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April 20, 1993

MEMORANDUM

SUBJECT: Analytical Results of Light Nonaqueous Phase Liquid Samples. From the Rockwell International NPL Site

FROM: Kenneth W. Brown
Manager, Technology Support Center

TO: Karen Sikora
Remedial Project Manager
Region 5

Karen, As per our conversation please find attached the following documents:

- Results for the Analysis of Light Nonaqueous Phase Liquid Samples from The Rockwell International NPL Site.
- Data Packages, including raw data, for:
  Total Metals and Cyanide
  Pesticides
  Semivolatiles and Volatiles

These documents were prepared by D.Dobb, V. Ecker, N. Amick, M. Silverstein and D. Youngmen (EMSL-LV), LESAT Chemists/Scientists. The analytical work was performed by J. Jeter (SVOCs); M. Abdel-Hamid and V. King (PCBs and pesticides); D. Dobb, D. Cardenas, and P. Nowinski (TAL Metals); G. Cooper (cyanides (LAS); N. Amick (hydrocarbon screen); and Dave Youngmen (VOCs and physical testing).

Karen, I hope this information will be helpful to you and your co-workers at The Rockwell Site. If you need additional clarification of the attached documents please call me at (702)798-2270.

Attachments

cc: (w/out attachments) Phil Malley

April 16, 1993

RESULTS FOR THE ANALYSIS OF

LIGHT NONAQUEOUS PHASE LIQUID SAMPLES

FROM THE

ROCKWELL INTERNATIONAL CORPORATION NPL SITE

prepared by

Lockheed Environmental Systems & Technologies Company
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Las Vegas, Nevada 89119

for

Technology Support Center
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Las Vegas, Nevada 89193-3478

NOTICE

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ABSTRACT

Lockheed Environmental Systems & Technologies Company (LESAT) was tasked to provide special analytical services in the analysis of light nonaqueous phase liquid (LNAPL) samples collected from wells located on the Rockwell International Corporation Superfund Site in Allegan, Michigan. This work was performed at the request of US EPA Region 5 to the US EPA Environmental Monitoring Systems Laboratory, Las Vegas (EMSL-LV) Technology Support Project. The Region was interested in four primary issues: (1) determining the organic and inorganic constituents in the LNAPL samples, (2) achieving low method detection limits for the analytes in the sample matrix, (3) obtaining detailed methodologies of the sample preparation and analysis methods, and (4) having the sample handling and data generation activities documented in detail sufficient to meet litigation requirements. The analytical classes of interest were the semivolatile organic compounds, polychlorinated biphenyls, pesticides, and volatile organic compounds from the EPA Contract Laboratory Program (CLP) Target Compound List; the metals from the Target Analyte List; and cyanide.

LESAT investigated, identified, and when necessary, modified technically appropriate analytical methods that would potentially meet the data quality requirements of the Region. The results of the semivolatile compound analysis, which was performed by GC/MS, revealed that the sample contained polynuclear aromatic hydrocarbons, phthalates, dichlorobenzenes, and dibenzofuran. The GC and GC/MS methods selected to analyze for PCBs and pesticides were unable to quantitatively or qualitatively determine the presence of these analytes because of matrix interference problems. Additional analytical work may be warranted for these fractions and is specifically recommended. The results of the VOC analysis by purge-and-trap GC/MS showed the presence of xylenes. The analysis for TAL Metals, using a hydrofluoric acid and microwave digestion followed by ICP-MS analysis, yielded no "harmful" levels of metals (with the possible exception of arsenic) and also indicated a potential chemical "fingerprint," linking each sample analyzed to one point-source, based on a sample-to-sample comparison of the metals and lanthanides detected. No cyanide was detected in the LNAPL matrix, based on sample preparation by Midi Distillation followed by spectrophotometric analysis.

This summary report provides details of the study design, the methods used in sample analysis, the analytical results (including instrumental and method performance data), and the conclusions and recommendations made from the data generated and observations made during the investigation. In addition, a complete and fully documented CLP-level data package for the organic and inorganic analyses was prepared for this project in the event the results are required for litigation purposes.

ABBREVIATIONS AND ACRONYMS

CLP	Contract Laboratory Program
CRDL	contract-required detection limit
CVAA	cold vapor atomic absorption
DQO	data quality objective
ECD	electron capture detector
EMR&D	Environmental Monitoring Research and Development
EMSL-LV	Environmental Monitoring Systems Laboratory, Las Vegas
EPA	U.S. Environmental Protection Agency
FASP	Field Analytical Support Project
FID	flame ionization detection
GC	gas chromatography
GC/MS	gas chromatography/mass spectrometry
GFAA	graphite furnace atomic absorption
GPC	gel permeation chromatography
HF	hydrofluoric acid
ICP-AES	inductively coupled plasma-atomic emission spectroscopy
ICP-MS	inductively coupled plasma-mass spectrometry
ICV	initial calibration verification
LAS	Lockheed Analytical Services
LESAT	Lockheed Environmental Systems & Technologies Company
LNAPL	light nonaqueous phase liquid
MDL	method detection limit
m/z	mass-to-charge ratio
NPL	National Priorities List
PCB	polychlorinated biphenyl
PNA	polynuclear aromatics
PRP	potentially responsible party
QA	quality assurance
QAPjP	quality assurance project plan
QC	quality control
QTM	Quick Turnaround Method
ppb	parts per billion
ppm	parts per million
RCRA	Resource Conservation and Recovery Act
RI/FS	remedial investigation/feasibility study
rpm	revolutions per minute
RPM	Remedial Project Manager
RT	retention time
SOW	Statement of Work
SPE	solid phase adsorbent extraction
SVOC	semivolatile organic compound
TAL	Target Analyte List

TCL	Target Compound List
TCLP	Toxicity Characteristic Leaching Procedure
TIC	tentatively identified compound
TSP	Technology Support Project
VOC	volatile organic compound
WAM	Work Assignment Manager

ACKNOWLEDGEMENTS

The preparation of this document required the collaborative effort of many individuals from a number of organizations. The following individuals were instrumental in the project design, the analysis of the samples, preparation of data reports, and preparation of this document:

D. Youngman, J. Jeter, M. Abdel-Hamid, V. King, J. Donnelly, N. Amick, J. Kilduff, P. Nowinski, D. Dobb, D. Cardenas, D. Hillman, G. Cooper, J. Parolini, V. Ecker, M. Silverstein, P. Malley, and R. Plumb, Lockheed Environmental Systems and Technologies Company; G. Robertson and K. Brown, Environmental Monitoring Systems Laboratory, Las Vegas; and K. Sikora and A. Alwan, EPA Region 5.

SECTION 1

PROJECT DESCRIPTION

Under the Environmental Monitoring Research and Development (EMR&D) Contract to the US EPA Environmental Monitoring Systems Laboratory in Las Vegas (EMSL-LV), Lockheed Environmental Systems & Technologies Company (LESAT) was tasked to provide special analytical services in support of EMSL-LV's Technical Support Project (TSP) for EPA Region 5. This support included multiple activities relevant to the analysis of light nonaqueous phase liquids (LNAPLs) collected from the Rockwell International Corporation National Priorities List (NPL) Site for all analytes contained in the Contract Laboratory Program (CLP) organic and inorganic Statements of Work (SOWs). Standard EPA methods appropriate for the analysis of low concentrations of the analytes of interest in common oil matrices (e.g., transformer oil) were not applicable, due to the nature of the LNAPL samples collected at this site. Consequently, specialized procedures were identified or standard methods modified and optimized for use with a mixture of water-soluble and petroleum-based products found on this site (Anon., 1993), and their performance characterized prior to and in conjunction with sample analysis. All phases of the sample preparation and analysis activities conducted by LESAT were completely documented in order to provide technically and legally sound data indicating the composition and concentrations of contaminants in the LNAPL samples.

1.1 ROCKWELL INTERNATIONAL NPL SITE BACKGROUND

The Rockwell International Corporation NPL Site (Rockwell Site) is located adjacent to the Kalamazoo River in Allegan, Michigan (Figures 1a and 1b). Operations at this site (until closure in July 1992) included machining, hardening, and assembly of drive-line components for large vehicles. Various petroleum-based cutting and quench oils, water-soluble cutting oils, and cleaning compounds were employed in the manufacturing operations. Waste disposal at the site included settling ponds, an oil flotation house, and waste water treatment plant lagoons. In the course of measuring static water levels during the second phase of site characterization field work, LNAPLs were detected in eight piezometers and monitoring or recovery wells. Three locations (PZ-17, MW-10, and RW-3) were selected by the EPA and the site's potentially responsible party (PRP) for sampling based on the thickness of the LNAPL layer present, the proximity of the well/piezometer to possible LNAPL sources, and other technical considerations discussed in the site's Supplement to the Work Plan Addendum (Anon., 1993) and Revised Quality Assurance Project Plan (QAPjP) Addendum (Remcor, Inc., 1993). These sample locations are shown in Figure 1b.

1.2 PROJECT OBJECTIVES AND PRODUCTS

The project objectives and consequent data quality objectives (DQOs) were based on the technical support letter of request from the Region 5 Remedial Project Manager (RPM) (Appendix A), the information contained in Supplement to the Former Rockwell International Corporation (Rockwell) Facility Work Plan Addendum (Anon., 1993) and the Revised Rockwell RI/FS QAPjP Addendum (Remcor, Inc., 1993), and communications with the EMSL-LV TSP Work Assignment Manager (WAM), the RPM, and a representative of the Region 5 QA Staff. The primary use of the data from the analysis of the LNAPL samples, as identified in Remcor, Inc. (1993), is as supplemental information for the RI/FS. More specific objectives for data use include the identification of the

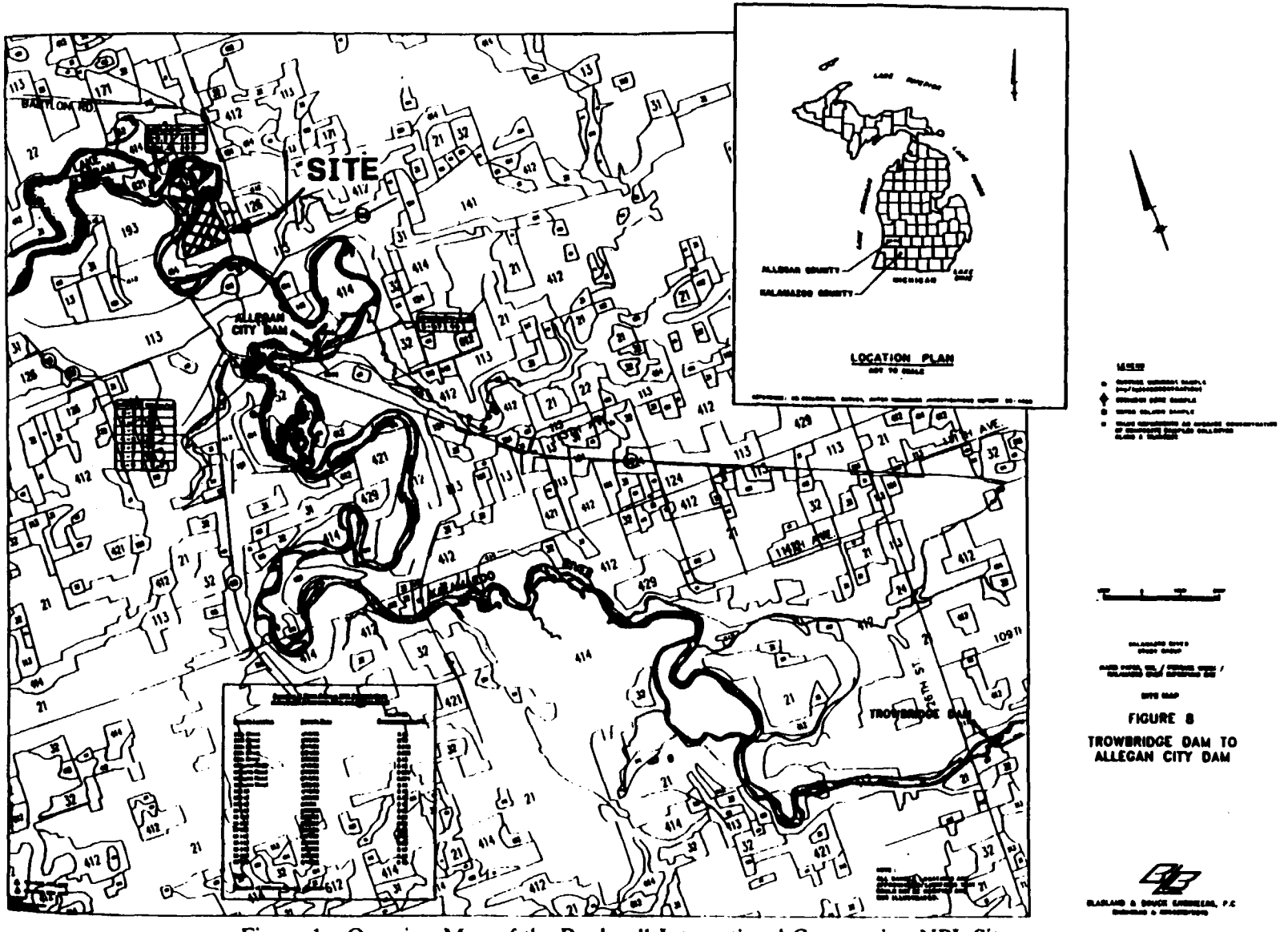


Figure 1a. Overview Map of the Rockwell International Corporation NPL Site.

(Source: Blasland & Bouck Engineers, P.C.)

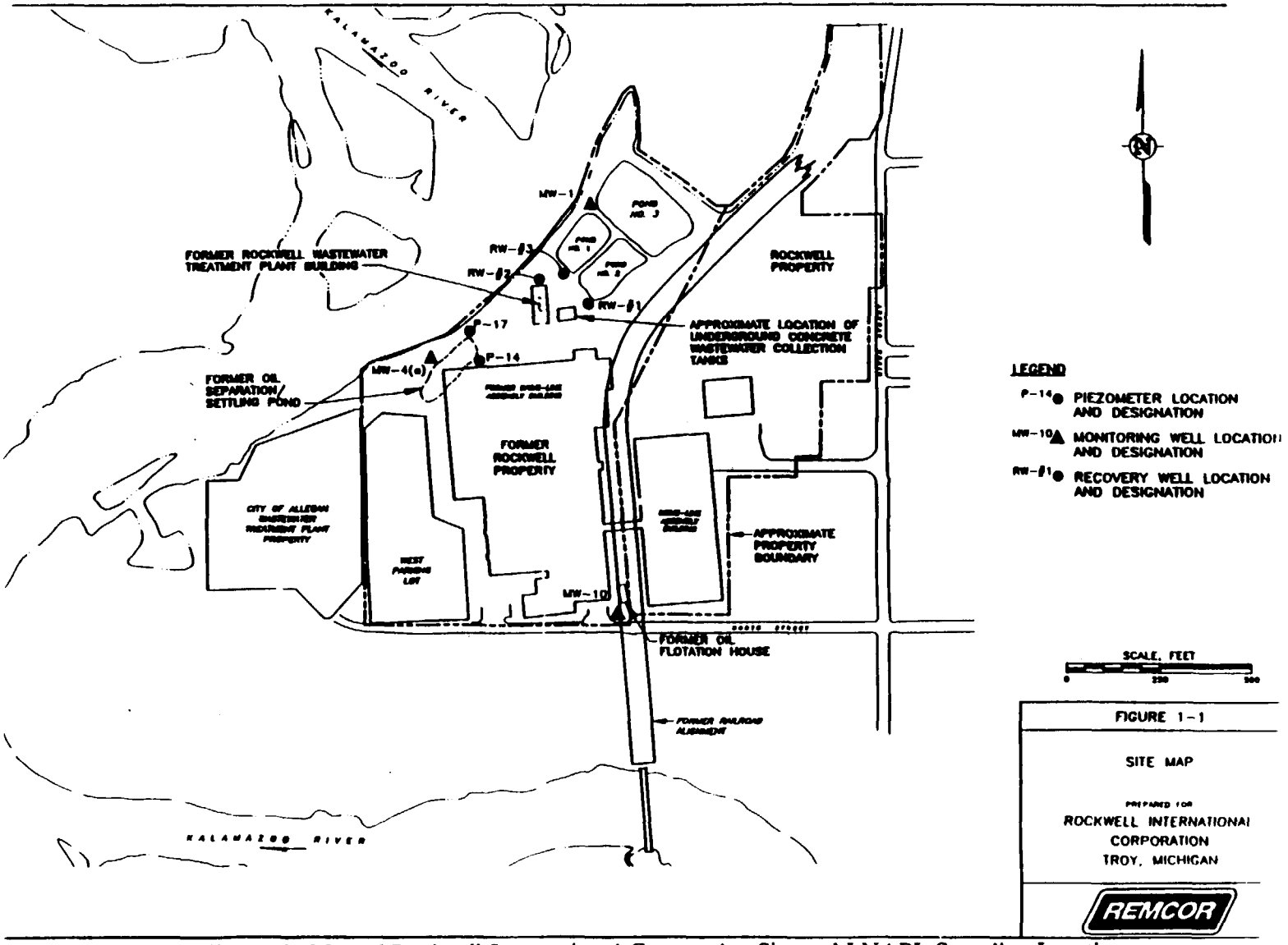


Figure 1b. Map of Rockwell International Corporation Site and LNAPL Sampling Locations.

(Source: Remcor, Inc.)

source(s) of the LNAPLs and the potential impact of their presence on site conditions. The primary objective of this project, as assigned to LESAT, was to perform and document the analysis of the LNAPLs for the designated volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), pesticides, polychlorinated biphenyls (PCBs), inorganic compounds (as total metals) and cyanide, using methods which were appropriate for the sample matrix. The organic compounds of interest were those on the Target Compound List (TCL) and the metals of interest were those on the Target Analyte List (TAL). The analytical priorities specified by Region 5 (Appendix A) were, from highest to lowest priority:

1. SVOCs
2. PCBs/Pesticides
3. VOCs
4. Inorganic Compounds (TAL Metals)
5. Cyanide

As described in guidance documents addressing the comparison of analytical procedures (e.g., EPA, 1988a), successful implementation of a project such as this one includes documenting the operational details of the methods, providing single laboratory performance data where this is feasible given the available matrix, and ensuring that the method can be used by at least one other laboratory. The specific products of this project are (1) a CLP-level data package documenting the LNAPL sample analysis results and associated quality control (QC) data, including instrument and method detection limits, (2) a case narrative documenting the observations made by the chemists and technicians during sample preparation and analysis, (3) detailed method write-ups stating exactly how the samples were prepared and analyzed, including instrument operating parameters, so that other laboratories can duplicate the analysis process, (4) complete raw data and sample tracking documentation for instances when such information is required in litigation, (5) a QAPjP and complementary audit report, and (6) this summary report, providing the overall processes by which the samples were analyzed and a summary of the results, conclusions, and recommendations.

1.3 PROJECT QUALITY ASSURANCE OVERVIEW

In light of the fact that the LNAPL samples originated from an NPL site, and the potential exists for the data generated during the project to be used in an enforcement action, a Category I QAPjP (EPA, 1991) was prepared (Appendix B). The DQOs specified in the Revised QAPjP Addendum (Remcor, Inc., 1993) include Level III analyses for pesticide/PCBs and Level IV analyses for all other contaminant classes. However, it was determined that it was more appropriate to apply Level V analyses to the LNAPL samples due to the potentially complex matrices and the unavailability of standard methods for this matrix (EPA, 1988b). DQOs for the LESAT analyses are provided in Table 1 of Appendix B.

In order to provide data which were of defined quality, project activities must include determinations of method precision, accuracy, and detection limits when applied to these matrices. The attainment and documentation of detection limits more sensitive than 1200 μg/Kg for VOCs and 10,000 μg/Kg for SVOCs were of particular interest to Region 5 (Appendix A). Consequently, an important aspect as well as a limiting factor involved in the selection of methods for the analysis of the LNAPLs was the need to achieve low method detection limits (MDLs).

To determine reasonable estimates of MDLs for the LNAPLs (i.e., method/matrix detection limits), laboratory investigators had to first obtain or concoct a matrix which was physically and chemically consistent with the actual LNAPL samples for performing MDL studies. Based upon preliminary physical characterization (sections 3.1 and 3.2) of the sample matrix, it was projected that a light-weight commercial motor oil (Pennzoil® 5W-30) would be a comparable matrix. The motor oil was then spiked with low levels of organic constituents appropriate to the analytical methods under investigation. QC samples employed in this study included VOC trip and holding blanks, matrix spikes, method/reagent blanks, and calibration check samples. In addition, a field duplicate from well RW-03 was collected by the field samplers; however, since laboratory performance was considered most crucial, this sample was not utilized as a field duplicate, except in the case of the VOC analysis (Section 3.6).

