



Interoffice Communication

To K. C. Hunt, Refining, Ponca City
From J. J. Mangelinkx, Refining, Lake Charles
Date September 19, 1977
Subject Sample Analyses

We are sending via the company shuttle three charcoal tubes for Benzene Content, data sheets are attached.


J. J. Mangelinkx

1b
CC: MEO, THM, FILE(2)

CONOCO INC.
PONCA CITY, OKLAHOMA
REFINING TECHNICAL SERVICES LABORATORY

Plt.: LC
File: 610
610.4
Date: 9/6/83

LABORATORY NO.: I-13-83
CHARGE: LC 49
SUBJECT: Analysis of Samples For Para-Xylene Study and Isomerization Unit
Evaluation - Lake Charles Refinery

DISCUSSION:

Samples of Lake Charles No. 2 and No. 3 CRU reformat were received for TBP distillation and compositional, physical and octane analyses. The TBP fractionation of each sample was done on an 8-plate still to produce IBP-250°F OH cuts and 250°F+ bottoms fractions. This work was done in connection with the Lake Charles para-xylene production study. In addition, samples of primary tower overhead, No. 2 and No. 3 CTU light straight run and denuded casinghead were analyzed to provide data for the preliminary evaluation of a straight run isomerization unit at Lake Charles.

PONA analysis including individual component breakdown through C8 hydrocarbons (excluding olefins) was run on all samples. The olefins are reported as C₄'s, C₅'s and C₆ plus. Octanes (clear and leaded) were run on all samples including the TBP fractions.

Trace determinations of F, Cl, S, H₂S, Pb, As, H₂O, basic/total nitrogen and oxygenated compounds were made on the reformat samples, primary tower overhead and denuded casinghead. Analysis for carbonyl compounds and active oxygen require special sampling and preservation which will virtually necessitate on-site analysis.

The denuded casinghead contained an appreciable level of olefins, i.e., 14.4 LV%.

DATA:

Attached.

REFERENCE:

Letter to K. C. Hunt from D. C. Griffith dated 8/9/83.

Approved:


Senior Technologist


Associate Technologist

bp

cc: (PWL-DFM)-RH-JM-WJW-MEO-JRU-DCG-USH-PAN-TGC-KCH-F

SAL 000009247

Lake Charles

Sample:	No.3	No.2	No.3	Primary	Denuded
Sample	Reformat	LSR	LSR	Tower	Casinghead
Sample Date:	8/8/83	8/11/83	8/11/83	8/11/83	8/11/83
L.C. Sample No.:	688-83	707-83	706-83	705-83	704-83
P.C. Sample No.:	1566	1579	1578	1577	1576
Gravity, "API @60°F	42.7	63.5	69.2	86.5	68.6
ASTM D-86 Dist. Corrected to 760 mm Hg., °F					
IBP	91	109	120	88	90
5% Recovered	148	147	141	100	106
10% Recovered	153	157	143	102	112
20% Recovered	204	172	149	105	124
30% Recovered	227	182	154	107	137
40% Recovered	248	193	159	111	155
50% Recovered	266	203	164	113	180
60% Recovered	282	212	170	118	212
70% Recovered	299	220	176	122	247
80% Recovered	306	230	184	129	297
90% Recovered	338	244	194	139	361
95% Recovered	361	254	202	144	416
End Point	388	264	209	149	447
% Recovered	98.0	98.5	99.0	98.0	98.0
% Residue	1.5	1.5	1.0	0.5	1.5
% Loss	0.5	---	---	1.5	0.5
RONC	----	65.0	68.0	76.4	75.0
RON + 3.17 gms. TEL/gal.	----	85.0	87.6	93.4	90.1
MONC	----	64.0	67.4	74.2	72.2
MON + 3.17 gms. TEL/gal.	----	85.1	87.8	92.8	88.4
Fluoride, ppm by Wt.				<1	<1
Chloride, ppm by Wt.				<1	<1
Sulfur, ppm by Wt.				50	75
Hydrogen Sulfide, ppm by Wt.				<0.5	<0.5
Basic Nitrogen, ppm by Wt.				<0.5	11
Total Nitrogen, ppm by Wt.				<0.5	12
Lead, ppm by Wt.				<0.01	0.03
Arsenic, ppm by Wt.				<0.005	0.03
Water, ppm by Wt.				<10	<10
Bromine No.				----	38
Oxygenated Compounds, ppm by Volume, ND indicates none detected					
Methanol				ND(<100)	ND(<100)
Ethanol				ND(<10)	ND(<10)
Isopropanol				ND(<10)	ND(<10)
Acetone				ND(<10)	ND(<10)
Methyl Ethyl Ketone				ND(<10)	ND(<10)
Tert-butyl Alcohol				ND(<10)	ND(<10)
Methyl tert-butyl ether				ND(<10)	ND(<10)

