bar{X}$	(PDFs-	105	103	102	100	99	103	96	74	74
SD	Istd)	7.3	11.5	2.3	6.4	8.1	18.0	13.2	30.6	29.7
$\bar{X}$	(PDFs-	108	105	102	100	98				
SD	Estd)	12.1	14.1	4.1	8.2	7.7				

notes:
1.) Explanation of Calibration methods under table 4.8.2
2.) Istd column: "yes" indicates internal standard was used; "no" indicates an external standard procedure used.
3.) "blank" under calibration methods #6, 7, 8 and 9 indicates no data was collected with an external standard procedure.

Table 4.8.2
Percent Found for Stoddard Solveant A

(see notes)			calibration methods								
sample	µg	Istd	#1	#2	#3	#4	#5	#6	#7	#8	#9
1	789	yes	104	96	102	111	98	96	91	101	93
		no	102	93	97	104	96				
2	3159	yes	101	94	103	106	94	99	93	102	94
		no	100	92	98	100	93				
3	4739	yes	102	94	104	107	95	99	92	101	93
		no	101	94	100	103	95				
4	237	yes	120	103	107	109	97	91	87	96	88
		no	108	98	102	101	94				
5	6318	yes	103	94	104	104	93	103	96	104	96
		no	101	94	101	101	93				
6	3159	yes	102	95	105	105	94	102	102	105	9
		no	103	95	101	101	94				
7	6318	yes	103	94	104	106	94	101	93	102	94
		no	101	95	101	103	95				
8	789	yes	102	94	101	107	95	91	86	95	88
		no	100	92	97	102	95				
9	4739	yes	103	95	105	107	95	102	95	104	96
		no	103	95	102	104	96				
10	2369	yes	102	95	104	108	96	97	92	101	93
		no	103	95	101	104	97				
11	237	yes	115	99	105	104	92	86	81	90	83
		no	105	95	101	99	91				
12	2369	yes	104	97	106	110	98	99	94	97	95
		no	106	97	104	107	99				

notes:
1) Calibration method #1 uses as analytical standards the source PDF, the basic program for peak integration and area summation of the standards for calibration.

2) Calibration method #2 uses as analytical standards a non-source PDF, otherwise the same as #1.
3) Calibration method #3 uses the source PDF, "valley reset" for peak integration and a single peak in the standards for calibration.
4) Calibration method #4 uses as analytical standards the source PDF, "hold the baseline" for peak integration and area summation of standards for calibration.
5) Calibration method #5 uses as analytical standards a non-source PDF, otherwise the same as #4.
6) Calibration method #6 uses as analytical standards the source PDF, the data system sets the baseline for peak integration, and area summation of standards for calibration.
7) Calibration method #7 uses as analytical standards a non-source PDF, otherwise the same as #6.
8) Calibration method #8 uses as analytical standards the source PDF, the data system sets the baseline for peak integration, and area summation of only one standard for calibration.
9) Calibration method #9 uses as analytical standards a non-source PDF, otherwise the same as #8.

Table 4.8.3
Percent Found for Stoddard Solvent B

(see notes)			calibration methods								
sample	µg	Istd	#1	#2	#3	#4	#5	#6	#7	#8	#9
13	3109	yes	112	119	111	116	128	103	95	103	103
		no	107	114	106	111	118				
14	777	yes	111	120	108	104	120	125	122	137	136
		no	108	116	103	100	111				
15	233	yes	122	141	103	89	96	79	132	136	136
		no	117	125	94	--	89				
16	5440	yes	106	113	106	106	117	107	98	105	105
		no	104	110	104	104	112				
17	7772	yes	106	114	104	105	116	107	103	106	105
		no	104	110	103	105	112				
18	233	yes	107	125	103	79	78	55	101	114	113
		no	108	116	103	--	76				
19	4663	yes	101	108	101	–	113	99	89	98	98
		no	107	114	106	107	115				
20	3109	yes	100	106	100	99	114	97	86	97	97
		no	109	116	107	106	119				
21	777	yes	99	108	100	97	109	105	102	118	118
		no	104	112	103	100	109				
22	7772	yes	104	112	103	104	114	105	101	104	104
		no	106	113	107	108	115				
23	5440	yes	103	110	104	104	115	104	95	103	103
		no	110	117	111	111	119				
24	4663	yes	100	107	101	102	113	99	89	98	98
		no	107	114	108	108	116				