As a part of QA oversight, LESAT conducted an internal on-site laboratory inspection which verified sample custody procedures and assessed the proper execution of the QAPjP. The results of the audit were documented in a formal audit report (Appendix C).

1.4 PROJECT SCHEDULE

The LNAPL samples were collected on February 18, 1993, shipped via overnight courier, and received by LESAT on February 19. The LESAT Technical Work Plan was approved by EMSL-LV on February 24. The analytical and data generation and reporting activities continued through the month of March 1993.

The holding times for each analytical fraction is given in the site's RI/FS Revised QAPjP Addendum (Remcor, Inc., 1993). While every effort was made to perform the sample preparations and analyses within the specified time limitations, the Region 5 RPM and QA representative indicated that, with the exception of the VOC analyses, the impact of exceeding the holding times would be less severe than the failure to provide analyses which would meet MDL and documentation requirements.

1.5 SAMPLE COLLECTION AND SHIPMENT

As documented in Remcor, Inc. (1993), the LNAPL samples were required to be collected from each well as follows: an oil/water interface probe measured the depth to the LNAPL surface; a sampling tube marked to the measured LNAPL depth was lowered into the LNAPL layer, at which time pumping commenced. When possible, sufficient sample to fill all sample bottle volumes were to be collected and all samples were immediately placed in shipping coolers at 4 °C for shipment to LESAT. The sample bottles were filled in the following order: TCL organics (VOCs, SVOCs, pesticides/PCBs), filling as many of six 40-mL glass vials as possible (approximately two per analysis class); inorganics (TAL metals, cyanide), filling two 4-ounce glass bottles (with Teflon-lined screw caps) with any remaining LNAPL sample. Since SVOCs were identified as the class of analytes with the highest priority for this project, success in achieving the project goals for all the analysis classes was highly dependent upon the quantity of sample available for method performance determinations. The samples actually collected and the numbers of bottles and volume collected are presented in Table 1. Because of the need for strict chain of custody, the condition and description of the samples was noted upon receipt on the Remcor Chain-Of-Custody forms (see Appendix B) which were kept by LESAT in a locked file cabinet. The samples, extract, and digestates were then kept in locked refrigerators or cabinets (as appropriate) prior to and throughout sample analysis.

TABLE 1. LNAPL SAMPLES COLLECTED FROM THE ROCKWELL INTERNATIONAL SITE FOR ORGANIC AND INORGANIC ANALYSIS.

SAMPLE ID	SAMPLE LOCATION	SAMPLE TYPE	SAMPLE BOTTLE (number/volume)	ANALYSIS REQUESTED
RAM-RW-03-0-0293	RW-3 (recovery well)	routine LNAPL sample	six 40-mL vials	organics
			two 4-oz jars	metals/cyanide
RAM-RW-03-0-0293D[a]	RW-3 (recovery well)	duplicate RW-3 LNAPL sample	six 40-mL vials	organics
			two 4-oz jars	metals/cyanide
RAM-MW-10-0-0293[b]	MW-10 (monitoring well)	routine LNAPL sample	five 40-mL vials	organics
RAM-PZ-17-0-0293[b]	PZ-17 (piezometer)	routine LNAPL sample	six 40-mL vials	organics
			two 4-oz jars	metals/cyanide[c]
RAM-TB-04-0293	NA	aqueous trip blank	three 40-mL vials	VOCs

[a] Although this sample was collected as a field duplicate, it was used as extra volume of the routine sample in the laboratory, with the exception of VOC analyses.

[b] These samples contained very little LNAPL; at least 90% of each sample was groundwater (visual observation).

[c] Due to the limited volume of LNAPL in the sample, cyanide analysis was not performed.

SECTION 2

STUDY DESIGN AND METHODS DESCRIPTIONS

As stated in Section 1, the analysis classes of interest for this project were the TCL organic compounds (SVOCs, PCBs, pesticides, and VOCs), the TAL metals, and cyanide, and, in the event that there was limited LNAPL sample volume, the analyses were to be conducted in the above order of analysis class or fraction. Therefore, the first step in the analytical process was to determine the sample volume available for each of the three LNAPL samples. Of the three samples only one, RW-03, contained a sufficient LNAPL volume to perform all the required analyses as well as any other supportive analyses (i.e., physical tests, hydrocarbon screen, test kit for organic chloride). The other two samples contained very small volumes of LNAPL (see Table 1) and were treated much more conservatively with respect to the prioritized order of analysis by fraction/analysis class. Once the sample volumes were determined, the samples were analyzed as depicted in Figure 2.

A minimal amount of the LNAPL matrix from RW-03 was allocated for physical testing and gas chromatographic (GC) screening in order to determine the matrix characteristics. These tests were performed primarily to assist in the organic analytical processes. Specifically, the purpose was two-fold: to provide initial information on how the sample would respond to typical sample preparation techniques (e.g., solvent extractions) and to facilitate the identification or concoction of a suitable material to simulate the LNAPL matrix in method performance testing (e.g., determining method detection limits). The remainder of the sample was reserved for sample preparation and analysis for the analytes of interest to the Region. In conjunction with matrix screening, candidate solvents were assessed for use in preparation/extraction of samples for analysis of SVOCs, PCBs, pesticides, and VOCs. After the physical testing and hydrocarbon screen was completed, the LNAPL samples were subjected to a battery of analyses for SVOCs by gas chromatography/mass spectrometry (GC/MS), for PCBs and pesticides by GC and by GC/MS, for VOCs by GC/MS, for TAL Metals by inductively coupled plasma-mass spectrometry (ICP-MS), and for cyanides by Midi distillation/spectrophotometry. Descriptions of each method follow. In instances where either nonstandard methods were used or standard methods were modified, detailed protocols have been provided in appendices or attachments to this report. The analytical work performed during this project was conducted by the LESAT Environmental Services Division staff under the EMR&D Contract, with the exception of the cyanide analysis, which was subcontracted to the Lockheed Analytical Services Laboratory (LAS).

2.1 PHYSICAL TESTING

Several tests were performed to determine the physical characteristics of the LNAPL matrices in order to minimize potential analysis problems and as an aid in selecting protocols that might be suitable for dilution or extraction of the matrix for organic analyses. These tests included sample miscibility with water and solvents, vortex emulsification, and centrifugation. Two grams of the oil matrix were added to each of six (conical-shaped) glass centrifuge tubes and an equal volume (2 mL) of the following solvents were added: (1) water, (2) methanol, (3) methylene chloride, (4) hexane, (5) acetone, and (6) toluene. The contents of the tubes were observed to note any physical characteristics (miscibility, density) which could be relevant to the analysis for SVOCs, PCBs, pesticides, and VOCs. The LNAPL/solvent mixtures were then processed using a Vortex mixer at half speed for a period of 15

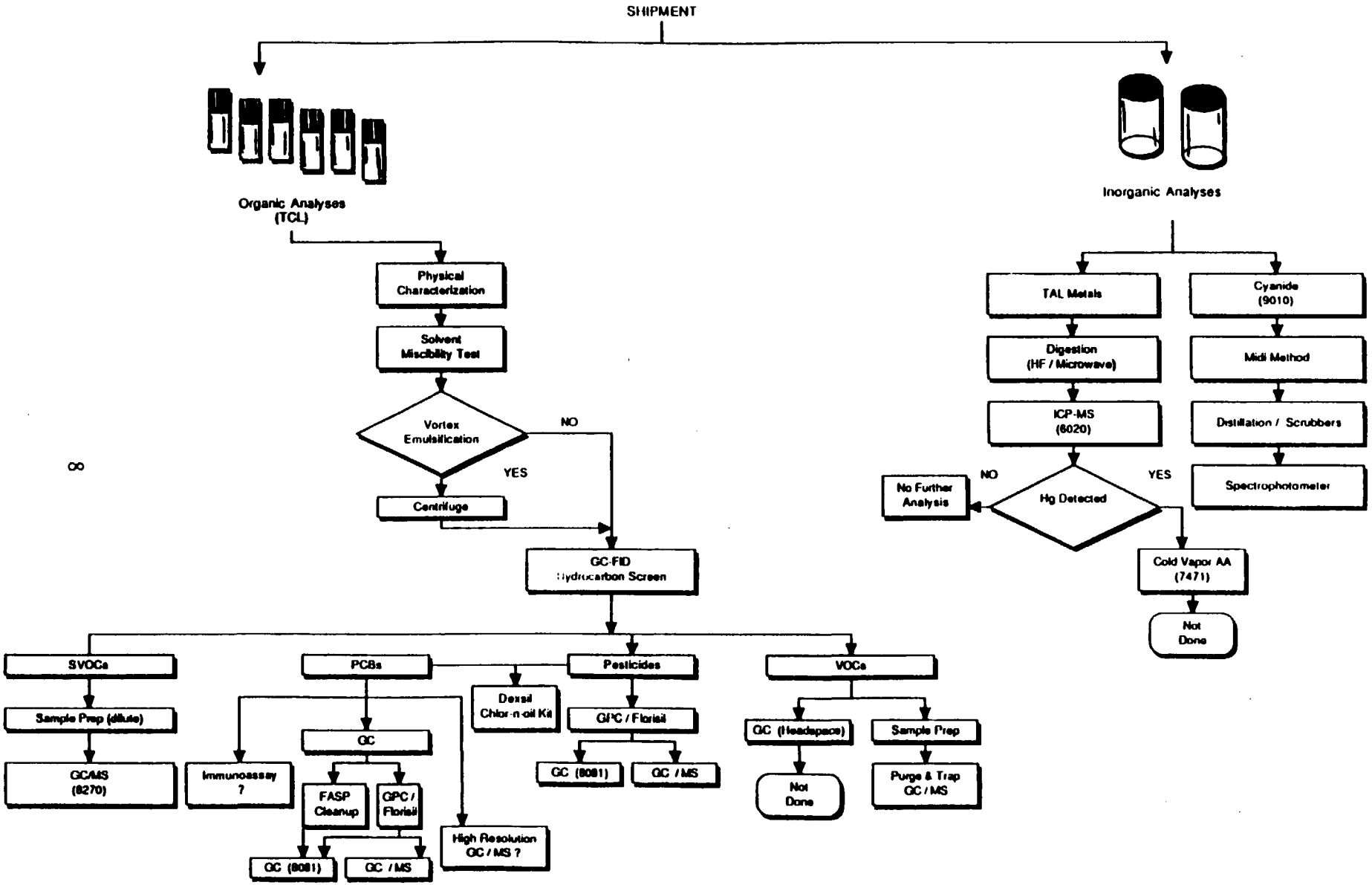


Figure 2. Schematic for analysis of organic and inorganic constituents in LNAPL samples. (? indicates method use is under consideration)

seconds and the physical characteristics were noted. The mixtures were then centrifuged in a Baxter Megafuge for 2.0 minutes at 2000 revolutions per minute (rpm) and the resulting characteristics observed and recorded. Section 3.1 presents the results of these tests.

2.2 HYDROCARBON SCREENING

Gas chromatographic (GC) screening (with flame ionization detection [FID]) of the LNAPLs was used to determine the approximate boiling points of the sample components. Separation of components by boiling point can be achieved with chromatography using a non-polar column. Thus, the variety and type of hydrocarbons present in the oil sample can be obtained using this method. By comparing the chromatogram of the sample with chromatograms of known substances, the nature of the oil can be inferred.

The GC screening was based on analyte separation procedures specified in SW-846 (EPA, 1986) Method 8015 for the analysis of VOCs. Sample RW-03 was diluted in methylene chloride and injected directly onto a capillary chromatography column (30m RTX-5, 0.53 mm ID) with 40 °C to 290 °C temperature programming. Serial dilutions (1:10, 1:100, etc.) in methylene chloride were made to achieve analyte responses approximately 50% of full scale. The nature and boiling point range of the LNAPL matrices was determined (Section 3.2) through comparison of the straight-chain hydrocarbon peak retention times (RTs) with those of a mixed alkane standard. Although the standard solution was prepared at a specific concentration range (80 to 100 μg/mL), compound quantitation was not performed on the basis of these analyses. The single-level standard was injected several times to verify instrument stability, and the RTs of the various alkanes were used to help characterize the unknown sample. Operational parameters, calibration specifications and sample preparation for this LNAPL hydrocarbon screening technique are provided in Appendix D.

2.3 SEMIVOLATILE ORGANIC COMPOUNDS

Semivolatiles sample preparation was accomplished using RCRA SW-846 Method 3580 (waste dilution). Samples were diluted 1.0 g into 10 mL methylene chloride. Samples were analyzed by gas chromatography/mass spectrometry using the US EPA 3/90 CLP SOW.

Standards and samples were run for semivolatiles during the period from 2/22/93 through 3/23/93. In addition to the analysis of the three LNAPL samples (RW-03, MW-10, PZ-17), a matrix spike and matrix spike duplicate at the 50 ppm level was analyzed on sample RW-03. The spiking solution contained all TCL SVOCs (at levels that resulted in a final concentration of 50 μg/g in the sample). These analyses were used to calculate recovery data. Matrix spikes and matrix spike duplicates were not run on samples MW-10 and PZ-17 due to the limited amounts of sample provided. A method detection limit study, which encompassed seven injections of Pennzoil® 5W-30 motor oil spiked at the 5 ppm (5 μg/g) level, was also conducted. MDLs were determined using the formula supplied in the QAPjP (Appendix B). The results of sample analyses, instrument detection limits, method detection limits and analyte recoveries are provided in Section 3.3 and Appendix E. GC/MS instrumental operating parameters for the SVOC analysis are provided in Appendix F.

2.4 POLYCHLORINATED BIPHENYLS

Four approaches to determine the concentration of PCBs in the LNAPL matrix were attempted, three

of which involved GC analysis with an electron capture detector (ECD) and a fourth employed a GC/MS. The three GC analytical schemes included analysis by Method 8081; the differences resided in the sample preparation procedures. An initial analysis of the LNAPL which was subjected to florisil chromatography cleanup (both undiluted and diluted 1:10 in hexane) of sample RW-03 was analyzed by GC. The second sample preparation procedure was based upon the Field Analytical Support Project (FASP) method of extraction, designed to determine aroclors in transformer oil. This sample preparation technique uses sulfuric acid treatment followed by a florisil chromatography cleanup and then analysis by GC. The third sample preparation scheme involved a gel permeation chromatography (GPC) cleanup step (Method 3640) of a 1:100 dilution of sample RW-03 in methylene chloride followed by florisil cleanup and a 1:10 dilution in hexane, followed by GC analysis. This extract was also analyzed by GC after being spiked with Aroclor 1254. The RW-03 sample that was GPC/florisil prepared was also analyzed by GC/MS.

In addition, the Dexsil Corporation's Chlor-N-Oil• kit for measuring total organic chloride in oil matrices was utilized to assess the level of organic chloride at the 50 ppm level. Appendix G provides the Dexsil Corporation's literature on this method.

Because the analysis of PCBs in the LNAPL samples proved difficult to measure (i.e., interferents prohibited peak identification, see Section 3.4) various contingencies were considered; however, they were not carried out due to time constraints on the project. One alternative considered is analysis by high resolution GC/MS. Another alternative is to have the matrix analyzed by a newly developed immunoassay technique (EnSys, Inc., Morrisville, NC) designed to analyze for PCBs in oil matrices. The immunoassay procedure only provides semiquantitative determination and will not identify specific aroclors. However, it will potentially determine if PCBs are present in the LNAPL matrix to approximately a 5 ppm detection limit (Personal communication, Dr. J. Mapes, EnSys, Inc.).

Section 3.4 presents the results of the PCBs analysis. Appendix H provides the GC instrumental operating parameters for the PCB analysis and the FASP extraction method used in this project.

2.5 PESTICIDES

The methods used for pesticides analysis were similar to the methods used for PCBs (Section 2.4). The only aspects of the analyses scheme for PCBs not directly applicable to pesticides determinations are the sulfuric acid cleanup step used in the FASP method (as sulfuric acid typically degrades pesticides when added to the sample) and the aroclor addition step employed after GPC/florisil treatments.

Section 3.5 provides the details on the results of the analysis for pesticides and Appendix H provides the GC instrumental operating parameters used in this project for the pesticides (and PCB) analysis.

2.6 VOLATILE ORGANIC COMPOUNDS

Two methods were investigated for use in the analysis of the LNAPLs for volatile organic compounds: the Quick Turnaround Method (QTM) by GC (EPA, 1993) and the CLP Multi-media, Multi-concentration Statement of Work (SOW) purge-and-trap GC/MS method (EPA, 1990). Because of instrumentation problems, only the purge-and-trap sample introduction/analytical technique was used in this project. The operating parameters for the VOC GC/MS analyses are provided in Appendix I.

VOC sample preparation was accomplished using a modified version of the QTM for the determination of volatiles in an oil matrix. Samples were extracted with purge-and-trap grade methanol (Appendix J). An aliquot of the extract was injected into reagent grade water and the sample introduced into the GC/MS via purge and trap as per the CLP 3/90 medium soil protocol. The associated VOC holding and trip blanks were analyzed using the US EPA CLP 3/90 low water protocol.

Standards and samples were run during a period from 2/23/93 through 3/4/93. Due to the limited amount of matrix available, the LNAPL sample from well RW-03 was the only sample analyzed. In addition to the RW-03 sample, a matrix and matrix spike on sample RW-03 and holding and trip water blanks were also analyzed. Instrument detection limits, method detection limits and sample recovery and precision data were determined during this time period. The results of sample analyses and applicable QC and method performance data are discussed in Section 3.6 and Appendix K.

2.7 TAL METALS

The techniques used for TAL Metals analysis of the LNAPL samples included draft or proposed EPA methods or protocols for the sample preparation and the ICP-MS analytical methods. The sample preparation and analysis methods used were considered by LESAT to represent the best available technology for analyzing oil matrix samples for metals. Sample preparation utilized a draft hydrofluoric acid (HF) microwave digestion method (developed by LESAT) being considered for adoption in the EPA CLP High Concentration SOW IHCO1.0 for oils, soils, and sludges. The HF microwave digestion method has been found to give excellent results when applied to oil and oil-containing soil samples (Suarez et. al, 1993; Appendix L). The method ensures total decomposition of the sample matrix, thereby providing the means of acquiring true total metals results. Unlike fusion methods, dissolved solids in the microwave-digested samples are tolerable by any analytical method. It should be noted that if this method is utilized, some problems with analyte carryover have been observed. Microwave vessel porosity and large surface area demand scrupulous cleaning and dedication of a set of vessels for digesting low level samples.

Analysis of the digested samples was accomplished by using ICP-MS Method 6020 CLP-M Version 8.1 which is included in the draft EPA CLP Low Concentration ILCO1.0 SOW (Appendix M). The main advantage of ICP-MS is the ability to analyze for all of the TAL analytes with one instrument, as opposed to conventional ICP-atomic emission spectroscopy (-AES), graphite furnace atomic absorption (GFAA), and cold vapor atomic absorption (CVAA). By employing the ICP-MS technology, major and trace metals can be analyzed within the same analysis batch without dilution and fewer analytical runs are required, resulting in shorter, more comprehensive data packages. ICP-MS also affords the advantage of screening for all other non-TAL analytes in the same analytical run. This allows for the identification of potentially hazardous elements that may be in a sample but are not normally analyzed for (i.e., targeted). In addition, ICP-MS also provides relative freedom from interferences which significantly reduces the occurrence of false-positives. All of these advantages were applicable to this case.

TAL Metals analyses were performed on two LNAPL samples (PZ-17 and RW-03) from the Rockwell Site. The sample preparation and analysis was performed from 2/25/93 to 3/09/93. The results are presented in Section 3.7.

2.8 TOTAL CYANIDE ANALYSIS BY MIDI DISTILLATION

The LNAPL sample matrix was analyzed for total cyanide using the Midi distillation protocol (CLP Method 335.2, Exhibit D) followed by Method 9010, Total Amenable Cyanide (Colorimetric, Automated UV).

Because of the limited volume of sample, only the LNAPL from RW-03 was analyzed, the results of which are presented in Section 3.8. The analysis was performed on 2/26/93 by Lockheed Analytical Services (LAS).

SECTION 3

ANALYTICAL RESULTS, CONCLUSIONS, AND RECOMMENDATIONS

This section provides detailed discussions of the results of the analyses performed on the LNAPL samples presented by analysis class. It also includes the significant conclusions drawn from those results, supporting information on the performance of the methods employed, and, when applicable, recommendations for potential additional analyses to further characterize the constituents of the LNAPL matrix.

