UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 4
ATLANTA FEDERAL CENTER
61 FORSYTH STREET
ATLANTA, GEORGIA 30303-8960

May 11, 2011

Reverend Steve Jamison
Maranatha Faith Center
716 Waterworks Road
Columbus, Mississippi 39701

Re: Response to Data Issues and Questions Submitted by Reverend Steve Jamison By Email Dated 4/26/2011

Dear Reverend Jamison:

Please find attached a memorandum from the U. S. Environmental Protection Agency (EPA) Science and Ecosystem Support Division which addresses technical issues raised in your email dated April 26, 2011.

EPA's review of the data deliverable determined that the laboratory adequately followed the procedures outlined in the Statement of Work for analyzing the samples. If you believe the issues were not fully addressed or need further clarification, please contact me at 731 394-8996.

Sincerely,

Steve Spurlin
On-Scene Coordinator
EPA Region 4

Attachment: SESD 5/4/11 Memorandum

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION 4

Science and Ecosystem Support Division
980 College Station Road
Athens, Georgia 30605-2720

May 4, 2011

4SESD-MTSB

MEMORANDUM

SUBJECT: Tronox, Inc., SESD's Findings in Support of a Response to the Reverend Steve Jamison's Email Dated 4/26/2011, Project 11-0019

FROM: Jeffrey R. Hendel, Chemist
Quality Assurance Section

THRU: Danny France, Chief
Management and Technical Services Branch

TO: Jim Miller, Chief
Superfund Program Support Branch

On April 26, 2011, USEPA's Science and Ecosystem Support Division (SESD) was in receipt of an email from Rev. Steve Jamison requesting technical clarification about the polycyclic aromatic hydrocarbons (PAHs) data deliverables prepared by Mitkem Laboratories. As a result of the inquiry, SESD's technical staff has evaluated the raw data packages associated with the samples that were collected from the Tronox, Inc. site during October 2010. This memorandum was prepared to address the technical issues raised by Rev. Jamison.

Inquiry - "Mitkem reported that the low level SOW was utilized in the performance of the Tronox/Columbus Samples."

> EPA's Response – Yes, Mitkem Laboratories was tasked with analyzing the samples for the Tronox/Columbus site following USEPA Contract Laboratory Program, Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration, SOM01.2 (SOW), Dated May 2005, Amended April, 2007. The laboratory utilized the Low Soil by Selective Ion Monitoring (SIM) procedure for the PAHs and the Low Soil procedure for the non-PAH compounds.

Inquiry - "Standards did not support this as levels were above the 100, 200, 400, 800, 1000 ppb levels in the method procedures"

EPA's Response – For the Low Soil procedure (non-PAHs), the laboratory prepared an initial calibration for the GC/MS in accordance with Exhibit D, Semivolatiles, Section 7.2.3.5.1 of the SOW, using the calibration standards at concentrations of 5, 10, 20, 40, and 80 ng/uL. For the Low Soil by SIM procedure, the laboratory prepared the initial calibration in accordance with Section 7.2.3.5.2 of the SOW, using the calibration standards at concentrations of 0.10, 0.20, 0.40, 0.80, and 1.0 ng/uL.

From the standards used to prepare the initial calibration, the absolute nanogram (ng) amount on column of each target analyte is used to calculate a response factor, see Section 9.3.4 of the SOW. An average response factor over the entire concentration range of the initial calibration is determined and is used for calculating concentration of the target analytes in the samples, see Section 9.3.4.2 of the SOW. The standards used by the laboratory were at the correct concentrations.

Inquiry - "Primary Ions were not always used in the calculation of the samples."