note: Explanation of calibration methods under Table 4.8.2

Table 4.8.4
Percent Found for VM&P Naphtha A

(see notes)			calibration methods								
sample	µg	Istd	#1	#2	#3	#4	#5	#6	#7	#8	#9
25	7528	yes	103	102	104	89	98	102	104	102	104
		no	120	105	106	94	98				
26	5270	yes	102	104	103	89	97	101	105	102	104
		no	112	107	107	95	99				
27	7528	yes	106	104	107	92	100	105	107	105	107
		no	119	105	106	94	98				
28	1506	yes	106	107	98	92	100	93	105	93	95
		no	110	109	105	98	102				
29	3011	yes	100	103	97	88	96	98	104	98	100
		no	106	106	104	94	98				
30	226	yes	172	119	96	100	110	72	148	65	66
		no	177	121	101	100	102				
31	753	yes	98	99	94	85	93	88	111	86	88
		no	99	99	99	88	92				
32	5270	yes	99	120	101	88	96	101	103	100	102
		no	106	103	103	92	96				

Table 4.8.4
Percent Found for VM&P Naphtha A

(see notes)			calibration methods								
sample	µg	lstd	#1	#2	#3	#4	#5	#6	#7	#8	#9
33	753	yes	101	103	94	91	99	91	114	89	91
		no	101	102	98	92	96				
34	1506	yes	100	106	98	92	100	93	105	93	95
		no	103	108	105	97	101				
35	226	yes	124	103	95	97	106	71	146	64	65
		no	126	103	99	93	96				
36	3011	yes	97	103	98	89	97	98	104	98	100
		no	103	106	105	95	99				

note: Explanation of calibration methods under Table 4.8.2

Table 4.8.5
Percent Found for VM&P Naphtha B

(see notes)			calibration methods								
sample	µg	lstd	#1	#2	#3	#4	#5	#6	#7	#8	#9
37	3768	yes	103	98	106	96	88	103	98	101	99
		no	95	93	97	86	83				
38	6029	yes	102	100	110	96	87	103	99	103	101
		no	95	98	97	86	82				
39	754	yes	102	100	101	87	80	106	84	87	85
		no	94	94	93	73	70				
40	2261	yes	106	100	105	97	89	100	92	95	93
		no	99	95	98	88	85				
41	301	yes	95	109	100	72	66	111	54	58	57
		no	90	106	94	52	50				
42	4522	yes	101	97	102	92	85	100	97	100	98
		no	104	105	104	94	90				
43	3768	yes	104	99	105	94	86	104	99	102	100
		no	107	106	107	96	86				
44	2261	yes	106	99	104	95	87	102	95	97	95
		no	109	104	108	98	94				
45	301	yes	113	124	101	77	70	127	70	74	73
		no	117	129	105	79	75				
46	6028	yes	102	100	111	95	87	103	100	103	101
		no	107	114	110	98	94				
47	754	yes	106	104	191	87	81	157	133	89	87
		no	113	111	108	95	91				
48	4522	yes	103	97	106	94	86	103	99	102	100
		no	109	111	112	100	95				

note: Explanation of calibration methods under Table 4.8.2

Table 4.8.6
Percent Found for Stoddard Solvent C

(see notes)			calibration methods								
sample	µg	lstd	#1	#2	#3	#4	#5	#6	#7	#8	#9
49	3897	yes	99	99	101	100	98	100	90	88	88
		no	98	97	98	98	97				
50	6235	yes	99	98	100	98	98	94	88	88	88
		no	97	96	99	97	97				
51	779	yes	96	92	97	106	106	96	78	61	61
		no	95	91	96	106	105				
52	545	yes	92	87	95	105	105	105	82	59	59
		no	91	85	94	104	104				
53	6235	yes	100	99	102	99	98	95	88	89	88
		no	100	99	102	99	99				
54	2338	yes	102	101	102	106	105	109	95	89	89
		no	100	99	100	104	104				
55	545	yes	99	94	101	112	112	69	82	60	60
		no	98	93	100	112	112				

Table 4.8.6
Percent Found for Stoddard Solvent C

(see notes)			calibration methods								
sample	µg	lstd	#1	#2	#3	#4	#5	#6	#7	#8	#9
56	3897	yes	101	100	102	101	100	101	91	89	89
		no	100	100	101	100	100				
57	1559	yes	100	99	101	105	105	94	79	70	70
		no	101	99	101	106	105				
58	2338	yes	101	100	101	103	102	89	77	71	71
		no	100	99	100	101	101				
59	1559	yes	100	98	101	105	104	93	79	70	70
		no	102	100	102	107	106				
60	779	yes	100	96	100	105	105	99	80	63	63
		no	767	739	769	810	809				