Table 2 provides an overview of the analysis of the LNAPL samples and associated findings, highlights of which are discussed below by analytical fraction. The physical testing provided useful information in the selection of the most effective extraction and/or dilution solvents for the SVOC and VOC analyses. The hydrocarbon screen by GC-FID showed that the LNAPL matrix was similar to a medium to heavy lubricating oil and provided a basis for selecting an oil matrix that would simulate the LNAPL for use in determining MDLs. The results of the semivolatile compound analysis revealed that the LNAPL sample contained compounds that may be expected to be found in oils: polynuclear aromatic hydrocarbons (PNAs), phthalates, dichlorobenzenes, and dibenzofuran. However, the MDLs required by the Region for the SVOC analysis (Appendix A) were not achieved for half of the compounds. The GC and GC/MS methods used to analyze for PCBs and pesticides were not able to quantitatively or qualitatively determine the presence of these analytes because of matrix interference problems. Additional work on this problem may be warranted and is recommended, including the use of a variety of cleanup methods not performed in this study, analysis by high-resolution GC/MS, and immunoassay. Samples analyzed for VOCs by purge-and-trap GC/MS showed the presence of xylenes; the demonstrated TCL MDLs were well below those required by the Region. The ICP-MS analysis for TAL Metals yielded no harmful levels of metals (i.e., at concentrations typically of concern in the Superfund Program), with the possible exception of arsenic. The ICP-MS analyses also indicated a chemical (metals and lanthanides) "fingerprint" in the two field samples analyzed (RW-03, PZ-17), possibly linking both samples to one point-source. No cyanide was detected in the LNAPL matrix.

Detailed discussions on the results for each analysis class/fraction follow.

3.1 RESULTS OF PHYSICAL TESTING

A set of physical tests were conducted to determine the solubility of the LNAPL sample from well RW-03 in various solvents (water, methanol, methylene chloride, hexanes, acetone, and toluene). Each LNAPL/solvent combination was mixed using a Vortex apparatus and then centrifuged. The observations made from these treatments to the LNAPL sample are summarized in Table 3.

As a result of performing these physical tests, insight was provided as to whether emulsion formation would be a problem during sample preparation for VOC analysis, as the QTM requires the samples be tested for methanol miscibility before analysis, and the RCRA waste dilution method used for SVOCs analysis requires that the sample be miscible with the solvent in which it is to be diluted.

TABLE 2. SUMMARY OF THE METHODS, RESULTS, CONCLUSIONS, AND RECOMMENDATIONS FOR THE ANALYSIS OF THE LNAPL SAMPLES

ANALYTICAL FRACTION	SAMPLE PREPARATION & ANALYSIS METHOD(S)	SUMMARY RESULTS	CONCLUSIONS	RECOMMENDATIONS
Physical Testing for Organics	Solvent miscibility/ Vortex emulsification/ Centrifugation	LNAPL miscible in toluene and methylene chloride	Helped to assess solvents for performing organic analyses; identified potential problems with PCB/pesticide (hexane) & VOC (MeOH) dilutions	Similar tests should be conducted on other LNAPL samples to assess how the matrix reacts to solvents expected to be used in organic analyses
Hydrocarbon Screen	Methylene chloride dilution/ GC-FID	Exhibits characteristics of medium to heavy lubricating oil	Helpful in determining matrix characteristics of samples; selected matrix (Pennzoil® 5W-30) for use in MDL estimation	Use an oil free of additives (detergents) to simulate matrix
TCL Semivolatile Organic Compounds	Method 3580 dilution/ GC/MS (3/90 CLP SOW)	Detected presence of PNAs, phthalates, dichlorobenzenes, dibenzofuran	Could not achieve 10,000 ppb MDL for every compound; peaks comprise typical compounds found in oil matrices	Consider high-resolution MS or ion-trap MS to achieve desired MDLs
TCL Polychlorinated Biphenyls	FASP Cleanup/GC; GPC & florisil cleanups/GC & GC/MS	Unable to confidently identify or quantitate aroclors	Quantity and composition of interferents precluded obtaining defensible GC determinations; Dexsil Chlor-N-Oil® Kit results indicate >50 ppm total organic chloride in sample.	Use Method 3665 (H_2SO_4 + $KMnO_4$) or 3611 (Alumina for Petroleum Wastes) combined with other cleanups and GC; consider high-resolution GC/MS after alumina and silica cleanup and/or immunoassay analysis

TCL Pesticides	GPC & florisil cleanup/GC	Unable to identify or quantitate pesticides	Available cleanups inadequate to allow quantitative or qualitative determination of individual pesticides; Dexsil Chlor-N-Oil® Kit used and determined that >50 ppm total organic chloride in sample.	Consider determination of potentially leachable compounds in LNAPLs based on pesticide results from associated stagnant water or through TCLP analyses
TCL Volatile Organic Compounds	Methanol dilution/ Purge & Trap GC	Xylene isomers only compounds detected	Able to achieve factor of 6 lower than requested MDLs	This method appropriate; GC headspace (QTM) possible alternative in lieu of GC/MS
TAL Metals	HF-Microwave Digestion/ ICP-MS	No TAL metals measured at levels of concern (except As); lanthanides detected.	Two wells with similar concentrations of metals and lanthanides (fingerprint), indicating LNAPL may come from single (point) source	Although Hg not detected, CVAA may be required, or the characterization of Hg performance on ICP-MS, if Hg is of concern at this site
Cyanide	Midi Distillation/ Method 9010	No cyanide detected ≥0.5 mg/Kg	No additional methods necessary	If MDL appropriate, the method should suffice for future LNAPL analyses

TABLE 3. RESULTS OF SOLVENT MISCIBILITY, VORTEX, AND CENTRIFUGATION TESTING OF THE LNAPL SAMPLE RW-03

SAMPLE TREATMENT	SOLVENT					
	Water	Methanol	Methylene chloride	Hexanes	Acetone	Toluene
Solvent Addition	T	B	T	T	B	M
After Vortex	T	B	M	T	B	M
After Centrifugation	T	B	M	T	B	M

T = solvent was not miscible with the LNAPL and the LNAPL remained in the top layer.
B = solvent was not miscible with the LNAPL and the LNAPL remained in the bottom layer.
M = solvent was miscible with the LNAPL.

3.2 RESULTS OF HYDROCARBON SCREEN BY GC-FID

The unknown LNAPL (RAM-RW-03-0-0293) was analyzed by GC-FID and was determined to be a medium to heavy lubricating oil. This conclusion was based upon a comparison of the boiling point range of the unknown oil, shown in Table 4 and Figure 3, to a chart depicting the boiling points of various petroleum products (Figure 4; Lowry et al, 1945). This conclusion is also supported by the chromatogram of the GC-FID analysis of the LNAPL sample shown in Figure 5, which is presented along with chromatograms of diesel fuel oil and motor lubricating oil. A visual analysis of these three chromatograms shows that the LNAPL exhibits chromatographic characteristics more similar to those of the motor oil than the diesel fuel.

The chromatogram comparisons in Figure 5 also show that the motor lubricating oil, Pennzoil® 5W-30 weight oil, was a reasonable selection of a matrix to simulate the LNAPL matrix in the MDL studies. Although the Pennzoil® 5W-30 weight motor oil is considered a light-weight motor oil, motor lubricating oils, as a class, are typically medium to heavy petroleum distillates.

TABLE 4. RESULTS OF GC-FID ANALYSIS - BOILING POINT RANGE OF LNAPL SAMPLE RW-03

BOILING RANGE (°C)	FRACTION (%)
< 240	0
240 - 260	0.2
260 - 280	0.6
280 - 300	2.1
300 - 320	5.5
320 - 340	9.9
340 - 360	13.1
360 - 380	14.4
380 - 400	14.2
400 - 420	12.9
420 - 440	10.7
440 - 460	8.3
460 - 480	5.4
480 - 500	2.2
> 500	0.5

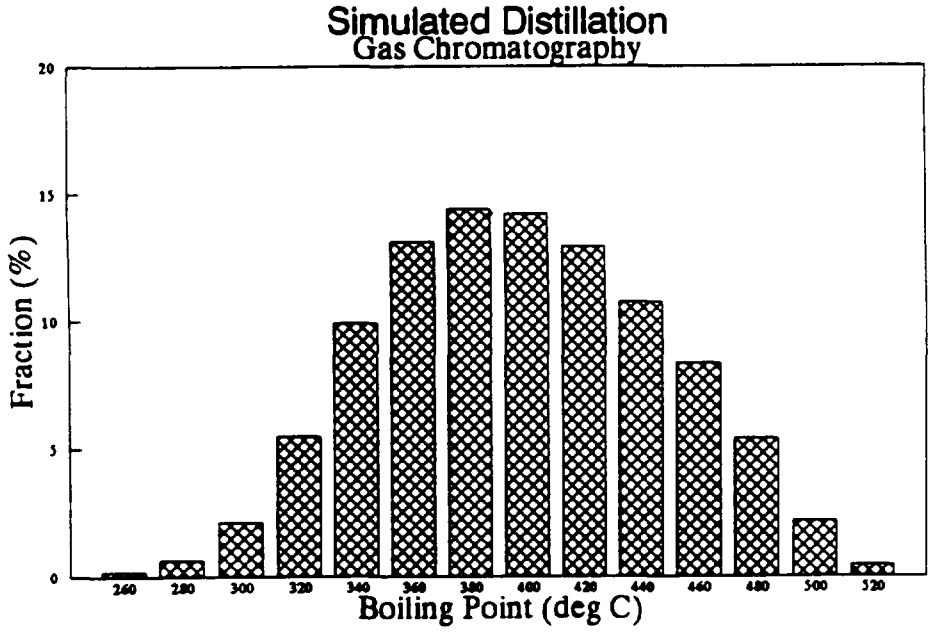


Figure 3. Histogram of GC-FID analysis - boiling point range of sample RW-03.

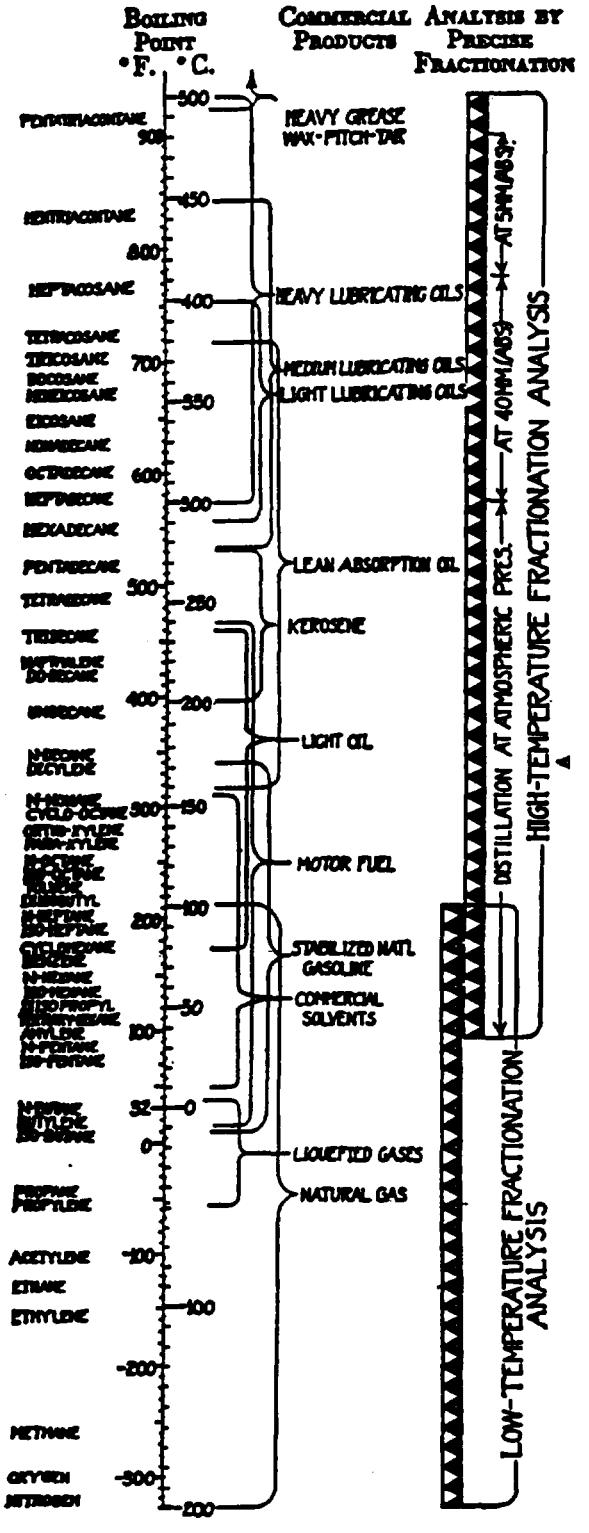


Figure 4. Boiling points of various petroleum products (Lowry et al, 1945).

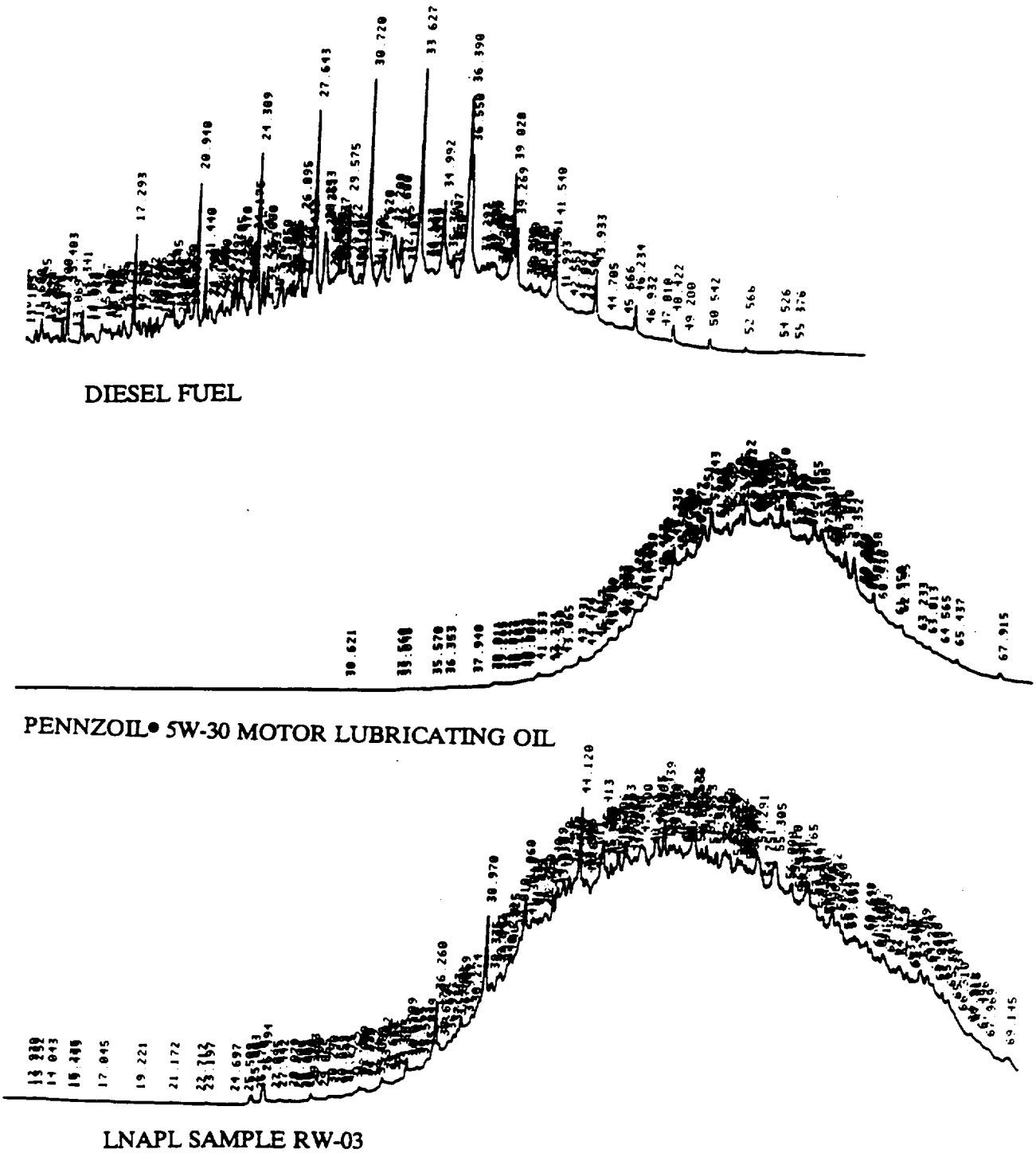


Figure 5. Comparison of GC-FID chromatograms for the LNAPL sample (bottom), diesel fuel (top), and motor oil (middle).

3.3 RESULTS OF SEMIVOLATILE ORGANIC COMPOUND ANALYSIS

Each of the three well samples (RW-03, MW-10, PZ-17) were analyzed for SVOCs. Sample preparation of the LNAPL samples was done using the waste dilution method, diluting 1.0 g of the sample into 10 mL methylene chloride. Samples were then analyzed by GC/MS using the US EPA 3/90 CLP SOW.

Analysis of the three samples showed the presence of varying amounts of polynuclear aromatic hydrocarbons (PNAs), phthalates, two dichlorobenzenes, and dibenzofuran. The results of the samples that yielded detectable concentrations of SVOCs are presented in Table 5.

The LNAPL sample matrix caused some chromatographic problems. Virtually all compounds exhibited a prepeak. This effect became more pronounced as the run progressed. Many of the manual integrations denoted on the quantitation reports were performed to correct instrumental errors caused by matrix effects. This problem also impacts the reported results, particularly in the case of benzo(a)anthracene. Benzo(a)anthracene elutes very close to and just before chrysene. The peak identified as benzo(a)anthracene on the quantitation list and Form I is probably a prepeak of chrysene. However, since both compounds have very similar mass spectra, the reporting decision has been made on the side of caution. Benzo(a)anthracene and chrysene also have very similar response factors, thus the actual concentration of chrysene may be the total of the reported concentrations of the two compounds.

The majority of problems encountered during the analysis for SVOCs were due to the fouling of the GC injector and the front of the GC column. This necessitated corrective maintenance and recalibration of the instrument during the project.

QA/QC performed for the analysis of the SVOC fraction consisted of seven instrument tunes, two 5-point calibrations, five continuing calibrations, surrogate spikes, and one set of matrix spike/matrix spike duplicate analyses. The CLP 3/90 SOW QC requirements were met for all instrument tunes, 5-point curves, continuing calibrations, and sample surrogate recoveries.

Using the 3/90 CLP SOW protocol, minor retention time shifts occurred on the GC column, however, these retention time shifts did not impact the identification of target analytes. This is demonstrated in the results for the matrix spike and matrix spike duplicate pair which were spiked with all SVOC analytes (Appendix E).

LNAPL matrix effects were determined by spiking the RW-03 sample in duplicate and calculating the average recovery and precision (as relative percent difference) as per the CLP 3/90 protocol. Results for this performance assessment are given in Appendix E.

IDLs were determined by running a standard containing 10 ppm (μg/mL) acids, 20 ppm (μg/mL) 3,3'-dichlorobenzidine, and 5 ppm (μg/mL) for all other analytes. The standard was analyzed seven times, the standard deviation for each analyte was determined, and the detection limit calculated by multiplying the resultant standard deviation by 3.143 (the 99% confidence level of the Student's t-test for six degrees of freedom where the number of degrees of freedom equals the number of determinations minus one). The SVOC IDLs are provided in Appendix E.