EPA's Response – SESD took a random look at multiple standards contained in multiple sample delivery groups that were used for quantifying samples. It was determined that the laboratory used the primary quantitation ions (m/z) for each of the target compounds, internal standards, and deuterated monitoring compounds (DMC), except for Phenol-d_5. For the DMC Phenol-d_5, the laboratory used m/z 71 instead of m/z 99. In accordance with Section 11.2.1.5 of the SOW, secondary ion quantitation is permitted when there are interferences with the primary ion. Since Phenol-d_5 elutes close to Bis(2-chloroethyl)ether-d_8, which has a secondary ion of m/z 99, the laboratory elected to used the secondary ion m/z 71 for Phenol-d_5 for quantitation. It should be noted that the laboratory provided a discussion for the use of the secondary ion m/z 71 for Phenol-d_5 in their case narrative accompanying the sample results.

Inquiry - "The contract only specifies the NIST or Wiley or equivalent mass spec library."

EPA's Response – The SOW specifies the use of the NIST, Wiley, or equivalent mass spectral library for qualitative determination of non-target compounds, or Tentatively Identified Compounds (TICs). The laboratory used the NIST 2002 mass spectral library for determining TICs in the samples associated with this project.

The SOW specifies that for qualitative determination of target compounds, comparison of standard and sample component mass spectra, the mass spectra must be obtained from a calibration standard on the laboratory's GC/MS instrumentation and meet the daily instrument performance requirements for decafluorotriphenylphosphine (DFTPP). The laboratory used to correct procedure for identifying the target analytes for this project.

Inquiry - "If analysis was low level why was the Spk not at 170 ug/Kg?"

EPA's Response – The standards used for preparing the initial calibration are in liquid units (ng/uL), however, the sample matrix from the Tronox site are solids. For determining a theoretical solids concentration of each of the target compounds in the standards, the units would need to be converted to solids units, ug/Kg. The following calculations are used for determining the theoretical concentrations of the low level standards in ug/Kg for the Low Solids and Low Solids by SIM methods:

Low Soil Procedure:

Theoretical Conc. 166.7 ug/Kg = $\frac{5\text{ng/uL} \times 500\text{uL}*2}{30\text{gms}}$

Low Soil by SIM Procedure:

Theoretical Conc. 3.3 ug/Kg = $\frac{0.01\text{ng/uL} \times 500\text{uL}*2}{30\text{gms}}$

Where:
500 uL is final volume of the extract
2 is the GPC cleanup value
30 gms is the initial weight of the sample

The use of these equations demonstrate the theoretical concentrations of the low level standards when converting them to solid units, ug/Kg. The calculated theoretical concentrations for the low level standards are consistent with the Contract Required Quantitation Limits presented on the Table in Exhibit C, Section 2, Semivolatiles Target Compound List and Contract Required Quantitation Limits. The actual concentration of target analaytes and DMCs are calculated using the description from the first inquiry above.

Inquiry - "D65A1 Benzo(a)Pyrene – Scan with Major Ion at 264 Subtracted major ion at 69, what happened?"

EPA's Response – For sample D65A1, Benzo(a)pyrene has a retention time of 13.405 minutes. A visual inspection of the total ion chromatogram for sample D65A1 shows a large amount of interferences at the end of the sample run, to include retention time 13.405 minutes (see Figure 1). In addition, Benzo(a)pyrene's primary quantitation ion is m/z 252 and secondary ions are m/z 253 and 125. The DMC Benzo(a)pyrene-d_{12} elutes very close to native Benzo(a)pyrene and has a quantitation ion of m/z 264 and secondary ions of m/z 132 and 104 (see Figure 1).

When performing qualitative determination for target compounds by GC/MS, the analyst has two sets of tools available for use, which include retention time and mass spectra. This is one of the benefits of using GC/MS over other GC techniques. In order to use mass spectra effectively for determining the positive identification of an unknown GC peak, it is necessary to subtract background interferences for visual and automated determination. As a result of the background subtraction, the m/z 264 from the Benzo(a)pyrene-d_{12} DMC was removed, and background ions from other sources were enhanced (i.e., m/z 69) (see Figure 2). This is standard practice when using the GC/MS technique, and is primarily used for qualitative determination of a peak. For quantitative determination of Benzo(a)pyrene, the entire peak area for m/z 252 is used in calculating concentration. Section 11.1.1.4 of the SOW includes specific requirements for qualitative verification by comparison of mass spectra.