note: Explanation of calibration methods under Table 4.8.2

Table 4.8.7
Percent Found for Stoddard Solvent D

(see notes)			calibration methods								
sample	µg	lstd	#1	#2	#3	#4	#5	#6	#7	#8	#9
61	3045	yes	102	100	102	103	102	102	104	34	34
		no	96	100	96	98	103				
62	3045	yes	102	101	102	104	103	102	104	34	34
		no	96	101	97	98	103				
63	6853	yes	103	102	104	102	102	103	105	34	34
		no	100	101	99	98	102				
64	1523	yes	98	94	96	101	104	100	102	30	31
		no	97	98	94	100	101				
65	761	yes	97	89	99	104	107	114	116	29	30
		no	100	92	97	102	104				
66	533	yes	99	97	119	107	110	125	127	28	28
		no	106	90	117	105	106				
67	6853	yes	99	97	100	98	101	98	100	33	33
		no	98	99	97	96	97				
68	533	yes	99	87	100	107	108	125	127	28	29
		no	105	88	96	103	106				
69	1523	yes	98	94	101	101	103	100	102	30	31
		no	96	97	97	98	100				
70	761	yes	101	93	119	108	109	117	119	30	31
		no	102	94	115	104	108				
71	4568	yes	100	99	99	100	101	99	102	33	34
		no	96	99	95	96	99				
72	4568	yes	100	98	104	100	102	99	101	33	34
		no	96	100	100	97	99				

note: Explanation of calibration methods under Table 4.8.2

Table 4.8.8
Percent Found for Stoddard Solvent E

(see notes)			calibration methods								
sample	µg	lstd	#1	#2	#3	#4	#5	#6	#7	#8	#9
73	7756	yes	104	94	103	99	92	106	102	35	35
		no	108	96	111	106	94				
74	2327	yes	103	98	103	103	95	153	105	35	34
		no	110	100	112	109	97				
75	3878	yes	104	97	102	100	93	132	102	35	34
		no	110	98	111	106	95				
76	776	yes	89	88	96	116	108	139	77	17	16
		no	99	88	103	122	109				
77	5429	yes	101	94	102	97	90	116	98	34	32
		no	108	96	109	104	93				
78	7756	yes	102	93	101	96	89	103	97	33	32
		no	110	97	112	106	94				

Table 4.8.8
Percent Found for Stoddard Solvent E

(see notes)			calibration methods								
sample	µg	Istd	#1	#2	#3	#4	#5	#6	#7	#8	#9
79	388	yes	78	81	99	130	125	206	112	17	16
		no	91	80	106	140	126				
80	3878	yes	101	94	103	98	91	129	99	34	33
		no	108	97	110	105	94				
81	5429	yes	102	94	103	99	92	118	100	35	33
		no	111	99	112	109	97				
82	2327	yes	100	96	102	101	94	151	109	34	33
		no	110	99	112	108	97				
83	776	yes	84	83	95	110	102	170	97	24	23
		no	96	86	104	117	105				
84	388	yes	77	79	98	122	114	199	108	16	15
		no	92	80	107	132	118				

note: Explanation of calibration curves under Table 4.8.2

Table 4.8.9
Percent Found for Mineral Spirits A

(see notes)			calibration methods								
sample	µg	Istd	#1	#2	#3	#4	#5	#6	#7	#8	#9
85	7673	yes	109	113	106	101	106	103	99	94	100
		no	100	98	88	91	90				
86	230	yes	186	200	108	90	88	57	109	43	46
		no	270	275	98	82	94				
87	1534	yes	149	158	119	129	135	110	93	86	92
		no	144	145	107	119	117				
88	5371	yes	107	110	103	102	107	100	92	86	92
		no	115	113	106	108	107				
89	7673	yes	106	110	103	96	101	107	104	99	106
		no	116	113	107	102	101				
90	537	yes	210	224	65	123	114	50	40	37	40
		no	226	228	67	108	106				
91	2302	yes	110	115	104	104	107	89	76	70	75
		no	112	112	101	102	99				
92	1534	yes	107	113	106	106	108	91	76	70	75
		no	112	112	103	103	102				
93	537	yes	61	65	71	62	56	39	32	30	31
		no	73	74	64	54	54				
94	230	yes	82	89	106	72	78	45	36	33	35
		no	143	149	96	67	66				
95	5371	yes	99	103	101	93	97	110	101	95	102
		no	106	105	106	99	97				
96	2302	yes	104	110	106	106	110	90	77	71	76
		no	103	103	104	104	102				