TABLE 5. RESULTS OF THE LNAPL SAMPLE SEMIVOLATILE ORGANIC COMPOUND ANALYSIS BY GC/MS

ANALYTE	CONCENTRATION (μg/Kg)		
	Sample ID		
	RW-03	MW-10	PZ-17
1,4-Dichlorobenzene	650[a]	21000	18000
1,2-Dichlorobenzene	3800[a]	33000	140000
Naphthalene	3800	39000	44000
2-Methylnaphthalene	7700[a]	110000	110000
Dibenzofuran	<2929	10000	6600
Fluorene	8600[a]	29000	26000
Phenanthrene	25000	180000	120000
Di-n-butylphthalate	9200[a]	<22889	<22889
Fluoranthene	5900[a]	<6825	5400[a]
Pyrene	19000[a]	70000	32000
Butylbenzylphthalate	21000[a]	33000[a]	29000[a]
Benzo(a)anthracene	4300[a]	24000	19000
Bis-2-ethylhexylphthalate	390000	180000	800000
Chrysene	55000	150000	87000
Di-n-octylphthalate	12000[a]	<14224	<14224
Benzo(b)fluoranthene	<11781	5200[a]	<11781
Benzo(k)fluoranthene	<9057	7800[a]	<9057
Benzo(a)pyrene	24000[a]	39000[a]	28000[a]

[a] Analyte detected below MDL (see Appendix E, Table E-2)

MDLs were determined by spiking a 1 g Pennzoil® 5W-30 oil sample with all SVOC analytes and diluting the sample 1:10 in methylene chloride. On the first attempt, the oil was spiked at a final concentration of 5 μg/mL (10 ng/analyte on column). Most of the later-eluting phenols gave no response during this set of runs, and some of the compound responses were erratic. A second MDL

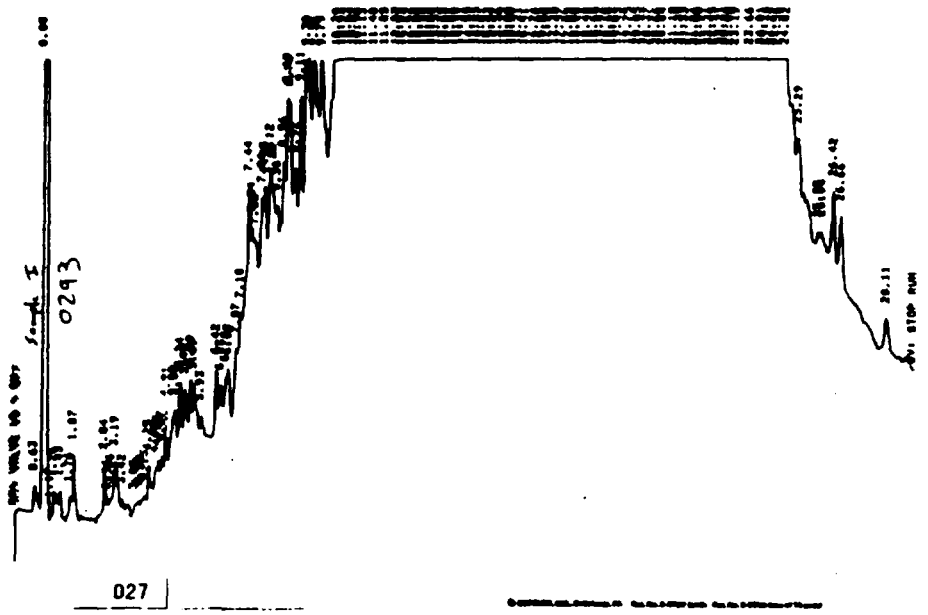
study was initiated after instrument maintenance which included cleaning the GC injection port and breaking off the front of the capillary column. Injections of diluted oil spiked to a concentration of 20 μg/mL (40 ng on column) also failed to show results for the later-eluting phenols. The response of the internal standard chrysene d-12 was well below QC limits during the experiments performed using both blank and spiked Pennzoil® motor oil. For the analytes that gave adequate response, MDLs were calculated using the results of the dilution and analysis of the seven original spiked motor oil samples (at 5 μg/mL). The SVOC MDLs are presented in Appendix E. Twenty-eight of the 57 compounds achieved the 10,000 ppb MDL desired by Region 5. Using a larger sample volume to achieve lower MDLs was not a viable option because of the detrimental affect of the matrix on capillary column performance. If the MDLs demonstrated in this project are not adequate to meet the data needs of the Region, lower detection limits may be attainable using the ion trap mass spectrometer.

Although using Pennzoil® 5W-30 motor oil for the matrix studies caused the problems discussed above, it also provided valuable information concerning the analytes detected in the samples. It appears that Pennzoil additives reacted with the chrysene-d12 internal standard and the late-eluting acidic compounds. This created problems in determining MDLs for the late eluting-phenols. However in application, these problems are moot, as no late-eluting phenols were found in the LNAPL samples. Additionally, the actual well and piezometer sample matrices did not react with the late-eluting phenols, as can be seen in the matrix spike data (Appendix E). The Pennzoil® also created an instrumental problem by fouling the injector after only one injection. In the future, a light-weight oil that is known to have no additives (e.g., detergents) should be considered for any method performance evaluations.

3.4 RESULTS OF POLYCHLORINATED BIPHENYLS ANALYSIS

The analysis of PCBs (and similarly, pesticides) proved to be the most difficult of the various analytical fractions to accomplish. The initial florisil cleanup (undiluted and 1:10 dilution in hexane) of sample RW-03 showed the presence of a large "hump" which had no discernable PCB pattern (figures 6a and 6b). The next cleanup technique attempted, the FASP method (sulfuric acid/florisil cleanup), produced a sample eluant which also gave a large chromatographic "hump." Again, no PCB isomeric pattern was recognizable on top of the hump. The GPC cleanup of a 1:100 dilution of sample RW-03 (followed by florisil cleanup and 1:10 dilution in hexane) also produced the "hump" (Figure 7). The analysis of the same cleaned-up sample on the GC/MS showed that the GPC and florisil treatments did not ameliorate the interference problems previously observed. The "hump" comprised of the oil constituents elutes from a retention time period of 18 to 44 minutes on a DB-5 column using the temperature program listed in Appendix F for SVOCs by GC/MS. An injection of a 1000 ppm Aroclor 1254 standard on the GC/MS using the same GC program showed the peaks comprising the aroclor eluting during the retention time period of 25 to 33 minutes, directly under the hydrocarbon envelope (Figure 8). An Aroclor 1254 standard was spiked into the cleaned-up extract (Figures 9a to 9o) to determine at what concentration this PCB could be detected, if indeed it was present in the LNAPL sample. While it was possible to match the retention times of the five largest peaks contained in the 1254 standard with the respective peaks in the spiked samples, the results of quantitation at a 5-ppb spike level show the values obtained were higher than expected by a factor of 18 to 26. The actual results were 92, 95, and 132 ppb for a sample injected in triplicate. These results may be attributed to other aroclors, halogenated compounds, phthalates, or high molecular weight contaminants present in the sample which are also being detected by ECD. The 5 ppb spike

(a)



(b)

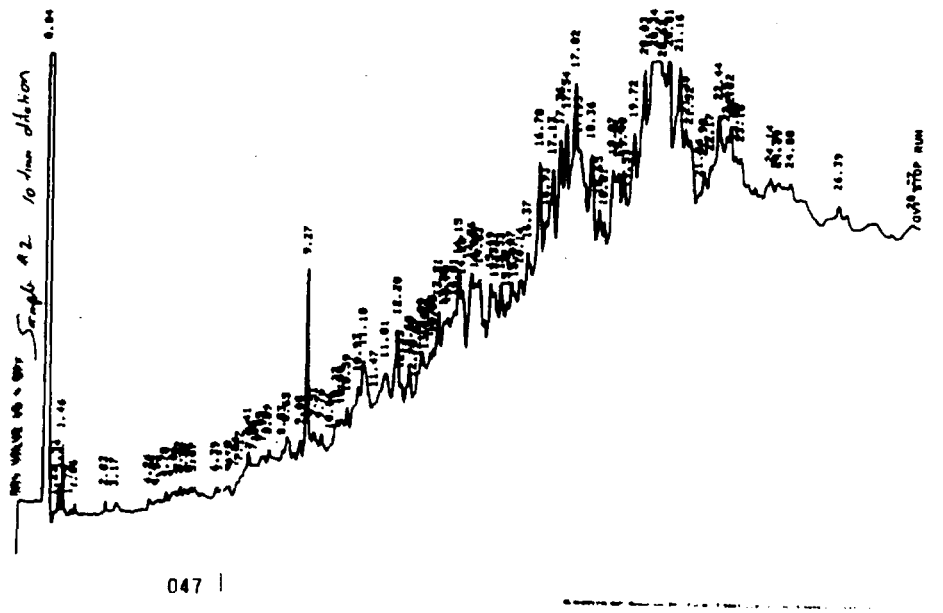


Figure 6. Chromatogram of sample RW-03: (a) florisil cleanup only; (b) 1:10 dilution in hexane with florisil cleanup.

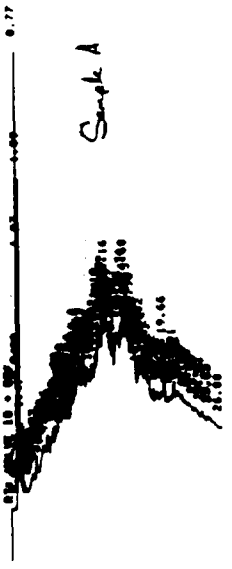


Figure 7. Chromatogram of sample RW-03 after 1:100 dilution in methylene chloride, GPC and florisil cleanup, and 1:10 dilution in hexane.

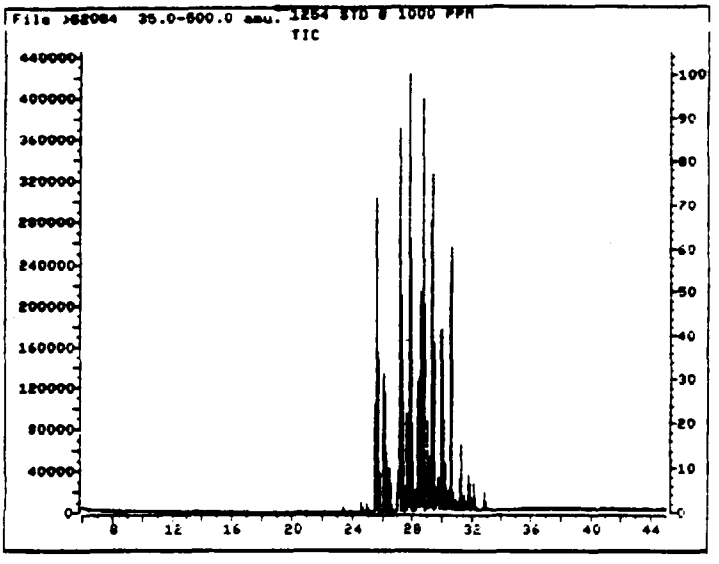


Figure 8. Chromatogram of Aroclor 1254 at 1000 ppm analyzed by GC/MS.

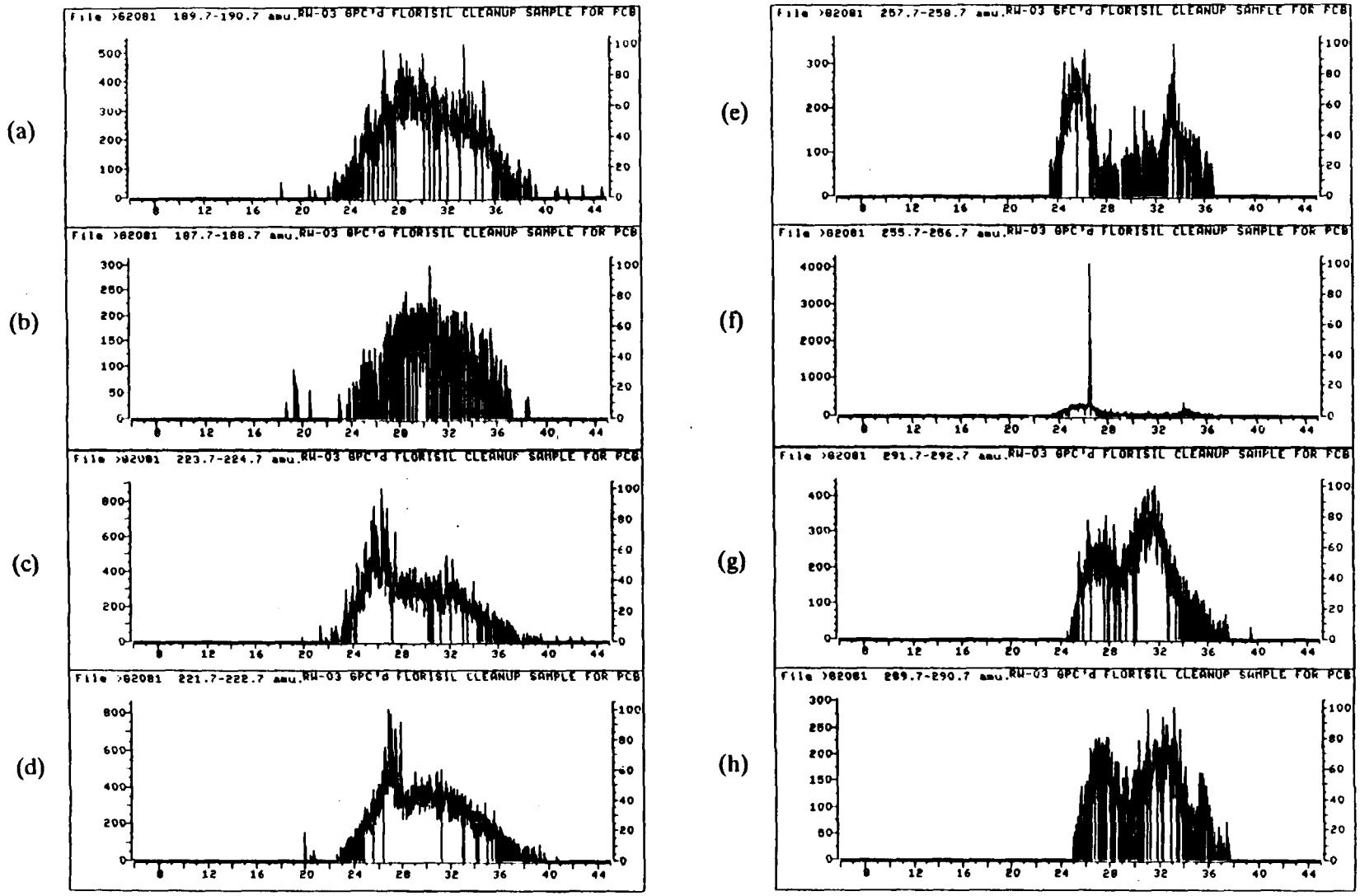


Figure 9. Extracted ion current profiles of PCBs analyzed by GC/MS for sample RW-03: (a) m/z 190 for monochlorobiphenyl, (b) m/z 188 for monochlorobiphenyl, (c) m/z 224 for dichlorobiphenyl, (d) m/z 222 for dichlorobiphenyl, (e) m/z 258 for trichlorobiphenyl, (f) m/z 256 for trichlorobiphenyl, (g) m/z 292 for tetrachlorobiphenyl, (h) m/z 290 for tetrachlorobiphenyl.

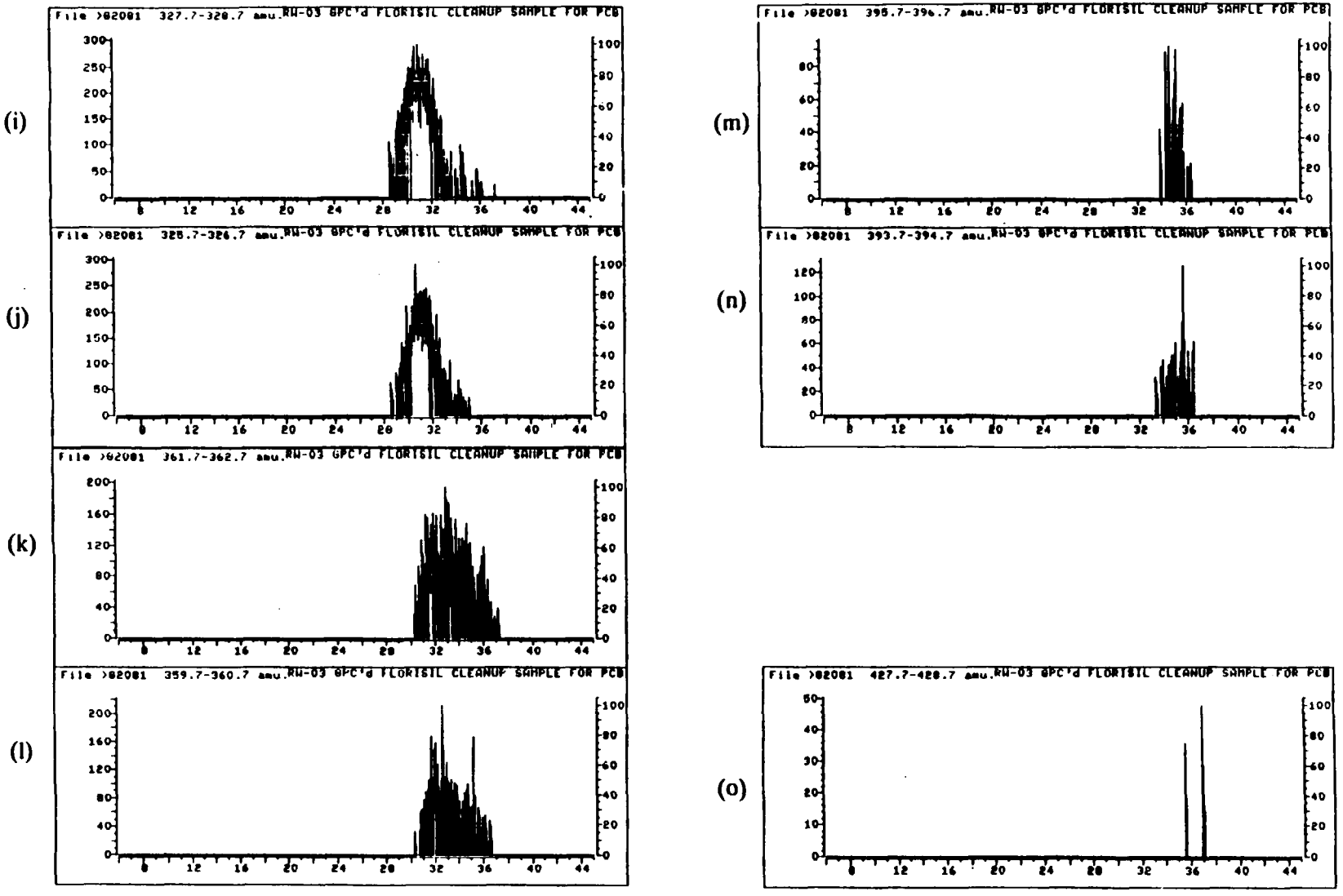


Figure 9 cont. Extracted ion current profiles of PCBs analyzed by GC/MS for sample RW-03: (i) m/z 328 for pentachlorobiphenyl, (j) m/z 326 for pentachlorobiphenyl, (k) m/z 362 for hexachlorobiphenyl, (l) m/z 360 for hexachlorobiphenyl, (m) m/z 396 for heptachlorobiphenyl, (n) m/z 394 for heptachlorobiphenyl, (o) m/z 428 for octachlorobiphenyl.

would represent a level of 5 ppm in the natural LNAPL matrix when dilutions and cleanup procedures are taken into account.

The Dexsil Chlor-N-Oil• field test kit (Appendix G) showed a positive result for the presence of PCBs at the 50 ppm level. It should be noted that this test was designed for the determination of PCBs in clean transformer oil. It is not specific for PCBs and will give positive results for any organic compound containing organically bound chloride. In this regard, it is also noted that the presence of at least two dichlorobenzenes were detected in the semivolatile analysis of RW-03.

Project time constraints precluded the use of additional alternative cleanup and analysis methods for these analytes (aroclors), however, it is recommended that such options be investigated. Methods 3611 (alumina column cleanup for petroleum wastes) and 3665 (sulfuric acid/potassium permanganate cleanup for PCBs, 1990 SW-846 revision) may provide sufficient sample cleanup to allow PCB identification/quantitation to be performed on GC. Additional analytical methods which may perform more effectively for this type of matrix include high-resolution GC/MS (used in conjunction with alumina/silica extract cleanup), immunoassay, and solid phase adsorbent extraction (SPE). Some communications have been held with EnSys, Inc., concerning the potential use of an immunoassay approach. Analytichem International, Millipore, Supelco, and other companies have developed SPE methods for PCBs in transformer oil which may be optimized for use with the LNAPL matrix.

3.5 RESULTS OF PESTICIDES ANALYSIS

Since the sample aliquot for pesticide analysis was prepared using cleanup procedures similar to those used for PCBs (except where sulfuric acid cleanup and the aroclor addition steps were employed), the discussion on problems encountered in PCB analysis (Section 3.4) applies to the pesticide results as well. The high-resolution GC/MS with the proper extract cleanup combinations may be a possible analytical option for pesticides. Communications between Region 5 and EMSL-LV indicated that a major concern is the contamination of the groundwater at the site by pesticide (and other) analytes present in the LNAPLs. Thus, an alternative approach in determining the impact of the LNAPLs on the groundwater may be to determine the quantity of pesticides which may be extracted or leached from the LNAPLs into an adjacent water matrix (e.g., the stagnant water from the piezometers or wells). Alternatively, the LNAPLs may be analyzed using the Toxicity Characteristic Leaching Procedure (TCLP) which is applicable to oily samples. If the LNAPLs are anticipated to be placed in a landfill, TCLP analysis may already be a RCRA requirement prior to such landfill waste disposal (RCRA, 1990).