Inquiry - "Deuterated monitoring compounds do not match SOW SVOA quant signal mass."

EPA's Response – As stated above, SESD took a random look at multiple standards that were used for quantifying samples, and it was determined that the laboratory used the primary quantitation ions (m/z) for each of the target compounds, internal standards, and deuterated monitoring compounds (DMC), except for Phenol-d_5. For the DMC Phenol-d_5, the laboratory used m/z 71 instead on m/z 99. In accordance with Section 11.2.1.5 of the SOW, secondary ion quantitation is permitted when there are interferences with the primary ion. Since Phenol-d_5 elutes close to Bis(2-chloroethyl)ether-d_8, which has a secondary ion of m/z 99, the laboratory elected to used the secondary ion m/z 71 for Phenol-d_5 for quantitation. It should be noted that the laboratory provided a discussion for the use of the secondary ion m/z 71 for Phenol-d_5 in their case narrative accompanying the sample results.

Inquiry - "What happened to the 1,4-Dichlorobenzene internal standard?"

EPA's Response – SESD was not exactly sure what this concern is in reference to and what is being asked. It was assumed that the question is in reference to the "Q" qualifier identified on the sample quantitation raw data reports, and defined as "Qualifier signal failed the ratio test". The GC/MS software allows for the operator to assign custom ratio criteria for the software to compare ion (m/z) ratios for each compound (target, DMC, and internal standard). These ratios are set by the GC/MS operator and are not routinely updated since they are not used for qualitative identification in accordance with the SOW. Often times, laboratories will err on the side of false positives by allowing wide ratios and through the manual review process, eliminate non-detects.

Inquiry - "What internal Standard was used to calculate Phenol d5?"

EPA's Response – In accordance with Exhibit D Semivolatiles, Section 17, Tables/Diagrams/Flowcharts, Table 2, 1,4,-Dichlorobenzene-d_4 is used to

quantitate the concentration of Phenol-d_5. The laboratory calculated Phenol-d_5 as per the requirements of the Low Soil method. 1,4- Dichlorobenzene-d_4 is not used in the Low Soil by SIM procedure.

Inquiry - If 1,4 Dichlorobenzene d4 failed the qualifier test what was used as the replacement IS?"

EPA's Response – Since the operator of the GC/MS assigns the custom ratio criteria for the software to compare ion (m/z) ratios for each compound and the ratios are not typically updated, no action would occur for an internal standard that failed the qualifier test. Since the laboratory knows that it injected the internal standard into the sample extract and assuming that it meets the minimum and maximum ratio requirements, and elutes at the proper retention time, the laboratory would use that internal standard for quantitation. A laboratory would never use an alternative internal standard for quantitating the concentrations of target compounds.

Based on a review of the laboratory deliverable in preparation of the responses to these inquiries, it was determined that the laboratory adequately followed the procedures outlined in the Statement of Work for analyzing the samples. If Rev. Jamison's inquiries were not fully addressed or if he has any specific examples of where the laboratory did not follow the SOW, please ask that he provide specific examples along with the sample number, sample delivery group reference, and page number of the report.