note: Exlanation of calibration methods under Table 4.8.2

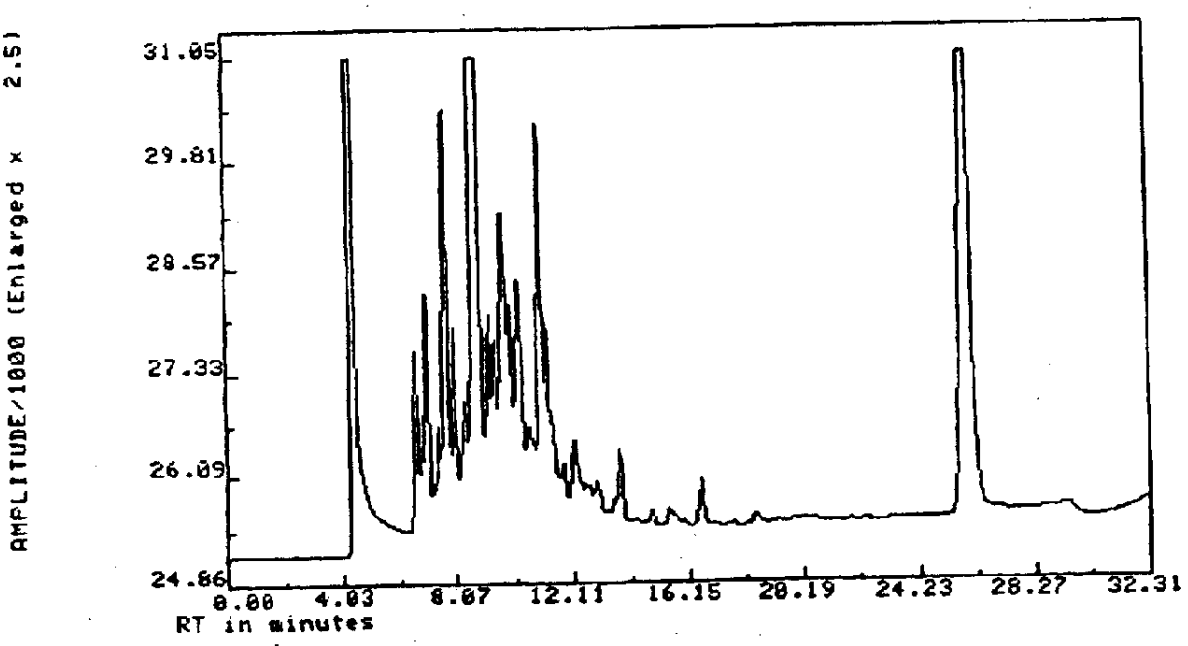

Figure 3.5.1. Chromatogram of PDF standard.

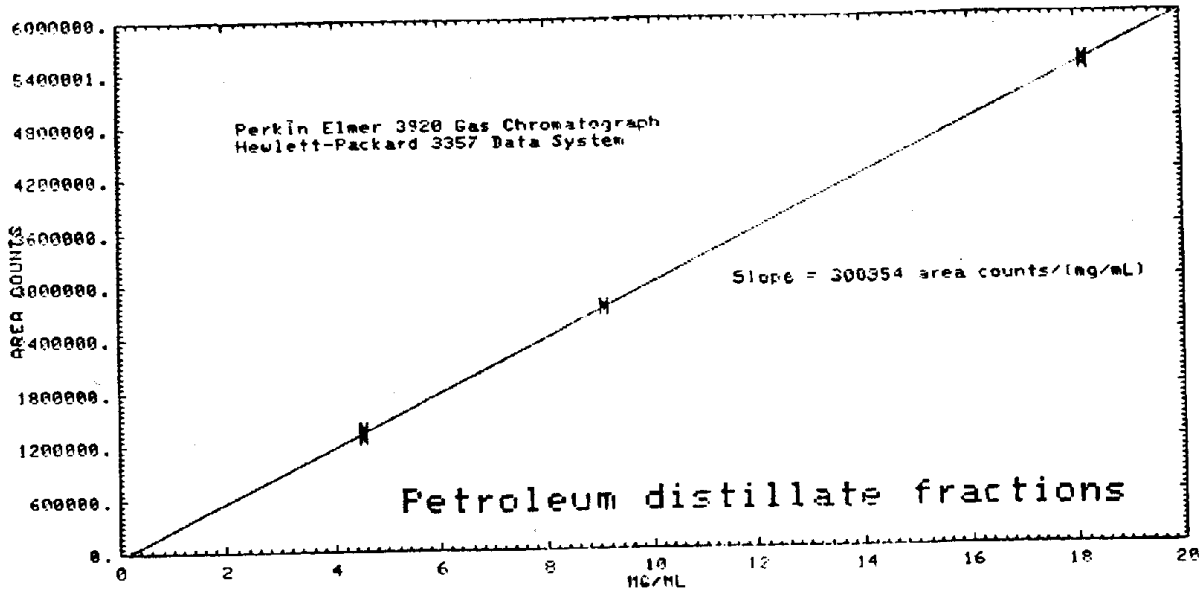

Figure 4.3.2. Sensitivity.

