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Date: February 12, 2003
Refer to: RRES-GPP:03-020

Mr. John Young, Corrective Action Project Leader
Permits Management Program
NMED – Hazardous Waste Bureau
2905 Rodeo Park Drive East
Building 1
Santa Fe, NM 87505-6303

FEB 2003

SUBJECT: REQUEST FOR DATA FROM THE GROUNDWATER FOCUS AREA'S INVESTIGATION OF LABORATORY ANALYSES OF HIGHEXPLOSIVE COMPOUNDS LOS ALAMOS NATIONAL LABORATORY (LANL) NM0890010515

Dear Mr. Young:

In response to your letter dated January 13, 2003, regarding the above subject, the following information is provided.

This letter provides an approach for avoiding misinterpretation of high explosive analytical testing results in water samples from drilled wells. Attached are the analytical data that show how contamination from polymeric compounds used during drilling can cause false-positive results for high explosive (HE) compounds. Included is spectral evidence that show a mismatch between the spectra of the contaminant and the reference spectra, water chemistry data that is evidence of a carbon-rich contaminant in the samples, and analytical results from a study using samples spiked with polymeric drilling fluids. Together, these results present a convincing argument that polymeric contaminants are causing interference during the analysis process and are the source of the false-positive results.

Beginning in late 2000, several wells installed at the Laboratory were drilled with additives to facilitate the drilling process. These additives included the trade name products QUIK-FOAM and EZ-MUD. Only a subset of all wells drilled at the Laboratory used drilling additives. When water samples from this subset were analyzed, the results showed detected values for several different HE compounds, most commonly 3-nitrotoluene (3-NT), an HE breakdown product. Until late 2000, this compound had rarely been detected in isolation from other HE compounds in Laboratory samples. Water samples from wells drilled without additives did not show a high detection rate for HE compounds.

This was the first indication that drilling additives may be contaminating water samples and causing false positives.

Because analytical results indicated potential HE in the samples, sampling was done in the field for the presence of HE using DTECH brand field test kits. However, the test kits yielded positive results only when drilling additives were added to a blank water sample. Therefore, something in the drilling additives was causing a false positive result in the field test kits. Investigation into the composition of the drilling additives and the details of the analytical method revealed a potential problem. The drilling additive EZ-MUD is a water-soluble polyacrylamide/polyacrylate copolymer (see Attachment 1). SW-846 Method 8330 for HE analysis uses an ultraviolet (UV) detector set at 254 nm to detect nitroaromatics and nitramines. The chemical bonds in explosives and in a polymer such as EZ-MUD are similar in structure and sensitive to UV light. Components of the EZ-MUD can be extracted into acetonitrile during analytical sample processing and might react similarly to HE compounds in a UV detector. If these contaminants produce positive peaks in specific retention-time windows for HE compounds on both columns, SW-846 Method 8330 requires that those HE compounds must be reported as detected, even if no HE is present in the sample. Therefore, SW-846 Method 8330 is not sufficient to accurately identify HE compounds in well samples.

Once the potential for problems from drilling fluid contamination of samples was identified, all further well samples were sent for more extensive analysis. SW-846 Method 8330 was used for all samples; however the analytical laboratories also were asked to provide an additional confirmation method that provides better identification of the detected compound. The analytical laboratories used diode array spectroscopy, which provides a multiwavelength UV spectrum of each detected compound. Each spectrum then is compared to reference spectra for the HE compound in question and the quality of the match between the two spectra is determined. Because each HE compound has a characteristic absorption spectrum, this detection method is more specific for identification purposes than the single-wavelength method specified by SW-846 Method 8330. It also provides additional confirmation data for compounds reported as detected on both columns, in accordance with SW-846 Method 8330. Attachment 2 shows the UV spectra for the suspected contaminant (top) and reference spectra of 3-NT (bottom) from the primary column used in SW-846 Method 8330 (left) and the secondary column used in SW-846 Method 8330 (right). This clearly illustrates the discrepancy between the spectral signature for 3-NT and the spectral signature of the contaminant. Note that the 3-NT spectra are missing the 220 nm peaks present in the contaminant spectra. This spectral evidence strongly supports our hypothesis that these reported detections are false positives.