	No.2 Reformate	1BP-250°F OH Cut From No.2 Reformate	250°F+ Stms. From No.2 Reformate	No.3 Reformate	1BP-250°F OH Cut From No.3 Reformate	250°F+ Stms. From No. Reformate
Sample:	8/11/83	8/19/83	8/19/83	8/11/83	8/22/83	8/22/83
Sample Date:	703-83			702-83		
L.C. Sample No.:	1575	1575A	1575B	1574	1574A	1574B
P.C. Sample No.:						
TBP Dist. Yield, LV% ----		61.1	38.9	----	57.3	42.7
Gravity, °API @60°F	49.5	63.3	31.9	44.7	57.4	30.4
ASTM D-86 Dist. Corrected to 760 mm Hg., °F						
1BP	88	87	273	89	87	271
5% Recovered	129	118	288	137	121	286
10% Recovered	147	129	289	160	135	288
20% Recovered	177	148	294	192	157	290
30% Recovered	200	152	296	214	170	294
40% Recovered	221	164	300	232	181	297
50% Recovered	240	185	305	250	191	301
60% Recovered	260	196	310	266	200	307
70% Recovered	279	207	317	282	210	313
80% Recovered	298	218	327	298	219	323
90% Recovered	321	229	341	323	230	340
95% Recovered	342	239	358	346	239	358
End Point	371	252	411	376	250	415
% Recovered	98.0	98.0	98.5	98.0	97.5	98.5
% Residue	1.5	1.0	1.5	1.5	1.0	1.5
% Loss	0.5	1.0	----	0.5	1.5	----
RONC	95.1	81.5	110.3 ⁽¹⁾	99.7	88.1	112.7 ⁽¹⁾
RON + 3.17 gms. TEL Gal.	102.6	96.4	109.9 ⁽¹⁾	104.7	100.6	113.4 ⁽¹⁾
MONC	85.0	76.0	94.9 ⁽¹⁾	88.8	81.4	96.5 ⁽¹⁾
MON + 3.17 gms. TEL Gal.	93.0	93.5	96.2 ⁽¹⁾	94.8	94.0	97.4 ⁽¹⁾
Fluoride, ppm by Wt.	<1			<1		
Chloride, ppm by Wt.	<1			<1		
Sulfur, ppm by Wt.	0.2			0.2		
Hydrogen Sulfide, ppm by Wt.	<0.5			<0.5		
Basic Nitrogen, ppm by Wt.	<0.5			<0.5		
Total Nitrogen, ppm by Wt.	<0.5			<0.5		
Lead, ppm by Wt.	<0.01			<0.01		
Arsenic, ppm by Wt.	<0.005			<0.005		
Water, ppm by Wt.	<10			<10		
Oxygenated Compounds, ppm by Volume, ND indicates none detected						
Methanol	ND(<100)			ND(<100)		
Ethanol	ND(<10)			ND(<10)		
Isopropanol	ND(<10)			ND(<10)		
Acetone	ND(<10)			ND(<10)		
Methyl Ethyl Ketone	ND(<10)			ND(<10)		
Tert-butyl Alco- hol	ND(<10)			ND(<10)		
Methyl tert-butyl ether	ND(<10)			ND(<10)		

(1) Octanes were run on blends of these samples and Ponca City base gasoline. The data reported is the calculated octane number of these samples.

LABORATORY NO.: 1-13-83

9/6/83

Page 4 Att.