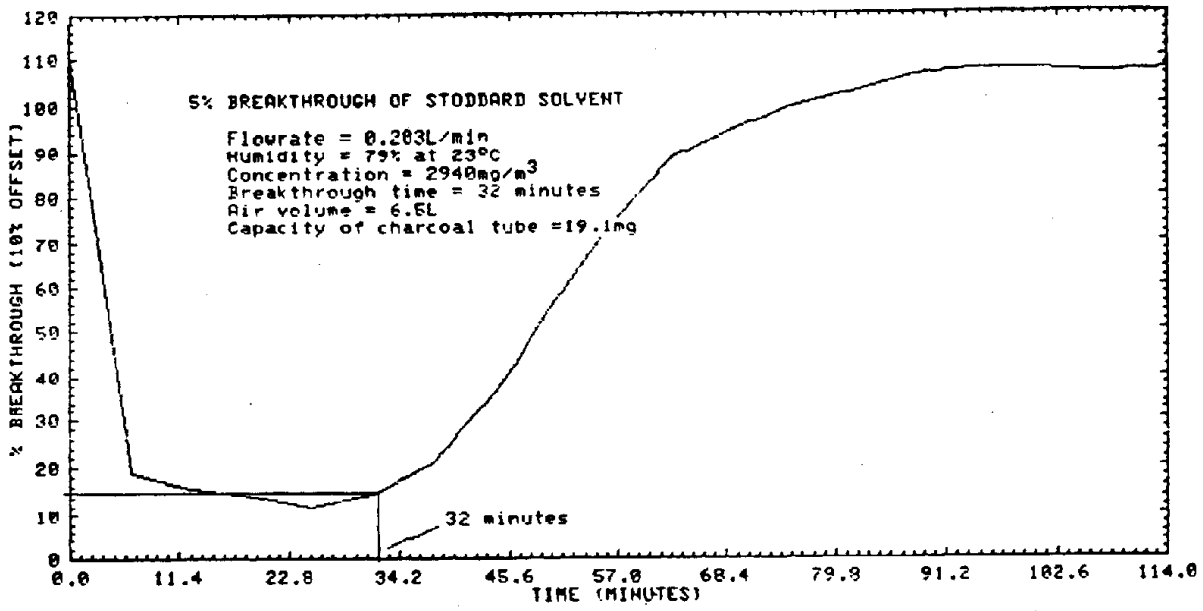

Figure 4.4. Breakthrough curve.

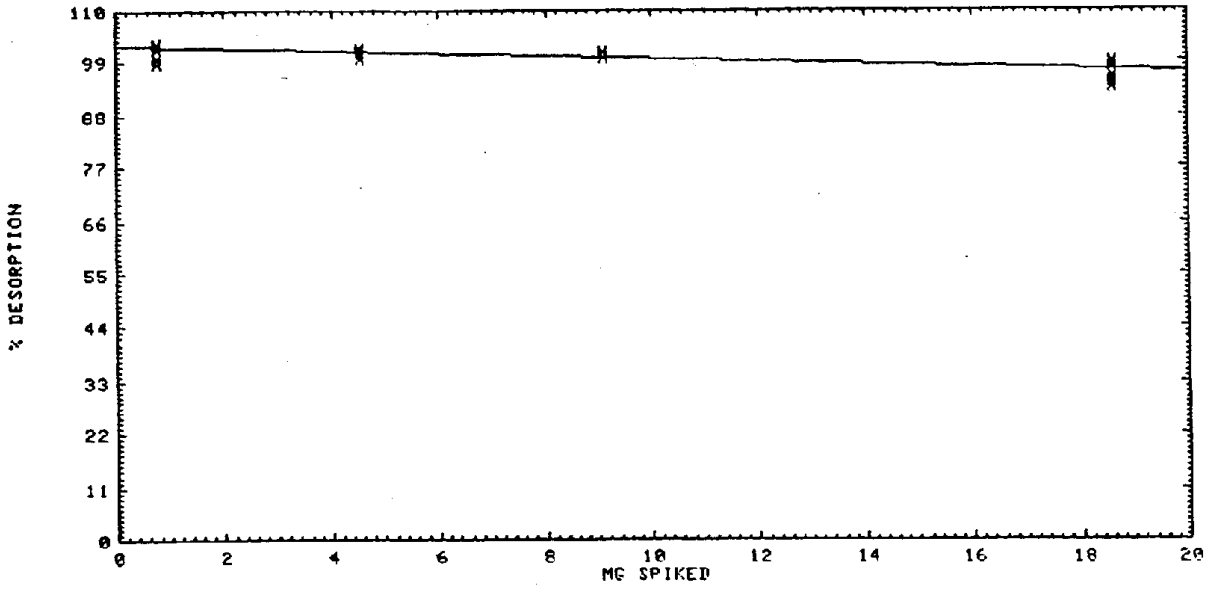

Figure 4.5. Desorption efficiencies.