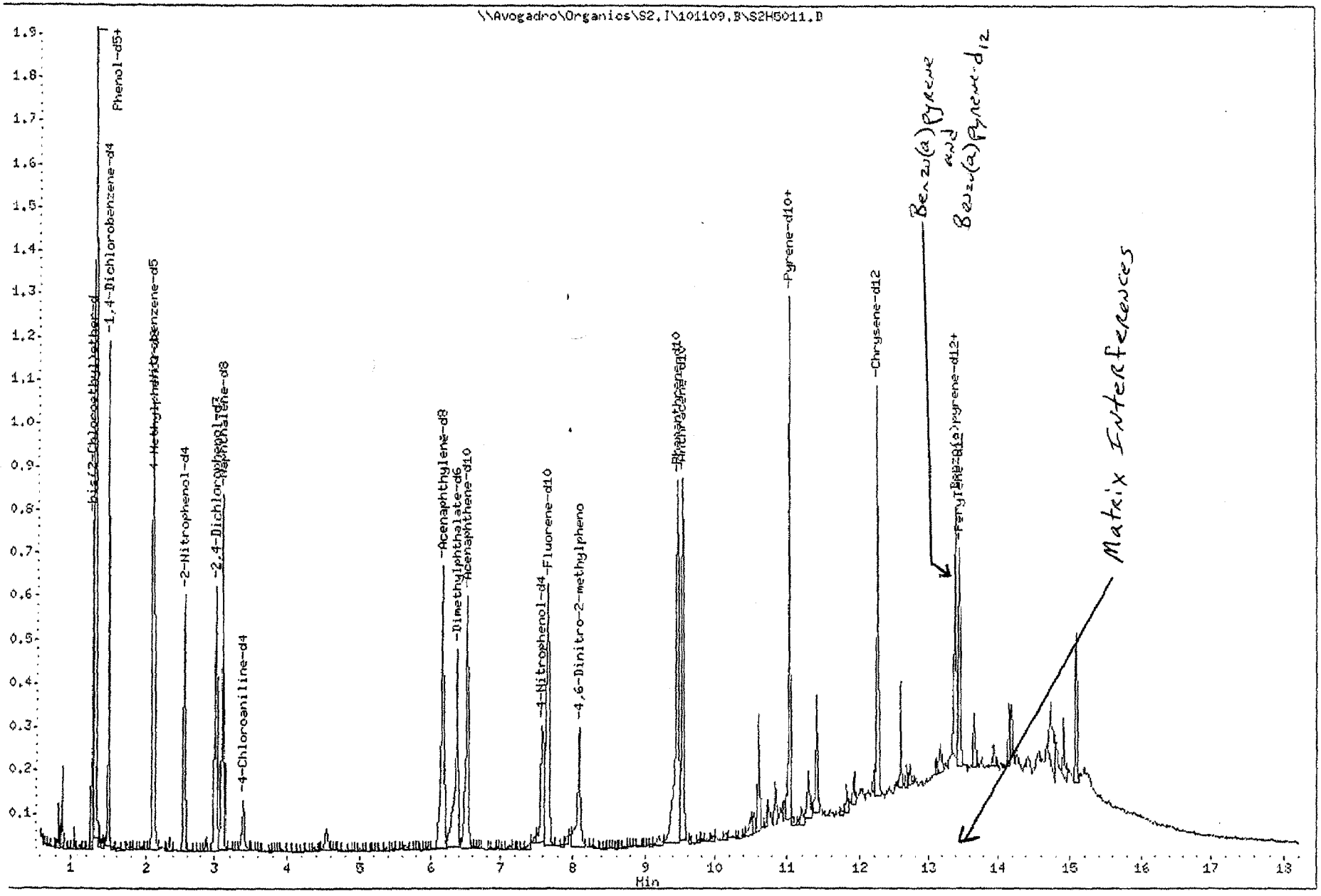
Attachment

cc: J. McGuire
G. Adams
S. Spurlin
A. Quinones
G. Bennett

Data File: \\Avogadro\Organics\S2.I\101109.B\S2H5011.D
Date : 09-NOV-2010 17:05
Client ID: D65A1
Sample Info: J2197-01A,,55277,,
Volume Injected (uL): 2.0
Column phase: RXI-5SILMS