There is also physical chemical evidence of contamination in well samples from residual drilling fluids. When water samples from wells that were drilled with additives were analyzed for total organic carbon (TOC) and dissolved organic carbon (DOC), the results were on the order of 3 to 6 mg of carbon per liter, higher than the 1 to 2 mg of carbon per liter expected for such samples. The organic nitrogen chemistry also supports these results. These elevated TOC and DOC levels indicate the presence of carbon- and nitrogen-rich compounds from the breakdown of the polymeric drilling additives. DOC and TOC concentrations in the wells decreased over time as the drilling additives were flushed from the well, providing further chemical evidence of drilling additive contamination. In

addition, the absence of detected tritium from past Laboratory discharges in some wells supports the argument that any detected HE results are false-positives and not from a Laboratory source. (see "Characterization Well R-19 Geochemistry Report," p. 27 (Longmire 2002, 73282).

To confirm that drilling additives were causing false-positive results for HE compounds, samples spiked with drilling additives were sent for analysis. Attachment 3 shows the chromatographic results of this study, i.e., chromatograms of pure water samples spiked with drilling additives. The chromatograms for samples spiked at 1000 µg/L EZ-MUD show multiple-peak responses on both columns required by SW-846 Method 8330. It is obvious that significant amounts of the EZ-MUD components are being extracted during sample processing and that these components can be detected at 254 nm. The high noise level in chromatograms such as these makes positive detected results likely, despite the absence of HE in the sample itself.

In conclusion, a wide range of evidence indicates that drilling additives in a subset of Laboratory wells are causing false-positive results for certain HE compounds. These false-positive results frequently occur in isolation without an obvious source term and in the absence of related breakdown products such as nitrotoluenes and aminodinitrotoluenes. These compounds were detected infrequently prior to 2001, at least for sites outside the Laboratory's HE corridor. The match between the spectral signature of the false-positive compound and known reference spectra is very poor. Water chemistry data support the presence of carbon-rich and nitrogen-rich compounds such as drilling additives in a subset of groundwater well samples. These drilling additives are known to cause false-positive results with field test kits for HE. Finally, analyses of the actual drilling additives show peaks that can masquerade as detected results in a typical SW-846 Method 8330 analysis. Given this information, we believe the best policy is to continue use of SW-846 Method 8330 as well as diode array confirmation for HE analysis, and the screen results for the possibility of false-positives from drilling additives. When false positives are found, they will be noted as appropriate.

If you have further questions regarding this response, please contact me at (505) 665-4681 or Mat Johansen at (505) 665-5046.

Sincerely,

Charles L. Nylander

Charles Nylander, Program Manager
Groundwater Protection Program
Los Alamos National Laboratory

Sincerely,

Mat Johansen

Mat Johansen, Groundwater Program
Program Compliance Manager
National Nuclear Security Admin.
Office of Los Alamos Site Operations

CN/MJ/th

Attachment: EZ-MUD, Attach. 1-1,1-2,2-1,3-1, and 3-2

Cy (w/att.):
C. Nylander, RRES-GPP, MS M992
N. Quintana, RRES-R, MS M992
B. Ramsey, RRES-DO, MS J591
D. Stavert, RRES-DO, MS J591
B. Enz, OLASO, MS A316
M. Johansen, OLASO, MS A316
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RRES-GPP File, MS M992
RRES-RPF, MS M992 (ER2003-0139)

EZ-MUD®

Shale stabilizer
& Viscosifier

EZ MUD is an anionic polymer emulsion (not suspension). It consists of 30% to 32% active copolymer of polyacrylamide/polyacrylate emulsified in a "petroleum distillate" (CAS #64742-47-8) which has been approved by the U.S. FDA for various food contact applications (21 CFR, Sec. 178.3650).

Baroid Environmental, Safety and Transportation Data Sheet

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EZ MUD®

PRODUCT IDENTIFICATION		
SUPPLIER BAROID DRILLING FLUIDS, INC.	REGULAR TELEPHONE NUMBER 281/871-5900 EMERGENCY TELEPHONE NO. 800 424-9300	
ADDRESS P.O. BOX 1675 HOUSTON, TEXAS 77251		
TRADE NAME EZMUD		
GENERIC DESCRIPTION PARTIALLY HYDROLYZED POLYACRYLAMIDE		
HAZARDOUS INGREDIENTS		
MATERIAL OR COMPONENT	%	HAZARD DATA
PETROLEUM DISTILLATE HYDRO-	24	400 PPM OSHA
TREATED LIGHT 64742-47-8		
PHYSICAL DATA		
BOILING POINT (Deg F) >200 F	MELTING POINT NA	FREEZING POINT ND
SPECIFIC GRAVITY (H2O = 1) 1.0	VAPOR PRESSURE (mm Hg) NA	
VAPOR DENSITY (AIR = 1) NA	SOLUBILITY IN WATER, % BY WT. APPRECIABL	
VOLATILES BY VOLUME 70	EVAPORATION RATE(BUTYL ACETATE = 1) <1	
APPEARANCE AND ODOR CLEAN COLORED LIQUID, SLIGHT ODOR	DENSITY @ 20 Deg C (Uncompacted) 8.3 lb/gal	
pH NA		