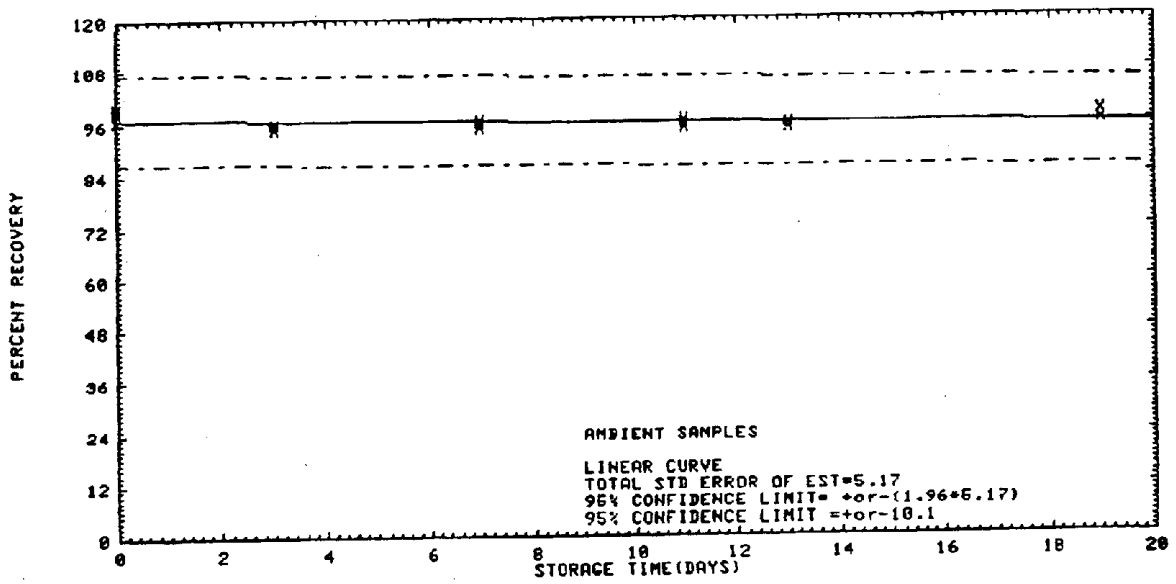

Figure 4.6.1. Ambient storage.

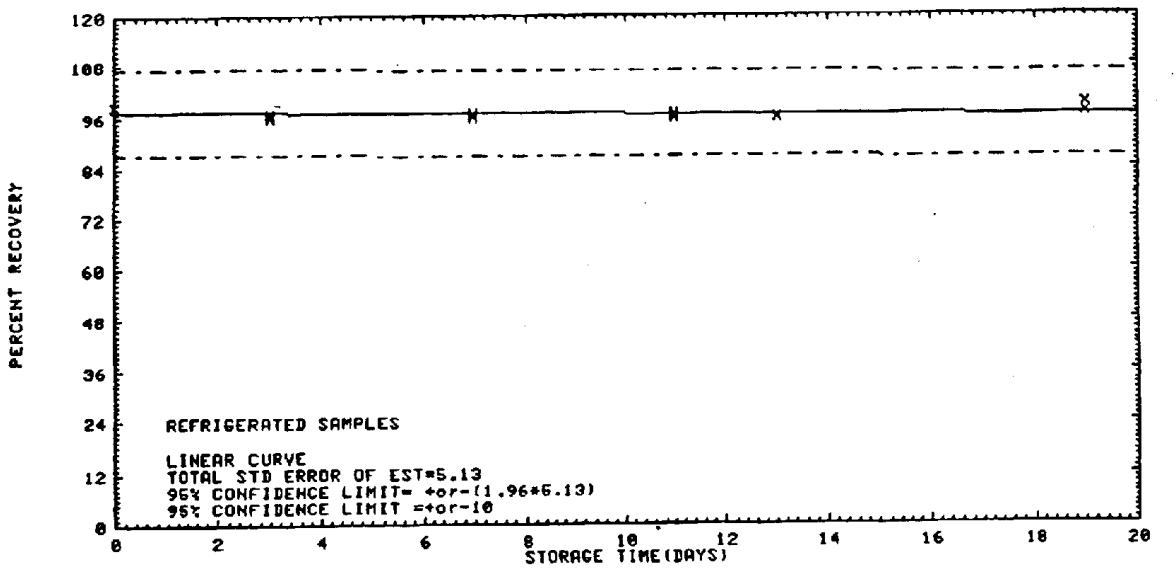

Figure 4.6.2. Refrigerated storage.