3.6 RESULTS OF VOLATILES ORGANIC COMPOUND ANALYSIS

Sample preparation for VOC analysis was performed using a modified version of the Quick Turnaround Method for the determination of VOCs in an oily matrix. Samples were extracted with purge-and-trap grade methanol. An aliquot of the extract was injected into reagent grade water. The volatile components in the aqueous phase were then introduced into the GC/MS via purge and trap as per the CLP 3/90 medium soil protocol. The associated holding and trip blanks were analyzed using the US EPA CLP 3/90 low water protocol. Due to the limited amount of matrix available, RW-03 was the only well sample that was analyzed. In order to provide precision data on the field sampling and analytical performance, the routine and the duplicate samples were analyzed as separate samples. This is the only instance in this project where the field duplicate was treated in this manner, i.e.,

analyzed as a true field duplicate sample. The analysis of this sample pair provided an estimate of system precision, calculated as the relative percent difference of the pair (Table 6).

Results of the analysis of sample RW-03 showed the presence of xylene isomers as the only volatile target compounds (Table 6). The remainder of the peaks in the chromatogram consisted of various other alkyl substituted benzenes and were quantitated as tentatively identified compounds (TICs) on the CLP reporting forms.

TABLE 6. RESULTS OF THE LNAPL SAMPLE VOLATILE ORGANIC COMPOUNDS ANALYSIS BY GC/MS

ANALYTE	CONCENTRATION (µg/Kg)			Relative Percent Difference
	Routine Sample (RW-03)	Duplicate Sample (RW-03)	Average	
m,p-Xylenes	386.5	346.5	366.0	10.9%
o-Xylene	332.5	307.0	319.0	8.0%

Instrument detection limits were determined by analyzing seven replicates of a 10 ppb standard and multiplying the resultant standard deviation by 3.143 (the 99% confidence level of the Student's t-test for six degrees of freedom, where the number of degrees of freedom equals the number of determination minus one). The results of the IDL study are presented in Appendix K.

Method detection limits were determined by extracting seven aliquots of 5W-30 Pennzoil® spiked at the 500 ppb level. The estimated detection limits were then determined as above. The data showed that the Pennzoil normally contains a high amount of toluene and o-Xylene and also appears to contain methylene chloride. The MDL for toluene should be similar to that of the xylenes due to its chemical properties. The MDL for o-Xylene can be assumed to be similar to meta and para Xylenes as these three compounds are isomers of each other and have nearly identical chemical properties. Methylene chloride is not of concern since it was not detected in the sample. The results of the MDL study are presented in Appendix K.

Analyte recoveries were determined by spiking the sample RW-03 in duplicate at the 2,500 ppb level. After analysis the average recoveries were calculated and the relative percent differences determined. The results of the matrix spike/matrix spike duplicate analyses are presented in Appendix K.

QA/QC associated with the analysis of the volatile samples consisted of six instrument tunes, one 5-point curve, 4 continuing calibration checks, surrogate spikes, and two sets of matrix spike/matrix spike duplicates (one for the aqueous trip blank and one for sample RW-03). The CLP 3/90 SOW QA criteria were met for all six instrument tunes, the initial 5-point curve and the four continuing calibrations. Surrogate recoveries were within limits for all aqueous samples (the trip blank and

associated spike and duplicate, as well as all instrument blanks). While the toluene-d8 and bromofluorobenzene recoveries were below the QC limits for the 3/90 multimedia SOW, these surrogate recoveries were within the Quick Turnaround Method criteria of 50 to 150 percent recovery for the analysis of volatiles in oil using methanolic extraction. Recoveries for all other analytes (as matrix spikes) were within the 50 to 150 percent range with the exceptions of carbon disulfide, carbon tetrachloride, tetrachloroethene, and ethyl benzene, which had recoveries lower than 50 percent. It should be noted that the 50 to 150 percent range is an advisory limit at this time.

The method of methanolic extraction does not work well for the ketones, vinyl acetate, and carbon disulfide. Vinyl acetate and the ketones use m/z 43 for quantitation and interference from the hydrocarbon C_3H_7 fragment causes their apparent recoveries to be high. The analyte 2-butanone uses m/z 72 as a quantitation ion and is interfered by the ^{13}C peak of the C_5H_{11} hydrocarbon fragment when hydrocarbons are present. Carbon disulfide is miscible with both methanol and oil and partitions itself accordingly.

3.7 RESULTS OF TAL METALS ANALYSIS

Target Analyte List Metals analyses were performed on two oil samples (PZ-17 and RW-03) from the Rockwell Site. Metals levels found in the samples were well below levels typically of concern at hazardous waste sites. Most metals were not detected or were below the contract required detection limit (CRDL). Of the few analytes that were detected, only arsenic merits comment, being detected at about 4 times the CRDL in both samples. Even at this concentration, the samples can be considered relatively "harmless" from a metals standpoint. Table 7 provides the results of the analysis of these two samples for TAL Metals by ICP-MS. Even though the samples did not contain significant levels of inorganic constituents, the choice of analytical methods (ICP-MS) did allow sample source identification from observation of inorganic parameters. There is a strong possibility that the two LNAPL samples originated from the same source, as can be observed by a visual comparison of the TAL Metals data histogram provided in Figure 10 and the detection of lanthanides (see below).

Mercury was not determined by CVAA. Instead, it was quantified from ICP-MS data, even though the IDL was above CRDL. The use of ICP-MS Hg data was decided after analyses for the other metals were completed. A dedicated run for Hg was not performed since the Hg level appeared to be undetectable in the samples and time did not allow extra analyses. If a dedicated run for Hg had been performed the CRDL would have been met. It can be stated that Hg is below 0.25 mg/Kg in the oil samples, which is typically not considered a level of concern for hazardous waste site monitoring.

One analytical problem was encountered during the metals analyses. The detector being used on the ICP-MS instrument was nearing the end of its useful lifetime and there was insufficient time to procure and install a new detector. High ion fluxes cannot be counted reliably when the detector is aged. The detector performed satisfactorily for low level analytes, however, one analyte, Al, was sufficiently high in the LNAPL samples (and initial calibration verification [ICV] standard) that upper linear ranges were affected. Al was present above the linear range and may be reported as much as 20% low. Given that Al is relatively harmless and just above CRDL (about 3X), the low bias will have no practical impact. Some other minor QA/QC problems were encountered and are discussed below and in the comments sections of the reporting forms of the data package. These problems had no impact on the data usability.

TABLE 7. TAL METALS RESULTS FOR LNAPL SAMPLES ANALYZED BY ICP-MS.

ANALYTE	MDL (mg/Kg)	CRDL (mg/Kg)	SAMPLE PZ-17	SAMPLE RW-03
			CONCENTRATION (mg/Kg)	CONCENTRATION (mg/Kg)
Aluminum	1.12	80	591[a]	320[a]
Antimony	0.20	24	0.52[b]	0.35[b]
Arsenic	0.91	4.0	15.7	13.8
Barium	0.60	80	40.5[b]	8.22[b]
Beryllium	0.20	2.0	2.73	2.49
Cadmium	0.31	2.0	0.31[c]	0.31[c]
Calcium	128.	2000	1850[b]	1043[b]
Chromium	0.28	4.0	12.4	6.15
Cobalt	0.09	20	0.93[b]	0.38[b]
Copper	0.43	10	6.66[b]	3.93[b]
Iron	20.3	40	787	1070
Lead	0.17	1.2	2.12	2.79
Magnesium	0.90	2000	46.7[b]	7.65[b]
Manganese	0.15	6.0	9.85	3.72[b]
Mercury	0.25	0.08	0.25	0.25[c]
Nickel	0.74	16	4.82[b]	4.31[b]
Potassium	8.21	2000	8.2[c]	9.60[b]
Selenium	2.02	2.0	2.02[c]	2.02[c]
Silver	0.15	4.0	1.21[b]	0.65[b]
Sodium	5.06	2000	41.4[b]	30.3[b]
Thallium	0.20	4.0	0.40[b]	0.20[c]
Vanadium	0.26	20	10.2[b]	4.69[b]
Zinc	0.29	8.0	5.70[b]	65.88

[a] PZ-17 measured above linear range, concentration may be up to 20% higher than reported value; RW-03 concentration may be 10% higher than reported (see data package).

[b] Sample concentration above IDL, but below contract required detection limit.

[c] Analyte not detected.

A few QA/QC parameters were out of control limits on several analytes due to technical difficulties. However, their resolution will result in no significant improvement in data quality at the levels of concern. Both Al and Ca were found above CRDL in the preparation blank for these analyses. The samples themselves contained Ca below CRDL, and Al just above the CRDL (<3X). Given the low levels and harmless nature of the affected analytes, the preparation blank contamination has very little practical impact.

NOTE: Reporting forms are not standard CLP and were adopted from the EPA's pending Low Concentration Waters Inorganics SOW (ILCO1.0). The SOW has not yet been released for contracts. Some forms (especially those devoted to ICP-MS) may be unfamiliar to the data auditor. A course in ICP-MS data reporting and auditing is available to the EPA regions from EMSL-LV. Contact Dr. Larry Butler at (702) 798-2114 for details. For questions regarding the forms as they were used in this case, please contact Dr. David Dobb, LESAT, at (702) 798-2124.

The choice of analytical methods (ICP-MS) for this case allowed quantitative analysis for TAL Metals and semiquantitative analysis for other analytes present in the samples. This included detection of several lanthanide elements (Table 8). Although levels were low, lanthanides can be used for fingerprinting and source identification purposes. In reviewing the TAL data in conjunction with the lanthanide data, there is an indication that both samples are related and, in fact, could be interpreted as duplicates of each other. Figures 10 and 11, respectively, show the high degree of overlap between samples PZ-17 and RW-03 for the TAL metals and for the lanthanides.

TABLE 8. LANTHANIDE RESULTS[a] OF LNAPL SAMPLES ANALYZED BY ICP-MS

ANALYTE	SAMPLE PZ-17		SAMPLE RW-03	
	CONCENTRATION		CONCENTRATION	
	µg/L	mg/Kg	µg/L	mg/Kg
Lanthanum (^{139}La)	9.0	3.6	5.0	2.0
Cerium (^{140}Ce)	40	16	40	16
Praseodymium (^{141}Pr)	5.0	2.0	2.0	0.8
Neodymium (^{142}Nd)	25	10	5.0	2.0
Samarium (^{148}Sm)	10	4.0	5.0	2.0
Europium (^{151}Eu)	6.0	2.4	3.0	0.6
Gadolinium (^{156}Gd)	7.0	2.8	3.0	0.6
Dysprosium (^{163}Dy)	10	4.0	5.0	2.0
Holmium (^{165}Ho)	4.0	1.6	2.0	0.8
Erbium (^{167}Er)	11	4.4	5.0	2.0

[a] Semiquantitative estimations of concentrations; samples not quantitated against primary standards.

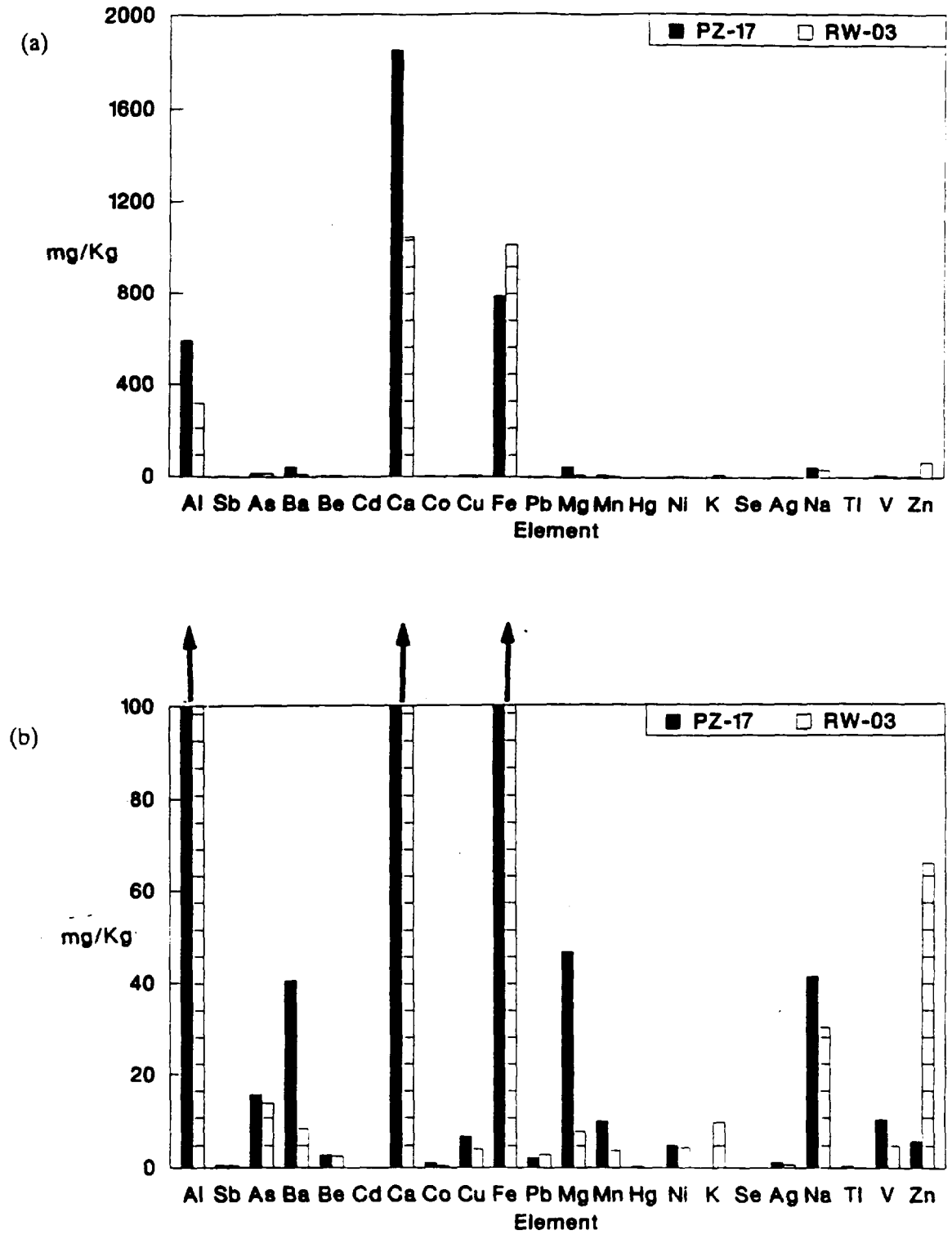


Figure 10. Histogram of the TAL Metals concentrations in LNAPL samples PZ-17 and RW-03: (a) plotted with all concentrations and (b) plotted to show resolution of lower concentration analytes.

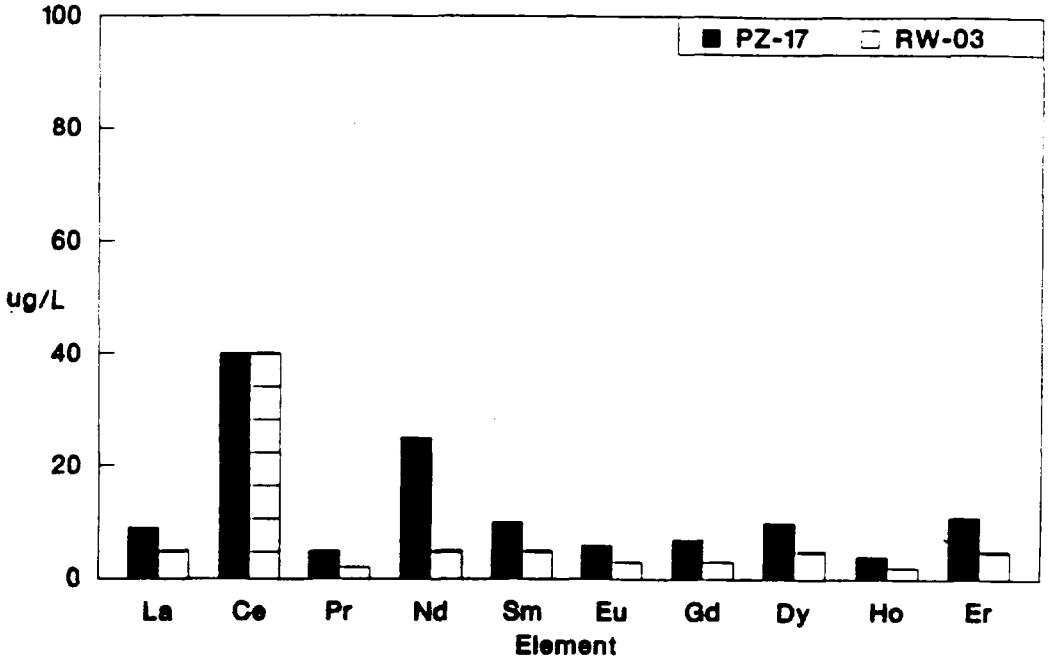


Figure 11. Histogram of the lanthanide concentrations in LNAPL samples PZ-17 and RW-03.

Except for minor differences between Ba, Ca, Mg, and Zn in the two samples, analyte levels go "up and down" in unison. The same is true for the lanthanides, however, the RW-03 sample generally contained half as much lanthanides as sample PZ-17. The source of the lanthanides in the samples is unknown, but the element-to-element ratios indicate the samples are related and there is a very good likelihood that they originate from the same source.

3.7.1 MDLs for Metals

In preparing oil samples for metals analysis, the digestion procedure destroys the matrix while solubilizing the analytes of interest. In such a case, the MDL is simply the IDL multiplied by the dilution factor resulting from sample preparation. An exception would be if the sample contained species which interfered with the determination of the analytes of interest as a result of spectral overlap. For these LNAPL samples no such interferences were observed. Since the IDL is determined as $\mu g/L$, the MDL in this case, as presented in Table 7, was calculated by converting liquid units of measure to solid units by multiplying the IDL by 0.4 (based on 0.25 g of sample being digested and diluted to 0.1 L).

3.8 RESULTS OF CYANIDE ANALYSIS

One sample, from well RW-03, was analyzed for cyanide by Method 9010. Since cyanide was the analysis class with lowest priority (Appendix A), it was decided that the single sample would be analyzed, reserving the other samples' volumes for the more urgent analyses. There was no cyanide detected at the 0.5 mg/kg level. The sample was analyzed within method-specific holding time. Based upon laboratory blank analysis, the sample analysis run was free of contamination, and all related internal quality control analyses were within acceptance limits for the method.

3.8.1 MDLs for Cyanide

In preparing oil samples for cyanide analysis, the distillation procedure separates the cyanide from the matrix. Since "total cyanide" is operationally defined, any cyanide tied up in the oil matrix so strongly that it is not liberated during distillation is not considered part of the "total cyanide." Consequently, the MDL is defined as the IDL multiplied by the dilution factor resulting from sample preparation.

3.9 SUMMARY ASSESSMENT OF DATA QUALITY

Data quality objectives (DQOs) for the LNAPL investigation are discussed in Section 1.3 and detailed in this project's QAPjP (Table 1 of Appendix B). With the exception of the MDLs for volatile and semivolatile analytes, the EPA Region 5 RPM and QA representative specified no quantitative limits for data quality (Appendix A). Therefore, the DQOs for accuracy, precision, and MDLs described in Appendix B were, for the most part, derived from results generated during interlaboratory studies using draft EPA methods or related technical procedures (Laing, 1989; Marsden, 1992; Suarez, 1993). While meeting the objectives was a desired output of the laboratory work, failure to do so in all cases does not invalidate the results of this investigation. A summary of the quantitative data quality indicators (assessed relative to the DQOs) is given in Table 9.