Sample:

Lake Charles Denuded

Casinghead

8/11/83

Sample Date:

704-83

L. C. Sample No.:

1576

P. C. Sample No.:

Compositional Analysis, LVZPARAFFINS, LVZ

Isobutane	Trace
Normal Butane	1.7
Isopentane	19.8
Normal Pentane	12.6
2,2 Dimethylbutane	0.75
2,3 Dimethylbutane	0.91
2-Methylpentane	3.90
3-Methylpentane	2.14
Normal Hexane	4.22
2,2 Dimethylpentane	0.18
2,4 Dimethylpentane	0.39
3,3 Dimethylpentane	0.11
2-Methylhexane	1.23
2,3 Dimethylpentane	0.59
3-Methylhexane	1.18
3-Ethylpentane	0.04
Normal Heptane	2.10
2,2 Dimethylhexane	0.15
2,5 Dimethylhexane	0.16
2,4 Dimethylhexane	0.14
3,3 Dimethylhexane	0.07
2,3 Dimethylhexane	0.11
3-Methyl, 3 Ethylpentane	0.20
Other C ₈ Isoparaffins	1.23
Normal Octane	0.94
C ₉ Paraffins, total	2.0
C ₁₀ Paraffins, total	2.4
C ₁₁ Paraffins, total	1.9
C ₁₂ Paraffins, total	2.0
Paraffins, Total	63.14

NAPHTHENES, LVZ

Cyclopentane	0.53
Methylcyclopentane	1.69
Cyclohexane	1.84
1,1 Dimethylcyclopentane	0.12
1-c-3 Dimethylcyclopentane	0.28
1-t-3 Dimethylcyclopentane	0.31
1-t-2 Dimethylcyclopentane	0.43
1-c-2 Dimethylcyclopentane	0.14
Methylcyclohexane	2.46
Ethylcyclopentane	0.15
1,1,3 Trimethylcyclopentane	0.11
1-t-2c-4 Trimethylpentane	0.16
1-t-2c-3 Trimethylpentane	0.16
Other C ₉ Naphthenes	1.35
C ₉ Naphthenes, total	1.3
C ₁₀ Naphthenes, total	1.5
C ₁₁ Naphthenes, total	1.2
C ₁₂ Naphthenes, total	0.9
Naphthenes, Total	14.63

AROMATICS, LVZ

Benzene	1.30
Toluene	1.33
Ethylbenzene	0.22
Para-Xylene	0.23
Meta-Xylene	0.49
Ortho-Xylene	0.08
C ₉ Aromatics, total	1.0
C ₁₀ Aromatics, total	0.9
C ₁₁ Aromatics, total	1.6
C ₁₂ Aromatics, total	0.7
Aromatics, Total	7.85

OLEFINS, LVZ

C ₄ Olefins, total	0.23
C ₅ Olefins, total	0.35
C ₆ Olefins, total	13.8
Olefins, Total	14.38
Total	100.00

SAL 00009250

Sample:	Lake Charles		
	Primary Tower	No. 2 CTU	No. 3 CTU
Sample Date:	Overhead	LSR	LSR
L.C. Sample No.:	8/17/83	8/17/83	8/17/83
P.C. Sample No.:	705-83	707-83	706-83
	1577	1579	1578

Compositional Analysis, LV%PARAFFINS, LV%

Propane	Trace	Trace	----
Isobutane	0.8	0.2	----
Normal Butane	3.4	0.9	----
Isopentane	24.0	6.2	3.1
Normal Pentane	28.6	6.0	12.2
2,2 Dimethylbutane	3.34	0.72	0.78
2,3 Dimethylbutane	4.23	1.12	1.87
2-Methylpentane	14.91	4.70	9.00
3-Methylpentane	8.06	2.91	6.03
Normal Hexane	6.87	5.96	12.40
2,2 Dimethylpentane	----	0.38	0.57
2,4 Dimethylpentane	----	0.77	1.15
3,3 Dimethylpentane	----	0.27	0.28
2-Methylhexane	----	3.19	4.08
2,3 Dimethylpentane	----	0.90	1.46
3-Methylhexane	----	3.23	4.55
3-Ethylpentane	----	0.25	0.31
Normal Heptane	----	6.55	5.77
2,2 Dimethylhexane	----	0.52	0.19
2,5 Dimethylhexane	----	0.66	0.16
2,4 Dimethylhexane	----	0.65	0.07
3,3 Dimethylhexane	----	0.25	0.02
2,3 Dimethylhexane	----	0.54	0.02
3-Methyl, 3 Ethylpentane	----	0.90	0.02
Other C ₈ Isoparaaffins	----	5.59	0.12
Normal Octane	----	4.47	0.02
C ₉ Paraaffins, total	----	2.7	----
C ₁₀ Paraaffins, total	----	0.1	----
C ₁₁ Paraaffins, total	----	----	----
Paraaffins, Total	94.21	60.63	64.17