Instrument: S2.i
Operator: MHS SRC: LIMS
Column diameter: 0.25

Figure 1



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Date : 09-NOV-2010 17:05

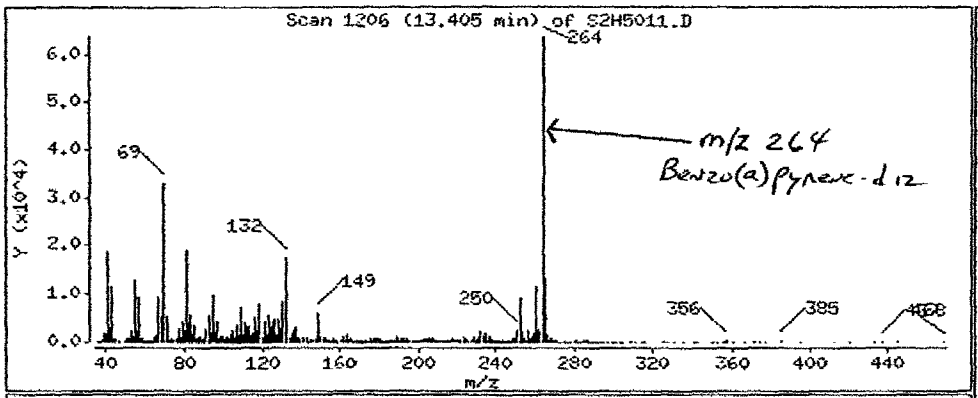
Client ID: D65A1 Instrument: S2.i

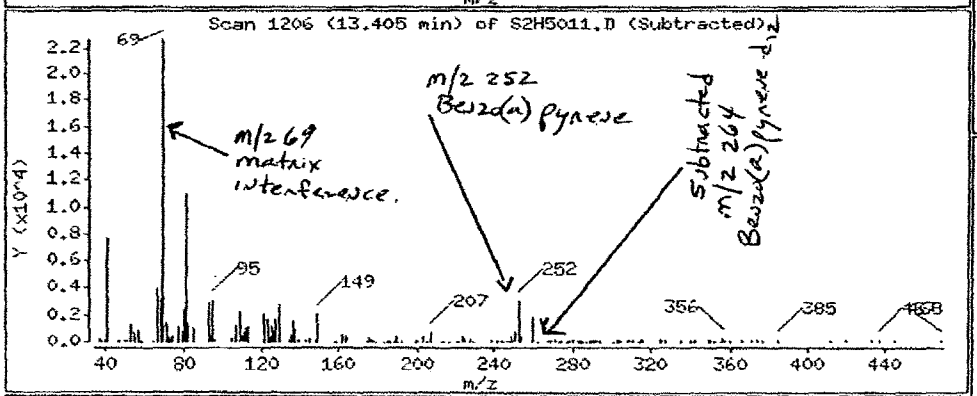
Sample Info: J2197-01A,,55277,,

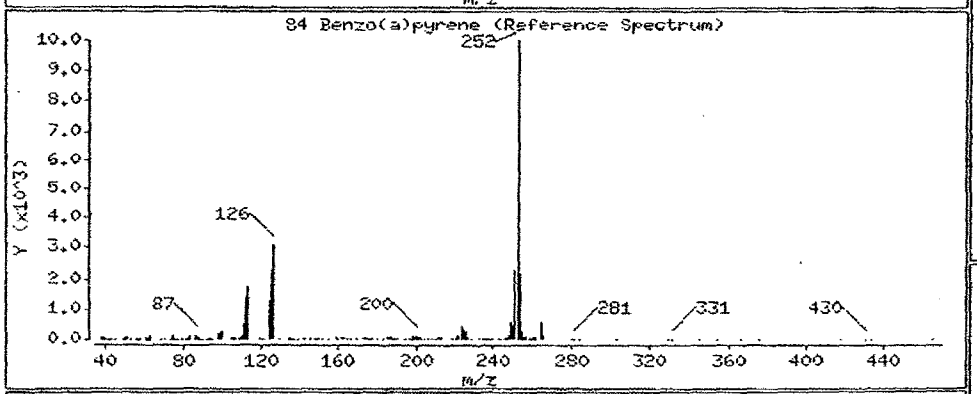
Volume Injected (uL): 2.0 Operator: MMS SRC: LIMS