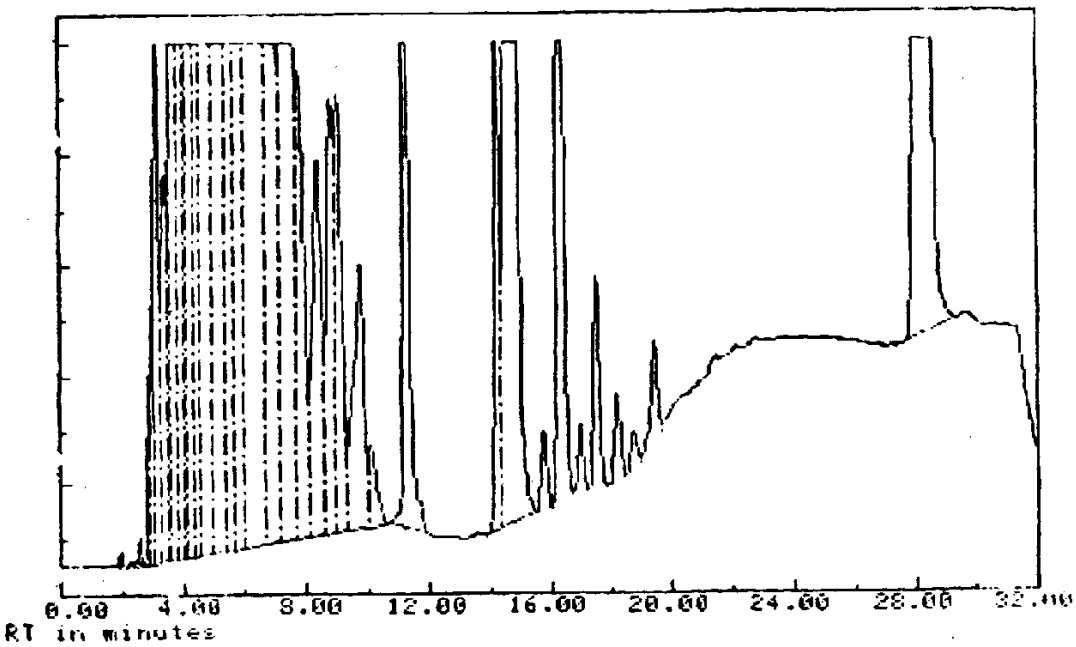

Figure 4.8.1. Automatic baseline set.

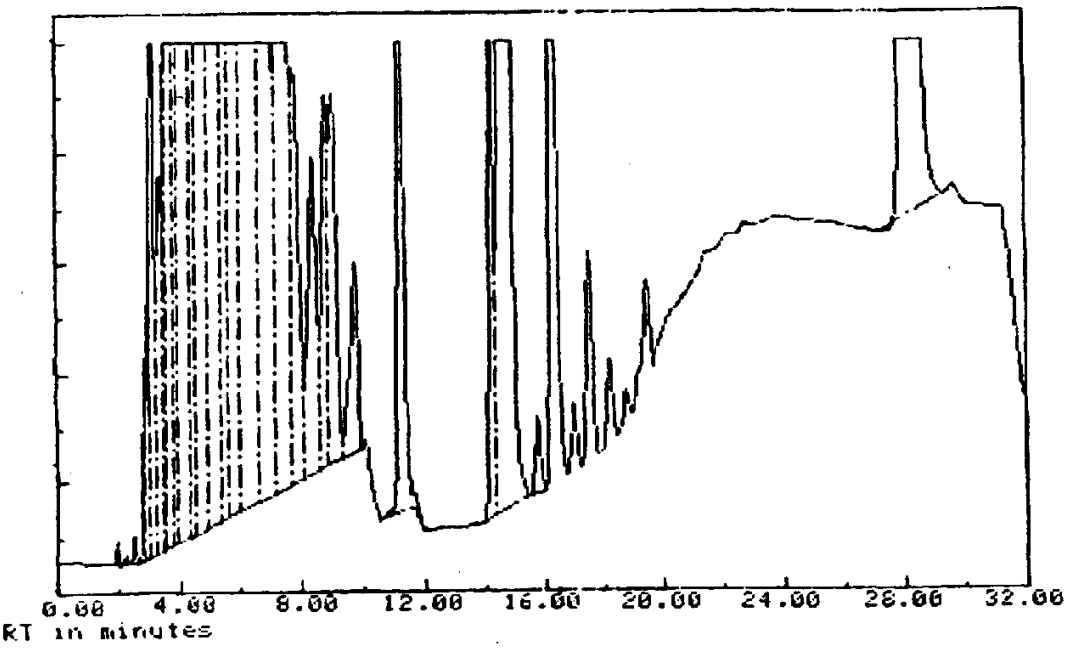

Figure 4.8.2. Automatic baseline set.