NAPHTHENES, LV%

Cyclopentane	2.98	0.53	1.99
Methylcyclopentane	1.38	3.22	7.80
Cyclohexane	0.09	4.11	7.62
1,1 Dimethylcyclopentane	----	0.80	1.24
1-c-3 Dimethylcyclopentane	----	0.90	1.62
1-t-3 Dimethylcyclopentane	----	1.03	1.73
1-t-2 Dimethylcyclopentane	----	1.42	2.70
1-c-2 Dimethylcyclopentane	----	0.50	0.26
Methylcyclohexane	----	8.91	4.55
Ethylcyclopentane	----	0.52	0.39
1,1,3 Trimethylcyclopentane	----	0.62	0.23
1-t-2c-4 Trimethylpentane	----	0.51	0.12
1-t-2c-3 Trimethylpentane	----	0.51	0.12
Other C ₈ Naphthenes	----	6.73	0.14
C ₉ Naphthenes, total	----	1.17	----
C ₁₀ Naphthenes, total	----	0.02	----
Naphthenes, Total	4.45	31.50	30.51

AROMATICS, LV%

Benzene	1.12	1.61	3.35
Toluene	----	3.85	1.82
Ethylbenzene	----	0.45	----
Para-Xylene	----	0.40	----
Meta-Xylene	----	1.17	----
Ortho-Xylene	----	0.33	----
C ₉ Aromatics, total	----	0.06	----
C ₁₀ Aromatics, total	----	----	----
C ₁₁ Aromatics, total	----	----	----
C ₁₂ Aromatics, total	----	----	----
Aromatics, Total	1.12	7.87	5.17

OLEFINS, LV%

C ₄ Olefins, total	0.02	----	----
C ₅ Olefins, total	0.10	----	0.05
C ₆ + Olefins, total	0.10	----	0.10
Olefins, Total	0.22	----	0.15

Total	100.00	100.00	100.00
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RECOMMENDATIONS FOR SAMPLING AIR FOR THE
SUBSEQUENT ANALYSIS OF THE BENZENE CONCENTRATION

1. Personal Sample Pump Calibration

The pump must be calibrated with a charcoal sampling tube attached. The tips of the charcoal tubes can best be broken off by first scoring them with a small file. The opening should be at least one-half the internal diameter of the tube.

The permissible total air volume range is 0.5 to 55 liter per sample. Therefore, for an 8 hour sampling period we recommend approximately 50 cc's/minute sampling rate (maximum allowable flow is 114 cc's/minute). For a 15 minute sampling period, we recommend approximately 200 cc's/minute sampling rate (maximum allowable is 1 liter/minute). For the recommended low flows, the soap-bubble graduated tube flow measurement procedure is suitable for calibration.

The atmospheric pressure and temperature must be recorded at the time of calibration.

2. Sampling

Insure the personal pump is calibrated for the flow required for the sampling time period desired.

Remove the white plastic guard from the clip-on-guard tube. Snap off the tips of the charcoal tube and insert the end with the shorter length of charcoal into the tubing connected to the pump. Replace the white plastic guard. Insure that the tube is in a vertical position for sampling.

Start the pump and maintain for the desired sampling time period. At the end of the sampling period, remove the tube and immediately cap with the supplied plastic caps. Insure the cap is firmly in place and cannot be easily dislodged. Refer to the attached data sheet, and log all required information. Attach the sample charcoal tube to an ID tag. Insure that the data sheet and ID tag are identically identified. An example of how to attach the ID tag to the sample tube will be enclosed with the sampling tubes.

3. Sample Tube Transmittal Back to TSL for Analysis

Insure that the sample charcoal tubes are effectively capped.

Break the tips off of a new charcoal tube and cap. This tube will be used as a blank for the analysis; please identify as blank.

Package all tubes in such a manner that will insure that the caps will not become dislodged. Return to TSL within as short a period of time as practical. Consider that the analysis of the tube must be made within 14 days from the time the sample was taken. Allow 24 hours for analysis after arrival at TSL

Submit a completed data sheet for each sample. These sheets will be returned to you for your records after we log the analysis data. We will retain a copy of each data sheet.