Data from the TAL Metals and cyanide show excellent accuracy with the recoveries of all but two spikes meeting the 80 to 120 % objective. Spike recoveries for silver were just below the window at 77% and 79%. Approximately two-thirds of the SVOC and VOC spiked analyte recoveries were also within the objectives for accuracy, set at 60 to 110% and 75 to 125% for the respective analytical fractions. The precision of the results for all of the above-mentioned LNAPL analyses was consistently demonstrated; all relative percent difference objectives of 25% were met for the metals, cyanide, and VOCs, and 61 of 65 of the SVOC analytes met the 35% goal. MDL determinations were performed on Pennzoil® light-weight motor oil, which proved to be an adequate but less than perfect artificial matrix. While all but mercury MDLs met the inorganic DQOs, and VOCs (with the exception of methylene chloride and o-Xylene) demonstrated method/matrix detection limits requested by the Region, in the case of SVOCs, detergents or other additives present in the Pennzoil® complicated MDL determinations or made them unattainable for some target analytes. Pesticide and PCB data from this investigation were so compromised by matrix interferences that none of the project goals for these compounds could be accomplished.

TABLE 9. DATA QUALITY ASSESSMENT SUMMARY FOR ACCURACY, PRECISION, AND METHOD DETECTION LIMITS BY ANALYTICAL FRACTION

ANALYTICAL FRACTION (Method)	ACCURACY (Spike % Recovery)	PRECISION (RPD)	METHOD DETECTION LIMIT
Semivolatile Organic Compounds (GC/MS: 8270)	Mean %R for MS/MSD: 45 of 65 analytes within 60-110% objective. Benzo(a)anthracene and chrysene showed matrix-related quantitation problems	MS/MSD for 61 of 65 analytes met ≤ 35% RPD objective	Objective of <10,000 µg/Kg achieved for 28 of 57 analytes (does not include phenols)
Polychlorinated Biphenyls (GC: 8081; GC/MS)	No data	No data	Unable to obtain 1000 µg/Kg MDL. Diluted/cleaned up LNAPL spiked at 5 mg/Kg 1254. These samples quantitated at ~100 mg/Kg
Pesticides (GC: 8081; GC/MS)	No data	No data	No data
Volatile Organic Compounds (Purge-and-Trap GC/MS)	Surrogates: all 50-150%. 23 of 36 spiked analytes within 75-125% objective (only 4 below 50%)	Field duplicates for m,p-Xylenes = 10.9%, o-Xylene = 8.0%. All MS/MSD ≤25% RPD (only 4 > 10%)	Objective of <1200 µg/Kg achieved for all but 2 analytes ($MeCl_2$, o-Xylene)
TAL Metals (ICP-MS: 6020)	All %R for spiked samples met 80-120% objective, except Ag (77%, 79%). Al of PZ-17 above linear range (conc. ~20% low); [Al] of RW-03 ~10% low (instrument problems)	All analytes above CRDL for laboratory duplicates of PZ-17 and RW-03 met ≤25 RPD, except Cu	All MDLs ≤ CRDL (Method 6020) except Hg (MDL = 0.25 mg/Kg, CRDL = 0.08 mg/Kg)
Total Cyanide (Spectrophotometer: 9010)	MS %R = 92.8% within (80-100% objective)	Laboratory duplicate of RW-03 below MDL	Objective of 500 µg/Kg achieved

MS/MSD = matrix spike/matrix spike duplicate
%R = percent recovery
CRDL = contract required detection limit
RPD = relative percent difference

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APPENDIX A

REGION 5 LETTER OF REQUEST

FOR TECHNICAL SUPPORT SERVICES

FOR LNAPL SAMPLE ANALYSIS

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 5
77 WEST JACKSON BOULEVARD
CHICAGO, IL 60604-3590

REPLY TO THE ATTENTION OF:

VIA FACSIMILE

February 3, 1992

Mr. Ken Brown
U.S. EPA EMSL-LV
944 East Harmon Drive
Las Vegas, Nevada 89119

Re: Request for Technical Support Services for Analysis of LNAPL Samples, Rockwell International Site, Allegan, Michigan

Dear Mr. Brown:

Per our telephone conversations, I am requesting technical support services from the U.S. EPA Environmental Systems Monitoring Laboratory (EMSL), Las Vegas, Nevada. This request is for the laboratory analysis of three (3) light non-aqueous phase liquid (LNAPL) samples that will be collected from the Rockwell International site in Allegan, Michigan.

The Rockwell International site is a former manufacturing facility located adjacent to the Kalamazoo River. Past operations at the site include machining, hardening, and the assembly of drive-line parts for large vehicles and construction equipment. Petroleum-based cutting oils, quench oils, water soluble cutting oils, and washer cleaning compounds are known to have been used at the site. Disposal of the waste oils has historically been into an oil flotation house, a series of settling ponds, and, more recently, a wastewater treatment plant and lagoons.

The LNAPL was first discovered in several existing on-site groundwater monitoring wells and piezometers during a second phase of field work undertaken during November, 1992. Since the time the LNAPL was unexpectedly discovered, our Quality Assurance Section (QAS) and I have been working with the potentially responsible party (PRP) to develop appropriate analytical methods for analysis of the LNAPL. The PRP has failed to submit appropriate analytical methods. As there are not, however,

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standard analytical methods available for analysis of an oil matrix, we are now asking for the expertise of your laboratory.

Our objective is to characterize the LNAPL in terms of chemical composition and concentration; and use the resulting analytical data in our Remedial Investigation and Feasibility Study. As such, we request that each LNAPL sample be analyzed for Target Compound List (TCL) volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), and polychlorinated biphenyls (PCBs) and pesticides; and for Target Analyte List (TAL) inorganic compounds and cyanide. Due to the potentially limited volume of LNAPL available for sampling, however, we may not be able to collect enough LNAPL at each of the three locations for analysis of every individual parameter. (The target sample volume is 80 mL of LNAPL per organic parameter, 50 mL per inorganic parameter.) As such, we have ranked the parameters in order of analytical priority. They are, in order from highest priority to lowest priority, as follows:

1) SVOCs
2) PCBs/pesticides
3) VOCs
4) Inorganic compounds
5) Cyanide

To give you an indication of what we are looking for in terms of analytical methods, I will be sending you (via overnight mail) a copy of the PRP's unapproved Quality Assurance Project Plan Addendum (QAPP) for LNAPL sampling and analysis; and a copy of QAS's final comments on the document. In general, QAS is asking for standard operating procedures (SOPs) that are designed for an oil matrix, have detection limits that are for oil, and have detection limits more sensitive than 1,200 ug/kg for VOCs, and 10,000 ug/kg for SVOCs.

Oil matrix interference has been a problem with this site previously during the analysis of oil-stained soil and sediment samples collected as part of the Phase I investigation. In addition to the disapproved QAPP and QAS comments, I will also send you a copy of the raw analytical data for some of the oil-stained samples (chromatogaphs and data system printouts), which may give a preliminary indication of the chemical composition and concentration of the LNAPL.

After you have had an opportunity to review the background information, we ask that you provide us with your general approach for analyzing the LNAPL samples, including the analytical methods you plan to use, and the detection limits those methods will yield. In addition, we also require documentation of the procedures and methods used during the actual analyses.

If you have any questions or require additional information, please feel free to contact me at (312) 886-1843. Questions

concerning our analytical requirements may be directed to Al Alwan of U.S. EPA's Region V Quality Assurance Section, at (312) 353-2004.

Sincerely,

Karen L. Sikora
Remedial Project Manager

cc: Wendy Carney, Section Chief
Al Alwan, QAS

APPENDIX B

QUALITY ASSURANCE PROJECT PLAN

FOR THE ANALYSIS OF LIGHT NON-AQUEOUS PHASE LIQUID SAMPLES

FROM THE ROCKWELL INTERNATIONAL CORPORATION NPL SITE

(February 1993)

February, 1993
J.O. 222101720

QUALITY ASSURANCE PROJECT PLAN
FOR
THE ANALYSIS OF LIGHT NON-AQUEOUS PHASE LIQUID SAMPLES
FROM THE
ROCKWELL INTERNATIONAL CORPORATION NPL SITE

PREPARED BY
LOCKHEED ENVIRONMENTAL SYSTEMS AND TECHNOLOGIES
LAS VEGAS, NEVADA 89119

CONTRACT No. 68-C0-0049
LESAT DCN QAO 90-93-01

WORK ASSIGNMENT MANAGER
K.W. BROWN
TECHNOLOGY SUPPORT CENTER
ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
U.S. ENVIRONMENTAL PROTECTION AGENCY
LAS VEGAS, NEVADA 89119

APPROVALS

V.A. Ecker, QA Coordinator, LESAT

K.W. Brown, WAM, EPA

J.E. Pollard, Scientific Supervisor, LESAT

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SECTION 1.0

PROJECT DESCRIPTION

Under the Environmental Monitoring Research and Development (EMR&D) Contract to the US EPA Environmental Monitoring Systems Laboratory in Las Vegas (EMSL-LV), Lockheed has been tasked to provide special analytical services to the Technical Support Project (TSP) and EPA Region 5. This support includes multiple activities relevant to the analysis of light, non-aqueous phase liquids (LNAPLs) for all analytes contained in the Contract Laboratory Program (CLP) organic and inorganic Statements of Work (SOWs). No routinely used EPA methods appropriate for the analysis of low levels of the target compounds in oil matrices are currently available. Consequently, specialized procedures must be identified, or methods optimized for use with petroleum-based products, and their performance characterized prior to or in conjunction with sample analysis. All phases of the sample preparation and analysis activities must be completely documented in order to provide technically and legally sound data indicating the composition and concentrations of contaminants in the LNAPL samples. Chain-of-custody (COC) records and procedural write-ups must be submitted with the CLP-formatted sample results.

1.1 GENERAL OVERVIEW

Because the LNAPL samples originated from the Rockwell International National Priority List (NPL) Site, and the potential exists for the data generated during the project to be used in an enforcement action, this document is being prepared using the format and content requirements designated for a Category I QAPjP (EPA, 1991). Certain sections of the document are not fully developed (e.g., Section 4.0, Site Selection and Sampling Procedures, Section 10.0, Performance and Systems Audits) due to the limited scope of the requested technical services and the short duration of the project.

1.1.1 The Rockwell International Site

The Rockwell International Corporation facility (Rockwell Site) is located adjacent to the Kalamazoo River in Allegan, Michigan. Operations at this site (until closure in July, 1992) included machining, hardening, and assembly of drive-line components for large vehicles. Various petroleum-based cutting and quench oils, water-soluble cutting oils, and cleaning compounds had been used in the manufacturing operations, and waste disposal at the site included settling ponds, an oil flotation house, and waste water treatment plant lagoons. In the course of measuring static water levels during the second phase of field work on the site, LNAPLs were detected in eight piezometers, and monitoring or recovery wells. Three locations (P-17, MW-10, and RW-3) were selected by the EPA and PRP for sampling, based on the thickness of the LNAPL layer present, the proximity of the well/piezometer to possible LNAPL sources, and other technical considerations discussed in the site Supplement to the Work Plan Addendum (Anon., 1993) and the Revised QAPjP Addendum (Remcor, 1993). These

sample locations are shown in Figure 1-1, attached to the above-mentioned Work Plan. The potential exists for the three LNAPL samples to exhibit quite different characteristics and contaminants due to their varying sources; a circumstance which must be anticipated in the project schedule and budget plans.

1.1.2 Project Objectives

The project objectives and consequent data quality objectives (DQOs) are based on the technical support request from the Region 5 RPM, the information contained in Supplement to the Former Rockwell International Corporation (Rockwell) Facility Work Plan Addendum and the Revised Rockwell RI/FS Quality Assurance Project Plan (QAPjP) Addendum, and communications with the TSP Work Assignment Manager (WAM), the RPM, and a representative of the Region 5 QA Staff.

The primary use of the data from these analyses, identified in the Region 5 letter of request, is as supplemental information for the RI/FS. More specific objectives for data use (given in the QAPjP addendum) include the identification of the source(s) of the LNAPLs and the potential impact of their presence on site conditions. The DQOs specified in the Revised QAPjP Addendum include Level III analyses for pesticide/PCBs and Level IV analyses for all other contaminant classes, however, it appears more appropriate to apply Level V analyses to the LNAPL samples due to the potentially complex matrices. DQOs will be discussed further in Section 3.0.

The objective of this project, as assigned to Lockheed, is to perform and document the analysis of the LNAPLs for the designated volatile organic compounds (VOCs), semi-volatiles (SVOCs), pesticides, polychlorinated biphenyls (PCBs), inorganic compounds (as total metals), and cyanide using methods which are appropriate to the sample types (NOTE: organic compounds of interest are those on the Target Compound List [TCL]; the metals of interest or those on the Target Analyte List [TAL]). In order to provide data which are of defined quality, project activities must include determinations of method precision, accuracy, and detection limits when applied to these matrices. The attainment and documentation of detection limits more sensitive than 1200 ug/Kg for VOCs and 10,000 ug/Kg for SVOCs have been identified as primary goals for this project. Success in achieving these goals will be dependent upon the quantity of sample available for method performance determinations, and the scientists' ability to concoct matrices which are physically and chemically consistent with the actual samples. As described in guidance documents (EPA, 1988a), successful implementation of the project will also include:

- Documenting the operational details of the methods
- Providing single laboratory performance data where this is feasible given the available matrix
- Ensuring that the method can be used by at least one other laboratory

1.2 EXPERIMENTAL DESIGN

The actual number of measurements made during the project will be dependent upon the quantity of each of the three LNAPL samples received from the Rockwell site. The target sample volumes are 240 mL (six 40-mL vials) for organic analyses and 150 mL (two 4-oz jars) for inorganic analyses from each location. A minimal amount of each matrix will be allocated for physical testing and gas chromatographic (GC) screening in order to determine the matrix characteristics. This will facilitate the identification or concoction of a suitable material to be utilized for method performance testing if insufficient real-world sample is available. The remainder will be aliquotted for sample preparation and analysis. The analytical priorities specified by Region 5 are, from highest to lowest priority:

1) SVOCs
2) PCBs/Pesticides
3) VOCs
4) Inorganic Compounds (Total Metals)
5) Cyanide

The Revised QAPjP Addendum indicates that, given sufficient matrix, seven QC samples were to be prepared for this project. These include a VOC trip blank and, in descending importance, a sample duplicate, a matrix spike, and a matrix spike duplicate (MS/MSD) for each LNAPL. Addition routine laboratory preparation/analytical QC samples would also include method/reagent blanks. A full complement of samples for the analytical portion of the project would number 18: three samples, three duplicates, six MS/MSDs, five preparation blanks, and a trip blank. Additional real-world or concocted matrix is required to determine matrix/method detection limits. A schematic of the planned analyses is given in Figure 1.

1.3 SCHEDULE

The holding times for each of the analytical parameters are given in Table 2-1 of the Revised QAPjP Addendum. While every effort should be made to perform the extractions and analyses within the specified time limitations (especially considering the legal implications), the Region 5 RPM and QA contact indicated that, with the exception of the VOC analyses, the impact of exceeding the holding times would be less severe than the failure to provide analyses which meet detection limit and documentation requirements.

According to the project Technical Work Plan (22210172), the results of the analyses are expected by March 9, 1993. Any preliminary analytical data or delays resulting from delays caused by such occurrences as instrumental downtime or resource (personnel or equipment) limitations will be reported to the WAM and appropriate documentation will be provided.

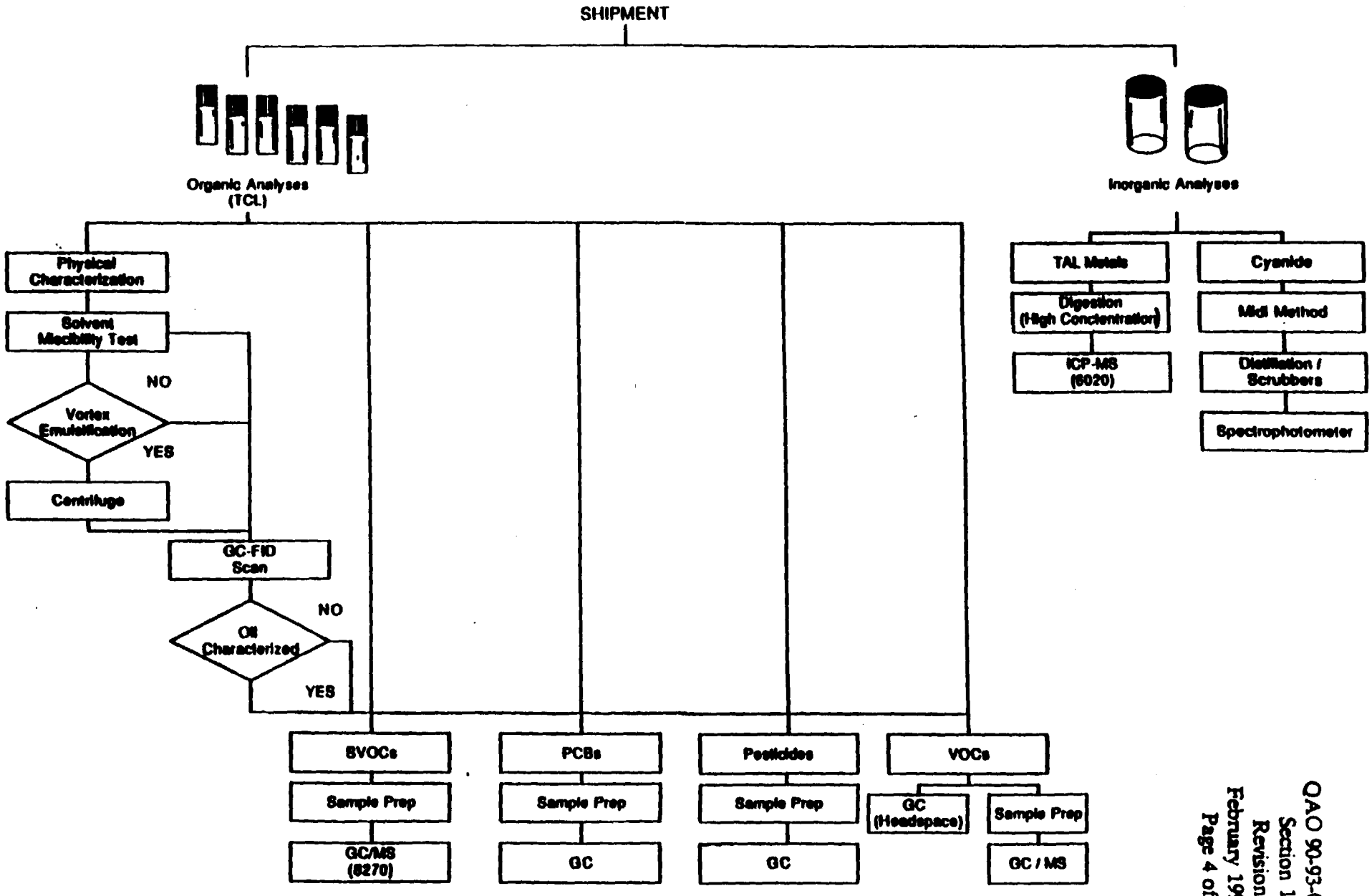

Figure 1. Schematic for analysis of organic and inorganic constituents in LNAPL samples.

SECTION 2.0

PROJECT ORGANIZATION AND RESPONSIBILITIES

This project, which primarily focuses on the analysis of LNAPL samples (including complete documentation of the methods used and sample and QA/QC data generated) from groundwater monitoring wells at the Rockwell International Superfund Site in Allegan, Michigan,, is being conducted under the Technology Support Project (TSP). As such, the request for technical support was made by the USEPA Region (Region 5: RPM, K. Sikora; QA Manager, A. Alwan) to the EMSL-LV TSP WAM (K. Brown; EMSL-LV Technical Lead, G. Robertson). The WAM, in turn, generated a Work Assignment for the LESAT TSP staff to perform the analytical work outlined above, described in Section 1, and detailed throughout this plan.

The specific roles and responsibilities of the EPA project management are not within the jurisdiction of this QAPjP, and are provided to show the overall flow of communication for this project. A flow diagram of project roles and responsibilities of key project personnel are provided in Figure 1.

The overall LESAT TSP operations are managed under the Field Methods Section of the Site Characterization Technologies Department. The **Field Methods Section Supervisor, J. Pollard**, is responsible for administering the TSP in reviewing, approving the Technical Work Plan (TWP) for this task (i.e., project), reviewing and approving the deliverables submitted to the WAM, and for assuring that the LESAT technical and support staff (within the section, and by coordinating with managers of other departments) are available to meet the project deadlines. The **Field Methods Section Quality Assurance Officer, V. Ecker**, is responsible for reviewing and approving QAPjPs for the section and for reviewing all data and data reports generated by tasks within the section. The Section QA Officer reports directly to the Section Supervisor and the Department Manager. The **LESAT TSP Coordinator, P. Malley**, is responsible for tracking all projects under the TSP and works with the Task Leader to prepare the TWP and identify the key personnel required to execute the task activities. The TSP Coordinator communicates with the WAM on a daily basis on issues including the status of the task and the need to utilize contingency planning. For each TSP task requiring analytical services, a project-specific QA lead is assigned. The **Project QA Lead, M. Silverstein**, is responsible for ensuring that the QAPjP is prepared, is complete, and is followed (and any discrepancies are documented). The QA Lead reports directly the TSP Coordinator and works directly with the Task Lead to ensure that the technical requirements of the project are being satisfied and that the analytical results and deliverables are of the required quality and documentation.