NA – Not Applicable ND – Not Determined

[illegible]

[illegible]

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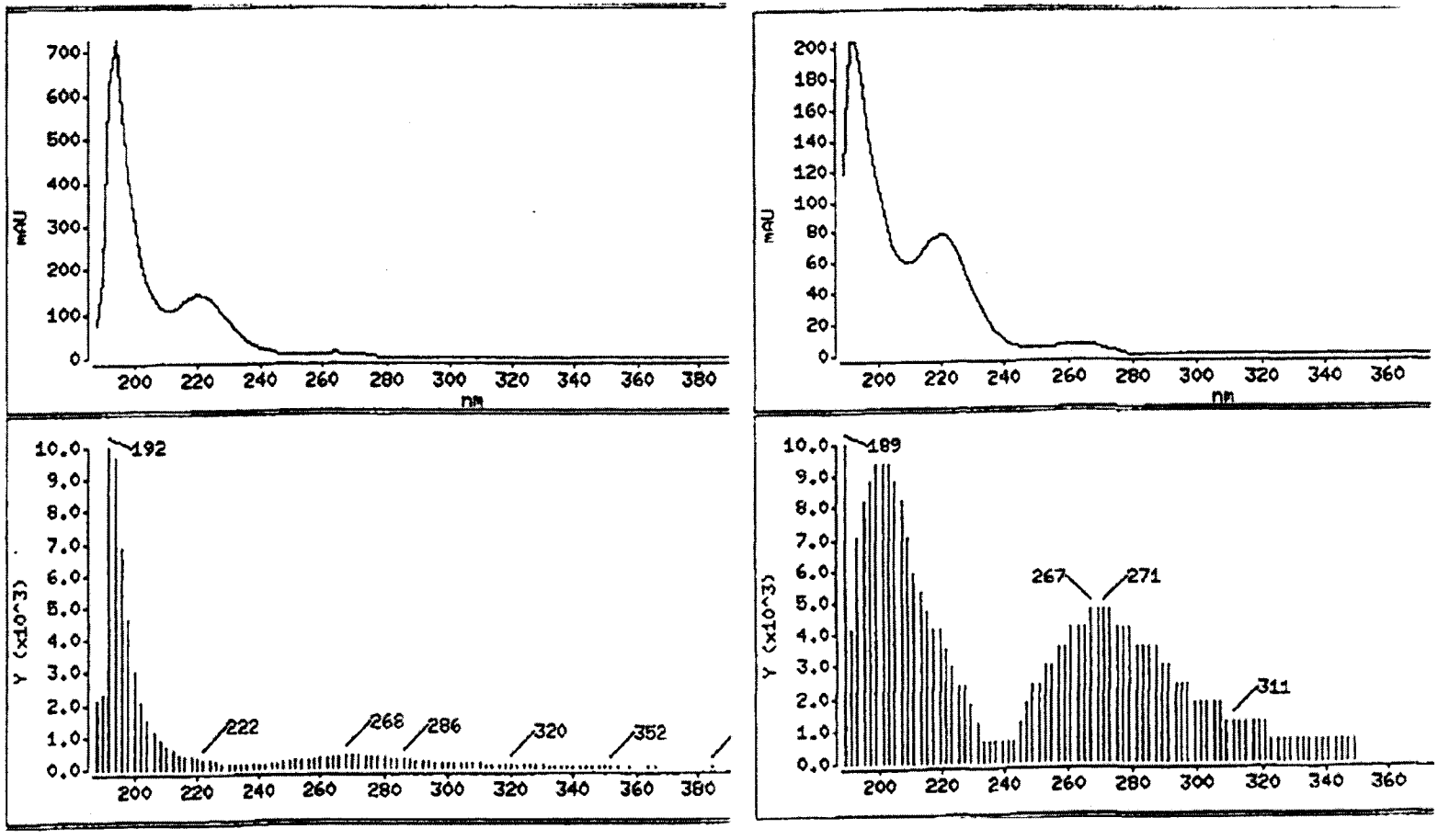
P.O. Box 1675, Houston, Texas 77251