SAL 000009168

$$8 \text{ hrs} = .1 \ell / 2 \text{ min} = 24 \ell$$

$$15 \text{ min} = .5 \ell / \text{min} = 7.5 \ell$$

N1024 Manual of ...
Element 1

ORGANIC SOLVENTS IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Organic Solvents (See Table 1)	Method No:	P&CAM 127
Matrix:	Air	Range:	For the specific compound, refer to Tables I&II
Procedure:	Adsorption on charcoal desorption with carbon disulfide, GC		
Date Issued:	9/15/72	Precision:	10.5% RSD
Date Revised:	7/15/74	Classification:	See Table 1

1. Principle of the Method

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, graduated test tube and desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

The lower limit in mg/sample for the specific compound at 16 x 1 attenuation on a gas chromatograph fitted with a 10:1 splitter is shown in Table 1. This value can be lowered by reducing the attenuation or by eliminating the 10:1 splitter.

3. Interferences

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more solvents are known or suspected to be present in the air, such information including their suspected identities, should be transmitted with the sample; since with differences in polarity, one may displace another from the charcoal.

- 3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity. For this reason it is important that a sample of the bulk solvent(s) be submitted at the same time so that identity(ies) can be established by other means.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperatures, etc.) must be changed to circumvent the problem.
4. Precision and Accuracy
- 4.1 The mean relative standard deviation of the analytical method is 8%. (Ref. 11.4).
- 4.2 The mean relative standard deviation of the analytical method plus field sampling using an approved personal sampling pump is 10% (Ref. 11.4). Part of the error associated with the method is related to uncertainties in the sample volume collected. If a more powerful vacuum pump with associated gas-volume integrating equipment is used, sampling precision can be improved.
- 4.3 The accuracy of the overall sampling and analytical method is 10% (NIOSH's unpublished data) when the personal sampling pump is calibrated with a charcoal tube in the line.
5. Advantages and Disadvantages of the Method
- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more solvents suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.
- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists. During sample storage the more volatile compounds will migrate throughout the tube until equilibrium is reached (33% of the sample on the backup section).

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 An approved and calibrated personal-sampling pump for personal samples. For an area sample any vacuum pump whose flow can be determined accurately at 1 liter per minute or less.
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 lpm.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (20 ft x 1/8 in) with 10% FFAP stationary phase on 80/100 mesh, acid-washed DMCS Chromosorb W solid support. Other columns capable of performing the required separations may be used.
- 6.5 A mechanical or electronic integrator or a recorder and some method for determining peak area.
- 6.6 Glass stoppered micro tubes. The 2.5-ml graduated microcentrifuge tubes are recommended.
- 6.7 Hamilton syringes: 10 μ l, and convenient sizes for making standards.
- 6.8 Pipets: 0.5 ml delivery pipets or 1.0 ml type graduated in 0.1 ml increments.
- 6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

- 7.1 Spectroquality carbon disulfide (Matheson Coleman and Bell)

7.2 Sample of the specific compound under study, preferably chromatography grade.

7.3 Bureau of Mines Grade A helium.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, the ends of the tube should be broken to provide an opening at least one-half the internal diameter of the tube (2mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be vertical during sampling.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 The flow, time, and/or volume must be measured as accurately as possible. The sample should be taken at a flow rate of 1 fpm or less to attain the total sample volume required. The minimum and maximum sample volumes that should be collected for each solvent are shown in Table 1. The minimum volume quoted must be collected if the desired sensitivity is to be achieved.

8.3.6 The temperature and pressure of the atmosphere being sampled should be measured and recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped tubes should be packed tightly before they are shipped to minimize tube breakage during shipping.
- 8.3.10 ~~Samples~~ of the suspected solvent(s) should be submitted to the laboratory in containers furnished by NIOSH for such purpose. These liquid bulk samples should not be transported in the same container as the samples or blank tube. If possible, a bulk air sample (at least 500 air drawn through tube) should be shipped for qualitative identification purposes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a small stoppered test tube. The separating section of foam is removed and discarded; the second section is transferred to another test tube. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, one-half ml of carbon disulfide is pipetted into each test tube. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period. The use of graduated glass-stoppered, microcentrifuge tubes is recommended so that one can observe any apparent change in volume during the desorption process. Carbon disulfide is a very volatile solvent, so volume changes can occur during the desorption process depending on the surrounding temperature. The initial volume occupied by the charcoal plus the 0.5 ml CS₂ should be noted and corresponding volume adjustments should be made whenever necessary just before GC analysis.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
1. 85 cc/min. (70 psig) helium carrier gas flow.
 2. 65 cc/min. (24 psig) hydrogen gas flow to detector.
 3. 500 cc/min. (50 psig) air flow to detector.
 4. 200°C injector temperature.

