

BUSINESS CONFIDENTIAL

PROJECT REPORT

TEXAS CITY PLANT

TOXIC POLLUTANT ANALYSIS OF EPA SPLIT-SAMPLES
TAKEN JUNE 12-15, 1978

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DATE: December 1, 1978
PROJECT NO: 510A16
FILE NO: 25749

SUMMARY Toxic pollutant analyses were completed for these
EPA split-samples taken at Texas City June 12-15, 1978.

Concentration, mg/l

	<u>Marine</u> <u>Terminal</u>	<u>No.3</u> <u>Olefins</u>	<u>Dilute</u> <u>Waste to</u> <u>Gulf Coast</u>	<u>Effluent</u> <u>From</u> <u>O.P.D.A.</u>
<u>Volatile Organics</u>				
Benzene	140.0(a)	160.0	0.69	0.27
1,2 Dichloroethane	250.0	(-)	0.72	(-)
Ethylbenzene	54.0	34.0	(-)	(-)
Toluene	380.0(a)	58.0	0.006	(-)
<u>Semi-Volatile Organics</u>				
Acenaphthene	0.16(a)	3.9	0.05	(+)
Acenaphthylene	(-)	18.0	0.12	(+)
Anthracene	0.009(a)	29.0	0.12	0.14(a)
Bis-2-chloroethyl ether	(-)	(-)	0.71	(+)
Dioctyl phthalate	2.2	2.8	0.10	(-)
Fluoranthene	(-)	6.6	0.01	(-)
Fluorene	(-)	13.0	0.058	(-)
Isophorone	23.0	(-)	(-)	(-)
Naphthalene	0.26	57.0	0.92	0.011
Phenol	57.0(a)	1.4	0.047	2.6
Polynuclear Aromatic				
Hydrocarbons	(-)	17.0	(-)	(-)
Pyrene	(-)	12.0	0.028	(-)

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RESEARCH AND DEVELOPMENT DEPARTMENT
CHEMICALS AND PLASTICS
UNION CARBIDE CORPORATION
SOUTH CHARLESTON, WEST VIRGINIA

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	<u>Marine Terminal</u>	<u>No. 3 Olefins</u>	<u>Dilute Waste to Gulf Coast</u>	<u>Effluent From O.P.D.A.</u>
<u>Metals</u>				
Chromium	0.20	0.52	4.2	0.66
Copper	0.48	0.15	0.20	0.15
Silver	0.20	0.15	0.12	0.15
Thallium	<0.35	<0.35	<0.35	<0.35
Zinc	2.0	0.32	0.89	0.31

- (+) Detected by GC-MS analysis only.
(-) Not detected by GC-MS analysis.
(a) The compound was detected as a multi-component peak, and the concentration may be high.

INTRODUCTION EPA sampled the Texas City plant June 5-15, 1978 for the verification phase of the BAT program. This sampling and analysis was to quantify those toxic pollutants detected by the screening analysis August 9-12, 1977. Carolyn Harvey, from the Texas City Plant, had requested that R/D take split-samples at four locations - Dilute Waste to Gulf Coast, Effluent from O.P.D.A., No. 3 Olefins Unit, and Marine Terminal - to provide a comparative analysis with EPA's results.

DISCUSSION Toxic pollutants were analyzed using the EPA protocol methods for screening wastewaters (1). The toxic organic pollutants were identified by GC-MS analysis, then quantified by a separate GC-FID analysis (Table I). The toxic metal pollutants were identified by flame or flameless atomic absorption analysis (Table II).

Four isomers of polynuclear aromatic hydrocarbons (PNAs) were detected by GC-MS, but not specifically identified, in the No. 3 Olefins sample. The total PNA concentration contributed by the isomers was estimated at 17 mg/l. These PNA isomers were not detected in the other samples.

The EPA screening analysis in August 1977 had detected metals at concentrations as high as 27 mg/l. Five of the EPA toxic metals - chromium, copper, silver, thallium, and zinc - were analyzed by flame or flameless atomic absorption. Chromium was detected in the Dilute Waste to Gulf Coast at a concentration of 4.2 mg/l. Zinc was detected in the Marine Terminal at a concentration of 2.0 mg/l. All other metals were detected at concentrations less than 1.0 mg/l.

EPA planned to analyze for the toxic pollutants using specific methods submitted for the verification phase. The methods include analysis of phthalate esters, polynuclear aromatic hydrocarbons, volatile organics, and metals.