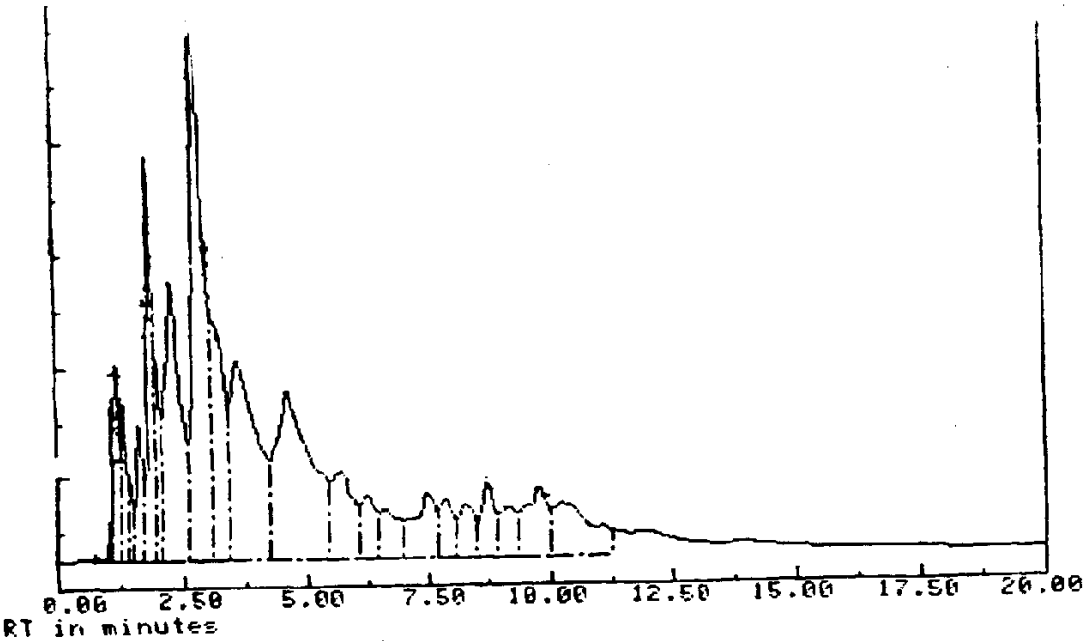

Figure 4.8.3. Controlled baseline with "hold the baseline" function.

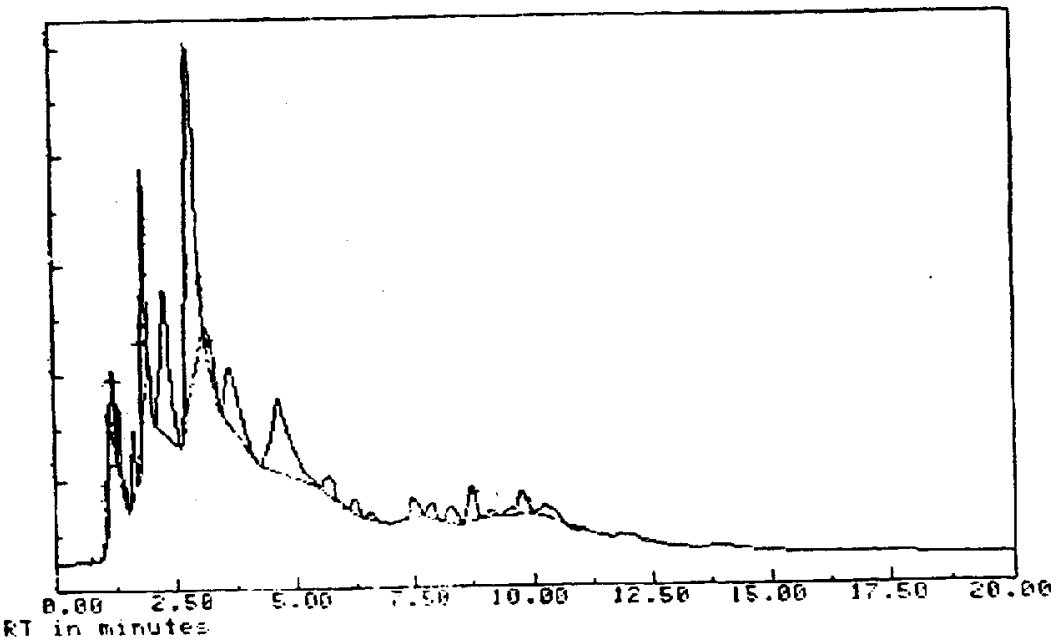

Figure 4.8.4. Controlled baseline with "valley reset" function.

5. References

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