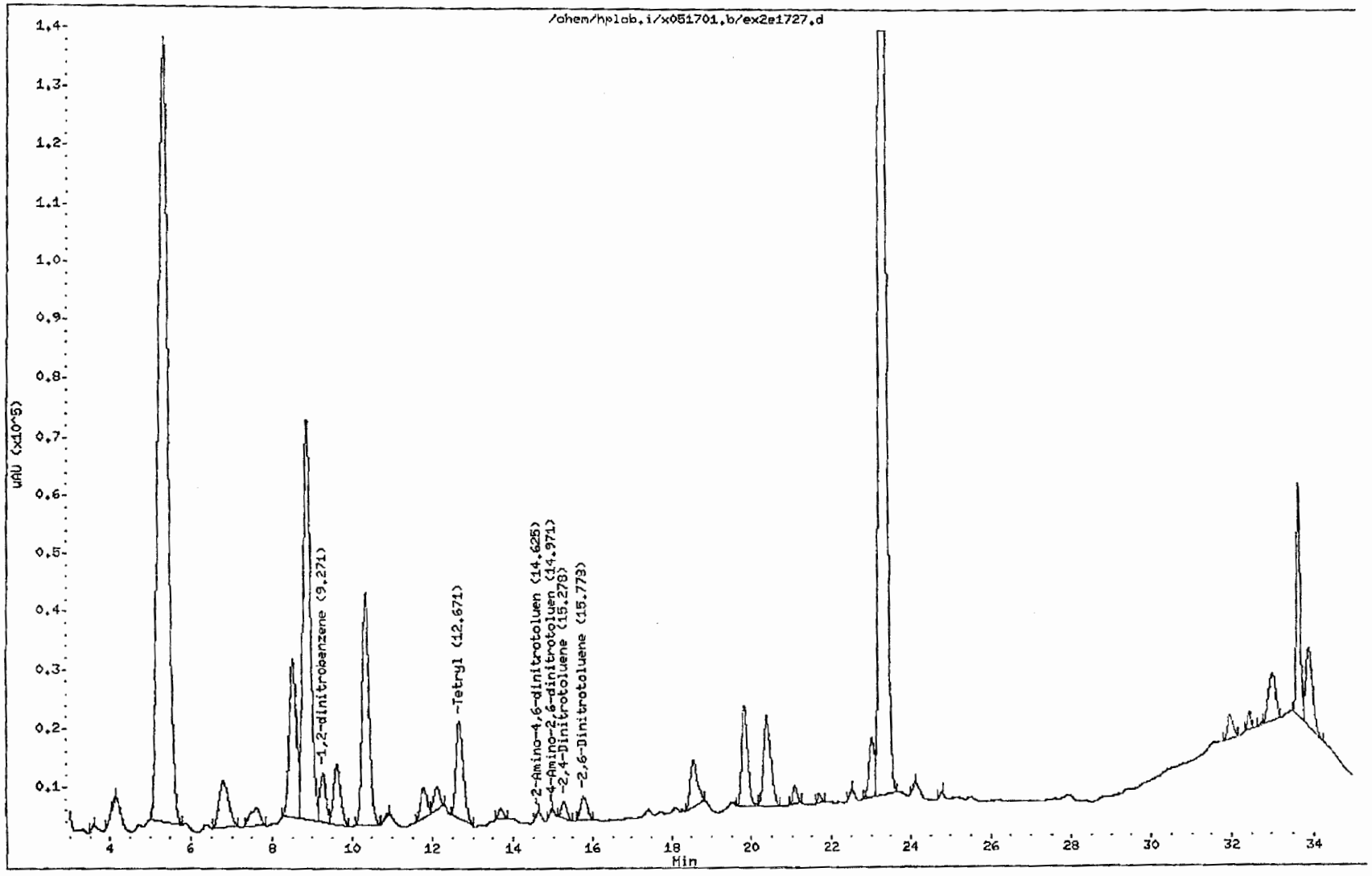


Attach. 2-1

Data File: /chem/hplcb.i/x051701.b/ex2e1727.d
Date : 18-MAY-2001 05:43
Client ID: GW15-01-0028
Sample Info: 142006004111
Volume Injected (uL): 0.1
Column phase: C18 BDS