The **Task Leader, D. Youngman**, is responsible for preparing the TWP and the QAPjP and is the technical leader and focal point for the daily task operations and personnel coordination. The Task Leader is responsible for ensuring that all analytical activities involved in chain of custody, organic and inorganic sample analyses (including sample preparation) are being performed to project specifications, that all data are reported in required format (e.g., CLP-quality data package), that all

analysis methods are and data generated by their use are documented and are valid, and that complete technical write ups are submitted from all key technical personnel (i.e., LESAT Chemist Leads), and that all deliverables are prepared and completed within time and budgetary constraints. The Task Leader anticipates, identifies, and facilitates the resolution of technical issues and any contingencies needed. The Task Leader communicates directly with the Project QA Lead, the TSP Coordinator, and the WAM and the EMSL-LV Technical (Chemist) Lead, and reports directly to the LESAT Chemistry Department Manager. The Chemistry Department Manager, D. Hillman, is responsible for ensuring that Chemistry Department analysis personnel assigned for this project, including the Task Leader, are available as needed (coordinating with the Section Supervisor via the TSP Coordinator, when necessary) to resolve any scheduling conflicts. The Chemistry Department Manager will review the output (analysis data, case narratives, etc.) of the work generated by department personnel assigned to this task. The Chemistry Department Manager is also responsible for coordinating any needed subcontracted analytical services (in this case, the analysis of the cyanide fraction). The Organic Chemist Leads on this task are D. Youngman for the physical analyses, the SVOC analyses, and the GC/MS VOC purge-and-trap analyses; Neal Amick for the GC-FID oil classification analysis and the GC headspace VOC analyses; and for the PCBs and the pesticides analyses, the lead(s) are to be determined (TBD) and will be the responsibility of the Task Leader for oversight. The Inorganic Chemist Lead, D. Dobb, is responsible for the metals analysis and incorporation the cyanide analysis from the subcontractor. Each Chemist Lead is responsible for overseeing and/or conducting the analysis of the samples, for conducting or overseeing the sample preparation activities and personnel, for reporting the results and performing preliminary data quality review of the results, and for preparing case narratives and detailed procedural write ups for the methods used in sample preparation and analysis. The chemist Leads work directly with the Task Leader on providing a status of their progress and need to assess contingencies, and report directly to their respective supervisors/managers for any possible scheduling conflicts.

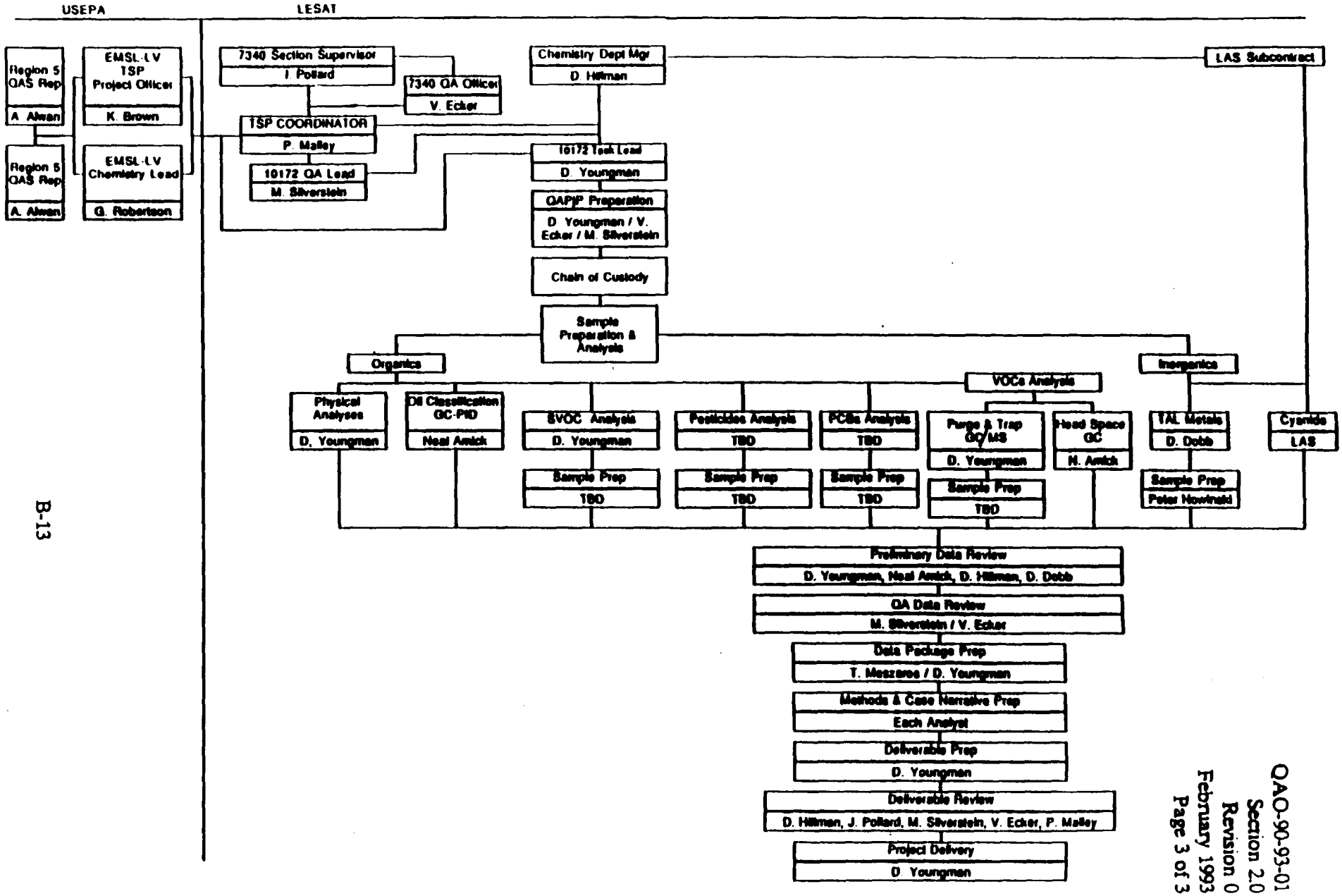

Figure 2. Overview of organization and key personnel roles for LNAPL sample analysis and reporting.

SECTION 3.0

QUALITY ASSURANCE OBJECTIVES

In order to properly utilize the information from this project, the sample results must be technically sound and of defined and documented quality. To achieve this end, and as required by the USEPA for all monitoring and measurement programs, objectives must be established for data quality based on their proposed end uses (Stanley and Verner, 1985). As stated in Section 1.1.2, the data produced here are intended to be used in support of the RI/FS, however the results will more specifically be used to discern the possible sources of the three LNAPLs and evaluate their impact on overall site conditions.

The Region 5 documents (QAPjP and Work Plan Addenda, with revisions) indicated that "The analytical levels applicable to this activity and defined by EPA are as follows:

- Level III - All analyses are performed in an off-site analytical laboratory. ....may or may not use the CLP procedures, but do not usually utilize the validation or documentation procedures required of CLP Level IV analyses. (Note: this analytical level is to be used for PCB/pesticide analyses.)

- Level IV - CLP routine analytical services (RAS). All analyses performed in an off-site CLP analytical laboratory following CLP protocols. Level IV is characterized by rigorous QA/QC protocols and documentation." (Note: this analytical level is to be used for all other LNAPL analyses.)

Later in this section of the Region 5 document, the above analytical levels are described as DQO Levels III and IV, however no project-specific objectives are given. According to the Agency, "QA objectives must be defined in terms of project requirements, and not in terms of the capabilities of the intended test methods (EPA, 1991)." Analytical Level V (Non-conventional parameters, method-specific detections limits, and modification of existing methods [EPA, 1988b]) seems to be more appropriate to these analyses, however, little guidance was available from the data users as to the actual quality of the results which would satisfy their technical and enforcement-related needs. To the extent possible, given the TSC/EMSL-LV/Lockheed understanding of the Region's request, more definitive statements of project quality objectives will be described in this QAPjP.

The parameters generally accepted as indicators of data quality include: precision, accuracy (which may be expressed as bias), representativeness, completeness, and comparability (Stanley and Verner, 1983). In this project method detection limits (MDLs) for the LNAPL matrix are also critical. The quantitative data quality objectives (DQOs) for this demonstration are given in Table 1.

The DQOs for precision and accuracy of the modified methods are derived from data generated by interlaboratory studies using EPA methods (Laing, 1989), since this is the data quality to be expected

Table 1. Data Quality Objectives for LNAPL Sample Analyses

Critical Measurement	Analytical Method	Accuracy (% Recovery)	Precision (RPD/RSD[a])	MDL (µg/Kg)
Volatile Organic Cmpds.				
Headspace	CLP Draft QTM,GC	50 - 150 [b]	≤ 30% [c]	400 [b]
Purge & Trap	CLP OLM01,GC/MS	75 - 125	≤ 25%	<1200
Semivolatile Org. Cmpds.	CLP OLM01/8270, GC/MS	60 - 110	≤ 35%	<10,000
Pesticides	CLP SOW/8081,GC	50 - 150	≤ 50%	100
PCBs	FASP Extr./CLP OLM01/8081,GC	50 - 150	≤ 50%	1000
TAL Metals	CLP High Con. Dig. CLP 6020-M,ICP/MS	80 -120% [b]	≤ 25% [b]	Same as 6020 Soils
Total Cyanide	CLP 335.2 Distil. 9012,Spectrophot.	80 - 120	≤ 25%	500

[a] RPD = relative percent difference or RSD = relative standard deviation of spiked/unspiked laboratory duplicates
[b] As specified in applicable published method
[c] As demonstrated in Helms, 1992

from a laboratory in the CLP, and appear to be acceptable to the Region 5 RPM and QA Staff. Although meeting the DQOs for these analyses is the optimal result of the laboratory work, failure to do so does not necessarily mean that the data will not meet the needs of the project, provided that the data generated is of defined quality, is adequately documented and is able to be reproduced in another laboratory.

3.1 REPRESENTATIVENESS

Representativeness is defined as "the degree to which the data accurately and precisely represent a characteristic of a parameter, variation of a property, a process characteristic, or an operational condition" (Stanley and Verner, 1985). In this project, the sampling collection program should have been carried out in such a manner that each sample taken is representative of the wells/piezometers and matrix type found at the three designated locations on the site. The integrity of the samples must be maintained by using the appropriate containers and shipping and storing them at 4 °C. In addition, the LNAPL phases must be separated from any stagnant water and extraneous materials in such a way so as not to jeopardize the character, composition, and contaminant content of the target matrices. VOC trip blanks and laboratory holding blanks must be prepared to qualitatively and quantitatively disclose interferents introduced prior to analysis.

3.2 COMPLETENESS

Completeness is defined as "a measure of the amount of data collected from a measurement process compared to the amount that was expected to be obtained under the conditions of measurement" (Stanley and Verner, 1985). The completeness goal relates not only to the number of samples successfully taken, but also to the proportion of valid data (i.e., data not associated with some criterion of potential "unacceptability" with respect to instrument calibration, detection limits, or results of QC samples) relative to the entire body of data. Because it is quite possible that only small quantities of LNAPL sample will be available for collection at one or more of the locations (Remcor, Section 2-16, 1993), it is not realistic to anticipate fulfilling a goal of 100% completeness for all analyses. Instead, the completeness goal for the various types of analyses which are able to be carried out with the available samples is 100%.

3.3 COMPARABILITY

Comparability is defined as "the confidence with which one data set can be compared to another" (Stanley and Verner, 1985). To the extent possible, the procedures used will be based on technically accepted, if not promulgated, Program-Level EPA methods (e.g., Draft CLP Quick-Turnaround Methods, Modified CLP ICP/MS, ESAT SOPs). Any modifications to those methods must be completely documented. Data verifying method performance for precision, accuracy, and detection limits, as well as those indicating evidence of systematic bias should be generated to enable utilization of the results in conjunction with other site information. All results must be reported as $\mu g/Kg$ of target analyte and tentatively identified compounds (TICs), to two significant figures.

3.4 ACCURACY and BIAS

Accuracy refers to the difference between a measured result and the true, or reference value. A systematic error in the accuracy of a method or measurement system is termed bias (Taylor, 1987). Bias may be exhibited in the results of the LNAPLs due to matrix interferences, detection of non-target compounds, systematic contamination or "carryover" of analyte, or loss of more volatile compounds during isolation of the LNAPL phase from co-sampled stagnant water. Accuracy and bias will be assessed using data from analyses of duplicate or split samples, concocted QC samples, and MS, MSD, and surrogate recoveries.

3.5 PRECISION

Precision, defined as the degree of mutual agreement among individual measurements, provides an estimate of random error (Taylor, 1987). In this project, for quantitative, continuous data, precision will be expressed in terms of the relative percent difference (RPD) between duplicate or split samples or the percent relative standard deviation (%RSD) between multiple analyses of concocted QC samples over the course of the evaluation.

3.6 METHOD DETECTION LIMITS

For this demonstration, Region 5 has requested that the demonstrated MDLs for VOCs and SVOCs be more sensitive than 1200 μg/Kg and 10,000 μg/Kg respectively. MDLs should be generated using clean LNAPL matrix (i.e., LANPL which has been shown to be free of the target analytes) or a matrix possessing physical characteristics similar to the LNAPLs which has been spiked with some or all of the compounds from the analytical fraction being investigated. The DQOs for MDLs are given in Table 1.

SECTION 4.0

SITE SELECTION AND SAMPLING PROCEDURES

The selection of the sites to be sampled and the procedures by which the samples will be collected are not within the control of LESAT and are, therefore, not an aspect of the QAPjP nor sample integrity for which LESAT can be responsible. LESAT has recommended the types of sample containers and volumes preferable. A brief discussion of the site selection and sample collection procedures are provided below.

4.1 SITE SELECTION

LNAPL samples will be collected from three locations on the Rockwell International site, from Piezometer P-17, Monitoring Well MW-10, and Oil Recovery Well RW#3 (Remcor, February 1993).

4.2 SAMPLING PROCEDURES

According to the Remcor, Inc., Work Plan Addendum (February 3, 1993), LNAPL samples will be collected from each well as follows: an oil/water interface probe will be measure the depth to the LNAPL surface; a sampling tube marked to the measured LNAPL depth will be lowered into the LNAPL layer, at which time pumping will commence. If possible, sufficient sample to fill all sample bottle volumes will be collected (see Section 4.3 for volumes); samples will be immediately placed in shipping coolers at 4 C for shipment to EMSL-LV/LESAT.

4.3 SAMPLE CONTAINERS AND VOLUMES

Sample bottles should be filled in accordance with the following order:

TCL Organics (SVOCs, pesticides/PCBS, VOCs), filling as many of six 40-mL glass (VOA) vials as possible (approximately two per analysis class).

Inorganics (TAL Metals, Cyanide), filling two 4-ounce amber glass bottles (with Teflon-lined screw caps) with any remaining LNAPL sample.

4.4 DECONTAMINATION

Decontamination procedures for field sampling equipment is provided on Page 3-6 of the Work Plan Addendum.

4.5 SAMPLING QUALITY CONTROL SAMPLES

Protocols for the collection of field quality control samples is provided on Page 3-7 of the Work Plan Addendum, and include field duplicates and trip blanks.

SECTION 5.0

SAMPLE CUSTODY

Since it is expected that the data generated from the LNAPL analyses may be used for litigation purposes, strict chain-of-custody procedures on the samples and the raw and supporting data generated from the analyses is required. LESAT has no control of the samples in the field, therefore, responsibility for ensuring sample custody procedures are followed begins, for LESAT, when the samples are transferred from the overnight courier into LESAT's possession at the Lockheed Analytical Services (LAS) laboratory in Las Vegas. The Task Leader, who will act as the Sample Custodian for this project, is responsible for ensuring proper chain-of-custody procedures are followed. These procedures are described below.

5.1 SAMPLE LOG-IN AND STORAGE

Once the shipping sample containers arrive at LAS, the sample shipment, by LAS policy, is considered physical evidence. Although, the sample handling will be managed by EMR&D staff via the EMR&D Task Leader, the samples will be housed in the LAS facility, whose chain-of-custody program is in compliance with procedures established by the National Enforcement Investigation Centers. Therefore, security within the facility applies to EMR&D activities and samples, as well.

The samples are to be accompanied with Chain-Of-Custody forms and Request for Analysis forms from Remcor (see Appendix A). Upon arrival at LAS, the Task Leader will first check the numbers and condition of the shipping containers and then inspect the contents of the containers against the information on the Remcor custody and analysis forms. The sample bottles will also be inspected for leakage or damage. Any bottles exhibiting a condition that may affect the integrity of the sample will be documented on the custody forms and in a logbook or other appropriate form, and the WAM will be notified. Once the samples have been inspected, they will be stored in a sealed box in a designated locked refrigerator (which includes a temperature log), and the accompanying paperwork filed in a locked cabinet. Refrigerator and file keys will be maintained by the Task Leader or designee.

5.2 SAMPLE TRACKING

Only the Sample Custodian or designee is permitted to remove the samples from the secured storage area. Therefore, sample preparation and sample analysis personnel can only obtain samples with properly prepared sample tracking forms. If sample containers are changed during processing (e.g., splitting, diluting, digestion), a new sample bottle label must be affixed to the bottle, and the activity documented in a logbook and sample tracking form. When required, samples will be transferred to the custody of personnel other than EMR&D staff or to off-site locations (e.g., cyanide fraction to the LAS subcontractor, TAL metal digestates to the EMSL-LV laboratory facility). In these instances samples will be tracked via appended sample tracking forms. For the LAS cyanide fraction, sample tracking and custody will also be ensured by following the laboratory's procedures #LAL-90-SOP-002

and #LAL-90-SOP-009.

5.3 SAMPLE DISPOSAL

Any sample or sample preparation fractions (e.g., diluents, digestates, extracts) will remain in the custody of the Sample Custodian until written notification by the WAM as to the final disposition of the samples (i.e., disposal or transfer to another facility, such as the Region or the PRP). Samples will be stored up to 60 days after the delivery of the data package to the WAM.

5.4 SAMPLE AND SUPPORTING DATA DOCUMENTATION

All sample preparation techniques and analytical methods used in sample analysis must be documented in logbooks or on preprinted forms. Experimental conditions and parameters, such reagent grades, lot numbers, operating temperatures, reaction times, and instrument settings must be noted, as appropriate. The results of all QC sample analyses should be recorded if generated using manual instrumentation; and proper annotation of instrument output for automated analyses for project samples and associated QC samples should be performed, including such output as properly marked chromatograms and ICP-MS data printouts. Supporting analytical data documentation must be secured in a locked file cabinet until the completion of the project data report, at which time all raw data will be submitted to the WAM. Copies of all sample data, instrument output, logs entries, and other raw and support data will be made and stored in the job order file for this project. No extraordinary security for this information is required.

SECTION 6.0

CALIBRATION PROCEDURES AND FREQUENCY

The calibration procedures and technical acceptance criteria described below are, unless otherwise indicated, taken from methods utilized in the Contract Laboratory Program (CLP), SW-846, or EPA Regional Laboratory SOPs. Because of time limitations on the LNAPL analyses, any failure to meet these criteria (e.g., an analyte calibration factor (CF) not meeting the %D limits in a continuing calibration) must be evaluated on a case-by-case basis by both technical and QA staff, based on the impact on data quality and overall project objectives.

6.1 PHYSICAL TESTING

Several tests are to be performed in order to determine the physical characteristics of the LNAPL matrices. These include sample miscibility with water and solvents, vortex emulsification, and centrifugation. Such testing involves no instrumentation or equipment-dependent measurements and consequently requires no calibration steps.

6.2 HYDROCARBON SCREENING

Gas chromatographic (GC) screening (with flame ionization detection [FID]) of the LNAPLs will be used primarily to determine the approximate boiling point(s) of the sample components. The analytes and their concentrations in the standard are given in Appendix B. Although the standard solution is prepared at a specific concentration range (80 - 100 ug/mL), compound quantitation is not performed on the basis of these analyses. The single-level standard must be injected several times to verify instrument stability, and the retention times (RTs) of the various alkanes are used to help characterize the unknown sample.