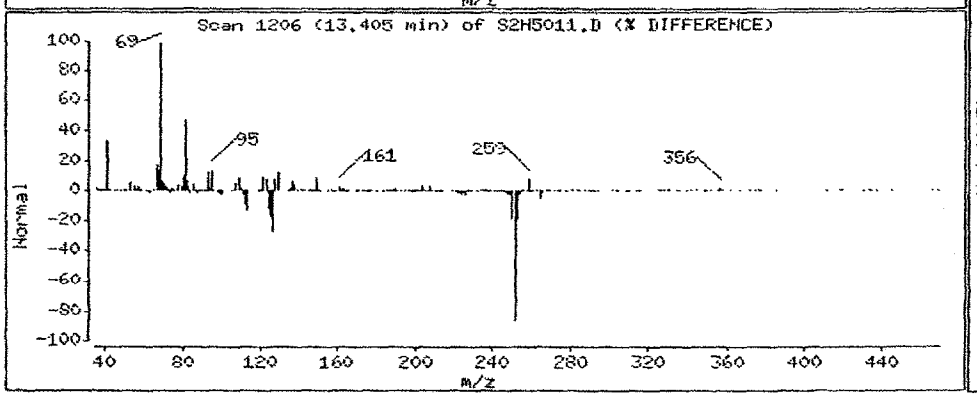
Column phase: RXI-5SILMS Column diameter: 0.25

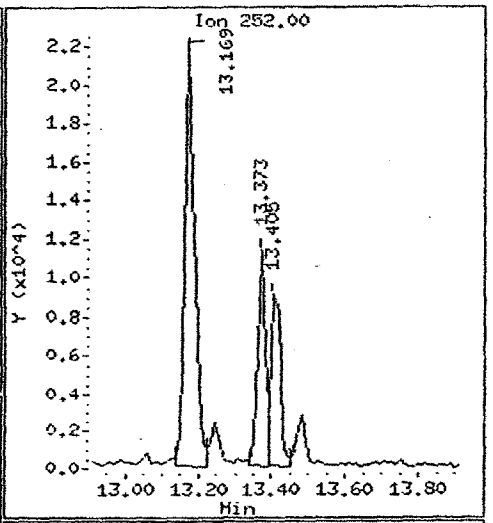
84 Benzo(a)pyrene Concentration: 66 ug/Kg

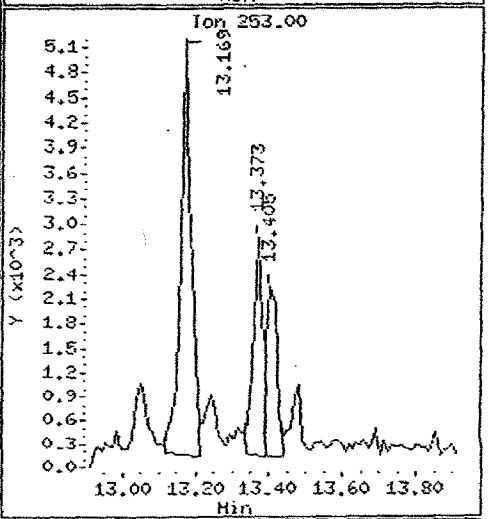












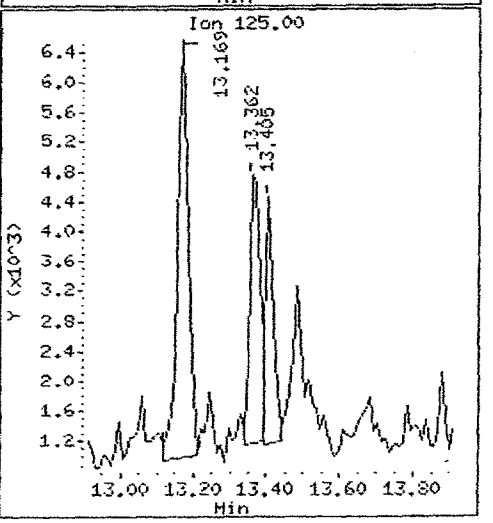


Figure 2

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