Instrument: hplcb.i

Operator: JSP
Column diameter: 4.00

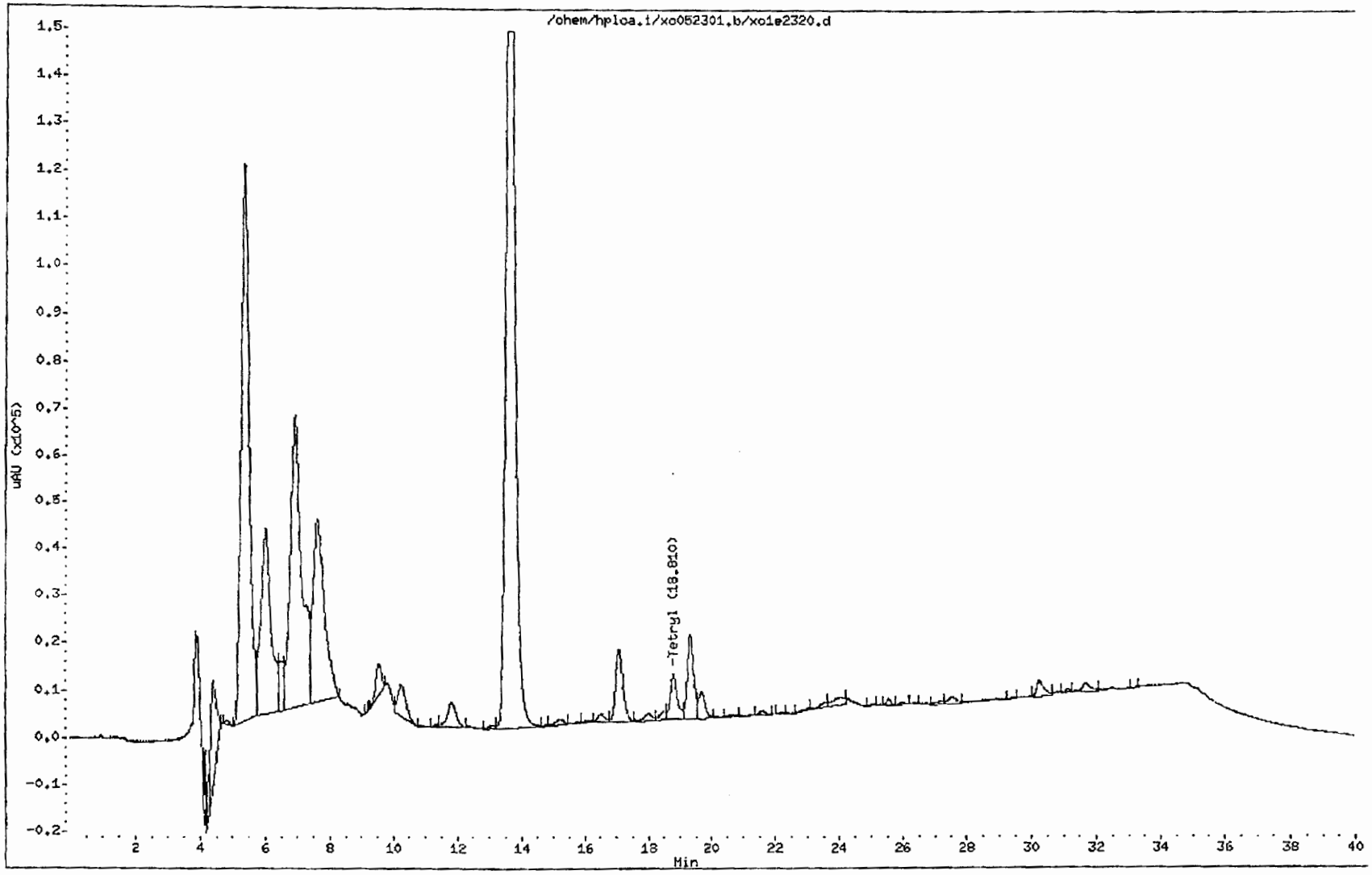


Attach. 3-1

Data File: /ohem/hploa.i/xc052301.b/xc1e2320.d
Date : 24-MAY-2001 03:07
Client ID: CW15-01-0028
Sample Info: |4200600411|
Volume Injected (uL): 0.1
Column phase: CN-UC-05

Instrument: hploa.i

Operator: JSP
Column diameter: 4.60



Attach. 3-2