5. 200°C manifold temperature (detector)
6. Isothermal oven or column temperature - refer to Table 1 for specific compounds.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10 µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process for a given compound, provided the same batch of charcoal is used. The Physical and Chemical Analysis Branch of NIOSH has found that the desorption efficiencies for the compounds in Table 1 are between 81% and 100% and vary with each batch of charcoal.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 5cm, 4-mm I.D. glass tube, flame-sealed at one end (similar to commercially available culture tubes). This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped

with Parafilm. A known amount of the compound is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. The amount injected is usually equivalent to that present in a 10-liter sample at a concentration equal to the federal standard.

At least five tubes are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the specific compound onto the charcoal. These five tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.3.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of CS₂ with the same syringe used in the preparation of the sample. These are analyzed with the samples.

The desorption efficiency equals the difference between the average peak area of the samples and the peak area of the blank divided by the average peak area of the standards, or

$$\text{desorption efficiency} = \frac{\text{Area sample} - \text{Area blank}}{\text{Area standard}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml CS₂ because samples are desorbed in this amount of CS₂. To minimize error due to the volatility of carbon disulfide, one can inject 20 times the weight into 10 ml of CS₂. For example, to prepare a 0.3 mg/0.5 ml standard, one would inject 6.0 mg into exactly 10 ml of CS₂ in a glass-stoppered flask. The density of the specific compound is used to convert 6.0 mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5ml versus peak area.

NOTE: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the PID response.

10. Calculations

10.1 The weight, in mg, corresponding to each peak area is read from the standard curve for the particular compound. No volume corrections are needed, because the standard curve is based on mg/0.5 ml CS₂ and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{Correct mg} = \text{mg}_s - \text{mg}_b$$

where:

mg_s = mg found in front section of sample tube

mg_b = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 The corrected amounts present in the front and backup sections of the same sample tube are added to determine the total measured amount in the sample.

10.4 This total weight is divided by the determined desorption efficiency to obtain the total mg per sample.

10.5 The volume of air sampled is converted to standard conditions of 25°C and 760 mm Hg.

$$V_s = V \times \frac{P}{760} \times \frac{298}{T+273}$$

where:

V_s = volume of air in liters at 25°C and 760 mm Hg

V = volume of air in liters as measured

P = Barometric pressure in mm Hg

T = Temperature of air in degree centigrade

10.6 The concentration of the organic solvent in the air sampled can be expressed in mg per m³, which is numerically equal to µg per liter of air

$$\text{mg/m}^3 = \mu\text{g/l} = \frac{\text{total mg (Section 10.4)} \times 1000 (\mu\text{g/mg})}{V_s}$$

10.7 Another method of expressing concentration is ppm, defined as µl of compounds per liter of air

$$\text{ppm} = \mu\text{l of compound} / V_s$$

$$\text{ppm} = \frac{\mu\text{l of compound}}{V_s} \times \frac{24.45}{\text{MW}}$$

where:

24.45 = molar volume at 25°C and 760 mm Hg

MW = molecular weight of the compound (Table 1)

11. References

- 11.1 White, L.D., D.G. Taylor, P.A. Mauer, and R.E. Kupel, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31:225 (1970).
- 11.2 Young, D.M. and A.D. Crowell, Physical Adsorption of Gases, Butterworths, London, 1962, pp. 137-146.
- 11.3 Federal Register, 37 (#202), 22139-22142 (October 18, 1972).
- 11.4 NIOSH Contract HSM-99-72-98, Scott Research Laboratories, Inc., "Collaborative Testing of Activated Charcoal Sampling Tubes for Seven Organic Solvents," pp. 4-22, 4-27 (1973).

TABLE I

PARAMETERS ASSOCIATED WITH PACAB ANALYTICAL METHOD NO. 127

A = recommended

Organic Solvent	Method Classification	Detection limit (mg/sample)	Sample Volume (l)		GC Column Temperature (°C)	Molecular Weight
			Minimum (a)	Maximum (b)		
Acetone	D		0.5	7.7	60	58.1
Benzene	<u>A</u>	<u>0.01</u>	0.5	55	90	78.1
Carbon tetrachloride	A	0.20	10	60	60	154.0
Chloroform	A	0.10	0.5	13	80	119
Dichloromethane	D	0.05	0.5	3.8	85	84.9
p-Dioxane	A	0.05	1	18	100	88.1
Ethylene dichloride	D	0.05	1	12	90	99.0
Methyl ethyl ketone	B	0.01	0.5	13	80	72.1
Styrene	D	0.10	1.5	34	150	104
Tetrachloroethylene	B	0.06	1	25	130	166
1,1,2-trichloroethane	B	0.05	10	97	150	133
1,1,1-trichloroethane (Methyl Chloroform)	B	0.05	0.5	13	150	133
Trichloroethylene	A	0.05	1	17	90	131
Toluene	B	0.01	0.5	22	120	92.1
Xylene	A	0.02	0.5	31	100	106