Flame ionization, electron capture and ultra-violet detectors would be used to detect or "identify" the toxic pollutants. No identifications would be made by GC-MS analysis. These methods have not been validated, and their precision and accuracy are not known. EPA asked the Texas City plant and R/D to use these methods for the split analysis, so that the data could be used as a partial validation of the methods. R/D chose not to use these specific methods. The GC-MS analytical scheme used by the Environmental Analytical Group unequivocally identifies the toxic pollutants to a detection limit of 10 ppb. A separate GC-FID analysis provides an accurate and precise quantitative analysis of the identified toxics. A comparison of R/D and EPA's results should agree within the same order of magnitude.

EXPERIMENTAL EPA sampled at Texas City June 5-15, 1978, sampling procedures were documented in an earlier memorandum (2). Grab samples were taken for volatile organics analysis (VOA). Composite samples were taken manually and with automatic samplers for semi-volatile organics analysis. Four split-samples were taken June 12-15 and the composites varied with each one: (1) The Marine Terminal was taken as a grab sample each of the three days; (2,3) The No. 3 Olefins Unit and the Dilute Waste to Gulf Coast samples were composited with an ISCOS automatic sampler; three 24 hour composites were taken; (4) the Effluent from O.P.D.A. was taken as a grab sample each day and combined for a 72-hour composite.

Volatile Organics

All grab samples collected for a particular wastewater were combined in the lab prior to analysis. Thus, VOA concentrations represent a three-day average value. A 5.0 ml volume was purged with nitrogen, adsorbing the volatile organics on Tenax/Silica gel columns. The organics were thermally desorbed at 250°C and chromatographed using these conditions:

Column: 0.2% Carbowax 1500 on 60/80
Carbopack C; glass; 6 ft. x 2mm I.D.

Detector: Mass spectrometry, then flame
ionization.

A direct aqueous injection technique was used to confirm concentrations detected greater than 5 mg/l.

Semi-Volatile Organics

Equal portions of the three 24-hour composite samples taken for a particular wastewater were combined for a final volume of 2.0 liters. The semi-volatile organics concentrations represent a three-day average value. The organics were separated by liquid - liquid extraction at pH 11 and 2 with methylene chloride. These gas chromatographic conditions were used:

Columns: 3% OV-17 on 100/200 Supelcoport,
glass, 6 ft. x 2 mm I.D.

Superpak 20 M, glass, 6 ft. x 2mm I.D.

Detectors: Mass spectrometry, then flame
ionization.

Metals

An aliquot of each sample was digested with acid, then analyzed by flame or flameless atomic absorption.

REFERENCES

1. "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants" EPA Publication, April, 1977.
2. Siegrist, S. A., "EPA Sampling at the Texas City Plant, June 5-16, 1978" R/D Memorandum, July 21, 1978, File No. 25313.

ACKNOWLEDGEMENTS The laboratory assistance of L. J. Priestly for GC-MS analysis and J. C. Boggs for quantitative analysis is greatly appreciated. The authors also thank R. A. Singer and D. E. Nixon for the metals analysis.

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Manuscript Date: November 14, 1978

Date Typed: December 1, 1978

Attachments: 2 Tables

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TABLE I

TOXIC ORGANIC POLLUTANTS DETECTED IN TEXAS CITY/EPA
SPLIT-SAMPLES FROM JUNE 12-15, 1978

	<u>Concentration, mg/l</u>			
	<u>Marine</u> <u>Terminal</u>	<u>No. 3</u> <u>Olefins</u>	<u>Dilute</u> <u>Waste to</u> <u>Gulf Coast</u>	<u>Effluent</u> <u>From</u> <u>O.P.D.A.</u>
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Pryene	(-)	12.0	0.028	(-)

(+) Detected by GC-MS analysis only.

(-) Not detected by GC-MS analysis.

(a) The compound was detected as a multi-component peak, and the concentration may be high.

TABLE I
TOXIC METALS DETECTED IN TEXAS CITY/EPA
SPLIT-SAMPLES FROM JUNE 12-15, 1978

	<u>Concentration, mg/l</u>			
	<u>Marine Terminal</u>	<u>No. 3 Olefins</u>	<u>Dilute Waste to Gulf Coast</u>	<u>Effluent From O.P.D.A.</u>
Chromium	0.20	0.52	4.2	0.66
Copper	0.48	0.15	0.20	0.15
Silver	0.20	0.15	0.12	0.15
Thallium	ND(a)	ND	ND	ND
Zinc	2.0	0.32	0.89	0.31

(a) Thallium was not detected (ND) at concentration greater than 0.35 mg/l, the thallium detection limit by flame atomic absorption.

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