(a) Minimum volume, in liters, required to measure 0.1 times the OSHA standard

(b) These are breakthrough volumes calculated with data derived from a potential plot (reference 11.2) for activated coconut charcoal. Concentrations of vapor in air at 5 times the OSHA standard (reference 11.3) or 500 ppm, whichever is lower, 25°C, and 760 torr were assumed. These values will be as much as 50% lower for atmospheres of high humidity. The effects of multiple contaminants have not been investigated, but it is suspected that less volatile compounds may displace more volatile compounds (See 3.1 and 3.2).

TABLE II

CHEMICALS WHICH HAVE GREATER THAN 80%
DESORPTION EFFICIENCY BUT HAVE NOT BEEN
THOROUGHLY TESTED BY NIOSH

Class E (Proposed)

Acrylonitrile	Isobutyl acetate
Allyl glycidyl ether	Isobutyl alcohol
n-Amyl acetate	Isoctane
2-Butoxyethanol	Isophorone
n-Butyl acetate	Isopropyl acetate
n-Butyl alcohol	Isopropyl glycidyl ether
n-Butylglycidyl ether	2,6-Lutidine
Chlorobenzene	Methyl acetate
Cyclohexane	Methyl acrylate
Cyclohexanone	Methyl n-butyl ketone
o-Dichlorobenzene	Methyl ethyl ketone
p-Dichlorobenzene	Methyl isobutyl ketone
Diethyl ether	Methyl methacrylate
N,N-Dimethyl aniline	o-Methyl styrene
Epichlorohydrin	p-Methyl styrene
2-Ethoxyethyl acetate	n-Octane
Ethyl acetate	3-Octanone
Ethylbenzene	Pentane
Ethyl butyl ketone	2-Pentanone
Fufural	α-pinene
Heptane	n-Propyl acetate
Hexane	1,1,2,2-Tetrachloroethane
Isoamyl acetate	Tetrahydrofuran
	Trichlorotrifluoroethane (Freon 113)

Recommended Sample Size = 10g

CONTINENTAL OIL COMPANY
PONCA CITY, OKLAHOMA
REFINING TECHNICAL SERVICES LABORATORY

File: LC
File: 652.1
921
Date: 5-19-77

LABORATORY NO. E-74-77
CHARGE: LC 49
SUBJECT: Benzene Content of Gasoline Streams and Blends - Lake Charles Refinery

ANALYTICAL DATA:

<u>Sample Number</u>	<u>Sample</u>	<u>Vol. % Benzene</u>
PC 1839 LC 640-77	Regular Gasoline	<u>1.1</u>
PC 1840 LC 641-77	Premium Gasoline	<u>1.0</u>
PC 1841 LC 642-77	Unleaded Gasoline	<u>1.1</u>
PC 1842 LC 643-77	Coker Gasoline	0.2
PC 1843 LC 644-77	Thermal Gasoline	1.3
PC 1844 LC 645-77	TCC Gasoline	0.5
PC 1819 LC 646-77	<u>No. 1 L.S.R.</u>	<u>1.5</u>
PC 1846 LC 647-77	<u>No. 2 L.S.R.</u>	<u>1.6</u>
PC 1847 LC 648-77	<u>Denuded Casinghead</u>	<u>3.7</u>
PC 1848 LC 649-77	<u>No. 1 Reformate</u>	0.9
PC 1849 LC 650-77	<u>No. 2 Reformate</u>	<u>1.0</u>
PC 1850 LC 651-77	<u>Primary Tower Overhead</u>	<u>2.8</u>

REFERENCE:

Letter from J. J. Mangelinkx to K. C. Hunt dated 5-12-77.

Approved:

J. D. Orrell
Senior Technologist

bp

cc: GAO-DRU-JRU-MEO-KCH-F

W. L. Tipton
Associate Chemist

SAL 000009180