6.3 SEMIVOLATILE ANALYTE ANALYSIS BY GC/MS

Calibration procedures will be followed as per RCRA Method 8270.

6.4 PESTICIDE ANALYSIS

Calibration procedures will be done according to CLP 3/90 SOW (or Method 8081).

6.5 POLYCHLORINATED BIPHENYL (AROCLOR) ANALYSIS BY GC

Calibration procedures will be done according to CLP 3/90 SOW (or Method 8081).

6.6 VOLATILE ORGANIC COMPOUND ANALYSIS

Two methods will be investigated for use in the analysis of the LNAPLs for volatile organic compounds (VOCs): the Quick Turnaround Method (QTM) (EPA, 1993), and the CLP Multi-media, Multi-concentration Statement of Work (SOW) (EPA, 1990).

6.6.1 Volatiles: Headspace

The CLP QTM requires calibration standards to be prepared daily and analyzed via headspace sample introduction (in the following order) at three concentrations: 500, 100, and 20 ng/mL (ppb) in water. The analyte composition of the standards are given in Appendix B. The initial calibration must be used to establish the calibration factors for compound quantitation, to define the RT windows for compound identification, and to determine the mean SMC RT for evaluating SMC shift during analyses. The technical acceptance criteria are:

- The %RSD of the CF for each target compound and the SMC in the initial calibration must be $\leq$ 25%. Up to two compounds may exceed the 25% limit, however all compounds must be $\leq$ 40% RSD.
- The RT of the SMC in each standard must be within $\pm$ 1.0% of the mean RT calculated from the three initial standards.
- Peak resolution must attain a valley $\leq$ 25% between cis-1,2-dichloroethene and chloroform in the low level standard.
- The response of all compounds in the low standard must be > 10% full-scale deflection.

A mid-point calibration standard (100 ppb) must be analyzed at least daily to check the on-going validity of the initial standard curve. The technical acceptance criteria are:

- %D between the CFs of each target compound and the SMC in the calibration check and the mean CF of that compound in the initial calibration must be $\pm$ 35%. Up to two compounds may exceed that limit, however all compounds must be within $\pm$ 45%.
- The absolute and relative RTs of all target compounds must be within the RT windows established by the initial calibration.
- The RT of the SMC in each standard must be with $\pm$ 1.0% of the mean RT calculated from the three initial standards.
- Peak resolution must attain a valley $\leq$ 25% between cis-1,2-dichloroethene and chloroform.

If sufficient time is available, experiments may be performed to examine the behavior of calibration standards prepared in a simulated LNAPL matrix. These attempts are also dependent upon the miscibility of the LNAPL with methanol and other solvents.

6.6.2 Volatiles: Purge and Trap

The CLP Multi-media, Multi-concentration SOW requires that calibration standards be analyzed at five target analyte concentration levels: 10, 20, 50, 100, and 200 ug/L. The relative response factor (RRF) and the %RSD across the five standards must be calculated for each analyte. With the exception of 12 compounds, all analytes must have a %RSD < 20.5%. The minimum acceptable RRF for all compounds, and the 12 compounds excepted from the %RSD limits are given in Table 2 and Section 7.4.6 of Exhibit D/VOA in the SOW.

The calibration curve must be verified once each 12 hours through the analysis of the 50 ug/L standard. The calculated RRFs for all but the 12 indicated compounds must show < 25% D versus the average RRFs from the initial calibration. In both the initial calibration and the continuing calibration check, up to two compounds in Table 2 may fail to meet the minimum RRF and either the %RSD or %D acceptance criteria, however the RRFs of those two compounds must be $\geq$ 0.010, and the %RSD or %D can be no greater than 40% for the calibration to be acceptable. Additional acceptance criteria for the initial and continuing calibration (e.g., internal standard responses, RT changes) are given in Section 7 of VOA Exhibit D.

6.7 METALS

See Section 9 for details.

6.8 CYANIDE

See Section 9 for details.

SECTION 7.0

ANALYTICAL PROCEDURES

Where applicable, standard EPA methods or SOPs should be used for sample preparation. Non-standard methods and specific modifications to EPA-approved methods are described below (to the extent possible prior to actual sample manipulation). Deviations, additions, and further modifications to the material given in this QAPjP must be completely documented and included in the case narrative, method descriptions, and/or summary write-ups submitted to the WAM and Region 5 RPM.

7.1 PHYSICAL TESTING

After arrival, 2g of the oil matrix will be added to five different conical-shaped glass centrifuge tubes and an equal volume of following solvents will be added: (1) water, (2) methanol, (3) hexane, (4) methylene chloride, (5) toluene. The tubes will be observed to note any physical characteristics (miscibility, density) which may be relevant to this project. The tubes will then be processed using a Vortex mixer for a period of 30 seconds and the physical characteristics will then be noted. Finally the tubes will be centrifuged for 2.0 minutes at 2000 revolutions per minute and their characteristics observed again.

7.2 HYDROCARBON SCREENING

The GC screening procedure is based on analyte separation procedures in SW-846 (EPA, 1986) Methods 8010/8015/8020 for the analysis of VOCs. Samples are diluted in methylene chloride and direct injected onto a capillary chromatography column (30m RTX-5, 0.53 micron film thickness) with 40° - 290° C temperature programming. Serial dilutions (1:10, 1:100, etc.) must be made to achieve analyte responses approximately 50% of full scale. The nature and boiling point range of the LNAPL matrices is determined through comparison of the straight-chain hydrocarbon peak RTs with those of the mixed alkane standard.

7.3 SEMIVOLATILE ANALYTE ANALYSIS BY GC/MS

RCRA Method 8270 will be used for the analysis of semivolatiles.

7.4 PESTICIDE ANALYSIS BY GC

Pesticides will be analyzed by GC using RCRA Method 8081.

7.5 POLYCHLORINATED BIPHENYL (AROCLOR) ANALYSIS BY GC

Aroclors will be analyzed using the Field Analytical Support Project (FASP) preparation method for transformer oils followed by GC/ECD using the current CLP 3/90 method.

7.6 VOLATILES ORGANIC COMPOUND ANALYSIS

7.6.1 Volatiles: Headspace

Volatiles for headspace will be done using the current revision of the quick turnaround method (QTM).

VOLATILES: PURGE AND TRAP

Volatiles for purge and trap will be done as prescribed in the CLP 3/90 SOW.

7.7 TAL METALS

7.7.1 Sample Preparation

Sample preparation for TAL Metals analysis will be achieved using a modification to the digestion procedures used in the High Concentration Inorganic Statement of Work (HCIn SOW) as documented in Suarez et al, 1993. This digestion procedure, Method 200.XX-A-CLP, is an alternative to the potassium hydroxide fusion method specified in the HCIn SOW, using microwave digestion with hydrofluoric acid for metals analysis of oils, oily soils, soils, and aqueous phase materials which are expected to be analyzed for TAL metals.

7.7.2 Sample Analysis by ICP-MS

The TAL metals will be analyzed using ICP-MS using EPA Method 6020-M, Version 8.1, after the digestion step described above and in Suarez et all, 1993. Method 6020 describes the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio-frequency inductively coupled plasma. NOTE: Since the data quality for the analysis of mercury has not been adequately assessed for this method, and since mercury is a TAL Metal, confidence in the results for mercury by this method may be in question. It is known that this method will confidently detect mercury and conversely, if mercury is not in the sample, a nondetect result is considered a valid analysis. Therefore, if mercury is not detected in the LNAPL samples, no further analysis is required. If mercury is detected, in order to adequately quantitate the concentration, cold vapor atomic absorption spectroscopy will be required. Method 7471, which includes sample preparation, will then be employed.

7.8 TOTAL CYANIDE ANALYSIS BY MIDI DISTILLATION

The LNAPL samples will be analyzed for total cyanide via subcontract to LAS using LAL-91-SOP-0098. The samples will be analyzed using the Midi distillation protocol (Exhibit D Method 335.2) followed by Method 9012, Total Amenable Cyanide (Colorimetric, Automated UV). See Section 9 for QA/QC and contingencies of analysis.

SECTION 8.0

DATA REDUCTION, VALIDATION, AND REPORTING

8.1 DATA REDUCTION

Data reduction is the respective responsibility of the analyst for each analytical class of measurements (SVOCs, Pesticides, PCBs, VOCs, Metals, Cyanide) as specified in Section 2 and displayed in Figure 2. Data reduction procedures will be conducted in accordance with protocols specified in each analysis method (Section 7). Any deviations from these protocols required to reduce the sample and QC data will be fully documented in the methods modification write up and delivered to the WAM.

8.2 DATA VALIDATION

Data validation will be the responsibility of the Task Leader for organic analyses and D. Dobb or D. Hillman for inorganic analyses. Because of the unique aspects of sample analysis and the small sample size, there are no plans for outlier detection. If applicable, data qualifiers applied to sample results data will be those typically used in the CLP program. If other data flags are required, these qualifiers will be defined in the data report, as will the definitions of CLP flags.

8.3 DATA REPORTING

Data for all organic analyses and inorganic analyses will be reported in $\mu g/Kg$.

A description of the data reports, data storage requirements, and the project deliverables are provided in Section 14. All deliverables will be reviewed by the Task Leader, the Project QA Lead, the Section Supervisor and QA Officer, the Chemistry Department Manager, and the TSP Coordinator.

SECTION 9.0

INTERNAL QUALITY CONTROL CHECKS

9.1 PHYSICAL MEASUREMENTS

Not applicable.

9.2 HYDROCARBON (GC-FID) SCREEN

Not applicable.

9.3 SEMIVOLATILE ANALYSIS

QA/QC procedure will be followed as per the RCRA method 8270. Such QA/QC methods involve surrogate recoveries, matrix spikes, control checks on internal standard areas, acceptable criteria for the initial and continuing calibrations.

9.4 PESTICIDES

QA/QC procedures will be done according to CLP 3/90 SOW (Method 8081) and Table 2. This includes addition of a surrogate standard and acceptable criteria for initial and continuing calibrations.

9.5 POLYCHLORINATED BIPHENYLS

QA/QC procedures will be done according to CLP 3/90 SOW (Method 8081) and Table 2. This includes addition of a surrogate standard and acceptable criteria for initial and continuing calibrations.

9.6 VOLATILES

9.6.1 Volatiles: Headspace

QA/QC procedures described in the CLP QTM protocol will be followed. These include criteria for initial and continuing calibrations, control checks on internal standard areas, and the addition of surrogate compounds and matrix spike/duplicates.

9.6.2 Volatiles: Purge and Trap

QA/QC procedures described in the CLP 3/90 SOW will be followed. These include criteria for initial and continuing calibrations, control checks on internal standard areas, and the addition of surrogate compounds and matrix spike/duplicates.

TABLE 2. METHOD 8081[a] QUALITY CONTROL REQUIREMENTS

QC ELEMENT	SPECIFICATIONS	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
1. Initial calibration	•Pesticides/PCBs plus surrogates at three concentration levels	•< 20% RSD of the analyte responses or CFs over the concentration range is required to use mean CF for quantitation	•Plot calibration curves for analytes with responses or CFs >20% RSD •Prepare new standards
2. Continuing calibration verification	•Analyze one midpoint standard after each group of 20 samples or less (and at end of analysis)	•CF or response (height or area) for each analyte ± 30% of the mean response for that analyte in the initial calibration standards	•Clean injection port, replace septum and recalibrate
3. Demonstration of the suitability of the extraction method, precision and accuracy, determination of method/matrix quantitation limits, and establishment of RT windows (Alternatively, RT windows may be determined by the analyses of 3 standard solutions)	•A minimum of four replicates of a clean oil matrix spiked with low levels of representative pesticides/PCBs carried throughout the entire extraction, cleanup, and analysis scheme	•No QC limits for oils are given in the applicable methods •Generate acceptance limits using the instructions in Method 8000 •The method detection limit calculated according to p. 19 of method 8081 must be sufficient to detect analytes at the levels required for site cleanup	•Perform maintenance and/or perform a new three-point calibration, and rerun the analyses •Utilize an alternative extraction method or solvent combination
4. Daily retention time windows	•Absolute retention time of each analyte in the daily standard ± 3 times the standard deviation of the RTs determined in number 3	•The RTs of major peaks in continuing standards must fall within the daily RT window	•Perform necessary maintenance and recalibrate
5. Instrument blank (Hexane or isooctane)	•Daily, prior to standard or sample analysis •Following samples containing analytes > the high standard	•No analytes present >PQL or low level standard, which ever is less •No QC-introduced interferences	•Repeat until blank meets the acceptance criteria •Decontaminate instrument
6. Method blank	•Blank matrix + surrogates •One/sample preparation batch •Carry through all extraction and cleanup steps	•No analytes present >PQL or low level standard •No reagent or glassware-introduced interferences	•Remove source of contamination •Reanalyze associated samples •If insufficient sample remains, flag sample results with "g"
7. QC check samples	•Spike clean matrix with a representative pesticide/PCB at the regulatory limit or 1 - 5 times the background conc. •Minimum of one/20 routine samples	•Recovery must be within the limits determined in number 3, above	•Identify and correct sample preparation or analytical problems •Recalibrate instrument •Reanalyze associated samples
8. Matrix Spike/Matrix Spike Duplicates	•Spike a routine sample in duplicate at 1 - 5 times the background concentration •Minimum of one/20 routine samples	•Recovery must be within the limits determined in number 3, above	•Analyze a QC check standard to verify that analytical system is in control
9. Surrogate Standards	•In each blank, routine sample, QC sample, and standard •2,4,5,6-tetrachloro-m-xylene decachlorobiphenyl	•Acceptable recovery limits must be determined by the procedures given in Method 8081	•Check calculations, surrogate and standard solutions •Reanalyze extract, reextract or flag results with "J"(estimated)

[a]EPA, 1990

RT = Retention time
%RSD = % Relative standard deviation
QC = Quality control
CF = Calibration factor
PQL = Practical quantitation limit
%R = % Recovery

9.7 TAL METALS BY ICP-MS

Table 3 provides the quality control specifications for the ICP-MS analyses.

9.8 TOTAL CYANIDE ANALYSIS BY MIDI DISTILLATION

This method uses the Midi distillation apparatus (Exhibit D Method 335.2) with a semi-automated spectrophotometer. Many laboratories use a completely manual spectrophotometer. The holding time is 12 days after receipt by which the complete (post-distillation) analysis for cyanide must be finished. LAS uses the Midi apparatus with a manual spectrophotometer (LAL-91-SOP-0098).

LAS's reporting limit for liquids is 20 μg/L. This is double the value specified in the SOW for Inorganics. LAS has a reporting limit of 0.5 mg/Kg for solid samples which equals the SOW for Inorganics. This is achieved using a 2 gram nonaqueous sample rather than 1 gram as specified in the method. Using a doubled sample size should not have any adverse effects if the total cyanide concentration if the concentration of the sample is low. One caution, if this oil sample is a sudsy sludge, there is the possibility insoluble particulate may contain large concentrations of cyanide. A high concentration of cyanide in the sample will yield low reported values for cyanide. But this cannot be determined until the analysis is performed. To ensure maximum data quality the following should be included in a request for cyanide analysis:

- Maximum holding time 12 days.
- The laboratory performing the work should meet a detection limit of 0.5 mg/Kg using a midi or equivalent distillation apparatus using either a manual or semi-automatic spectrophotometer.
- In addition to the normal QA/QC, a matrix spike should be performed on each sample to ensure reasonable cyanide data is obtained on each sample to be analyzed. Spike each 50-mL solution to be distilled, containing the 1 or 2 gram sample, with 2.5 to 5 μg of CN^- (yielding a CN^- solution concentration of 50 to 100 μg/L). The laboratory control sample should also use the same amount of cyanide as the matrix spikes.

TABLE 3. METHOD 6020 CLP-M QUALITY CONTROL REQUIREMENTS

QC ELEMENT	SPECIFICATIONS	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
1. Mass calibration and resolution check	• at the beginning and the end of each or twice per 8 hour working shift	• 0.1 amu difference from the true value • resolution <0.1 amu full width at 10% peak height	• adjust the mass calibration to the correct values
2. Tuning solution	• at the beginning and end of each run	• <10% RSD on 4 replicates	• check instrument hardware • allow more time for instrument warm-up
3. Initial calibration	• analytes of interest at least one concentration level and blank		
4. Initial calibration verification (ICV)	• immediately after the calibration has been established	• +/-10% of the true value for each analyte conc.	• recalibration of the instrument and new verification
5. Initial calibration blank (ICB)	• immediately after ICV	• concentration of the analytes < CRDL	
6. Memory test	• performed on the tuned and calibrated instrument	• concentration of the analytes in the memory test blank < CRDL	• increase the rinse time • change the instrument hardware • change the conc. of the element which is failing the test
8. Continuing calibration verification (CCV)	• after memory test • every ten routine samples	• +/-10% of the true value of the each analyte conc	• recalibration of the instrument
9. Continuing calibration blank (CCB)	• after every CCV	• conc. of the analytes <CRDL	• flush system for at least 30 sec. with the rinse blank
10. Interference check solution for ICP-MS (ICSA and ICSAB)	• at the beginning of the analytical run or once every 8 hours	• for A sol. conc. of the analytes <CRDL • for AB sol. <20% of the true value	
11. Detection limit sample (CRDL)	• at the beginning and end each sample analysis run • minimum twice every 8 hours	• <50% rsd of the true value	• instrument must be recalibrated

SECTION 10.0

PERFORMANCE AND SYSTEM AUDITS

10.1 PERFORMANCE AUDITS

Performance audits are generally based on data resulting from the analysis of standard reference materials. Samples having known concentrations may be tested as unknown in the laboratory or a sample may be analyzed for the presence of certain compounds. Performance audits are used to determine objectively whether an analytical measurement system is operating within established control limits at the time of the audit. The performance of personnel and instrumentation are tested by the degree of accuracy obtained. For this project, typical performance audits will not be used because of the scope, level of effort, and required turnaround time for the sample data. The only type of performance sample that will be attempted are analytes of interest spiked into motor oil.

10.2 SYSTEM AUDITS

Systems audits are qualitative on-site field or laboratory audits that evaluate the technical aspects of the operations (e.g., sample preparation, sample analysis) against the requirements of approved QA plans and protocols. System audit reports note problems and recommend or initiate corrective actions to be taken to ensure the validity of collected data. For this project, field systems audits are not applicable.

For this project, s system audit is a qualitative evaluation of the data acquisition program at the laboratory. The purpose of such audits is to ensure that sample and data collection activities for the demonstration are being conducted in accordance with the demonstration and QA project plans, designated methods and Standard Operating Procedures (SOPs). The systems audit consists of the evaluation of field and laboratory facilities, equipment, personnel qualifications, and operations such an sample collection and handling, record keeping, chain-of-custody/sample tracking, data reporting, and QA procedures. The results of any on-site evaluations conducted during this project will be summarized in a report that includes observations, substantive notes on interviews with personnel, problems and corrective actions, and recommendations.

A laboratory on-site evaluation will be conducted at the discretion of Project QA Lead. During the on-site laboratory evaluations, operations and instrumentation will be inspected. Laboratory analysts will be interviewed and their activities will be observed to ascertain the use of good laboratory practices during analytical operations. Key personnel should be prepared to make QC data available for auditor inspection. Sample receipt and chain-of-custody/sample tracking processes will also be observed and appropriate documentation reviewed.

SECTION 11.0

PREVENTATIVE MAINTENANCE

LESAT's Equipment and Systems Section maintains records on all analytical instruments, equipments, and computer systems used under the EMR&D contract. Personnel from this Section are responsible for performing preventative maintenance on all instruments and for updating maintenance and repair logs. The frequency of repair requests, number of downtime hours, repair hours, and repair costs are documented and reported to Lockheed management and to EMSL-LV by quarter and for the year-to-date. In addition, SOPs for each analytical instrument include routine maintenance and procedures that must be performed by personnel familiar with the equipment and, when performed, must be completely documented in individual logs.

As a precaution, and because of the oil matrix to be analyzed in this project, GCs will be equipped with guard columns. Instrument performance will be verified prior to and following sample analysis.

SECTION 12.0

CALCULATION OF DATA QUALITY INDICATORS

The assessment of data quality with respect to the QA objectives and the DQOs described in Section 3.0 will be conducted using several approaches. The results of different types of sample analyses or measurements will be used to assess completeness, accuracy, precision, and MDLs. The assessment procedures to be used on the results generated from the measurements and the applicable calculations are described below.

12.1 COMPLETENESS

Degrees of completeness will be assessed at two levels. The first level of completeness is determined based on the number of samples or measurements actually collected in proportion to the number that could have been collected. Incompleteness at this level is due to the inability to collect the appropriate sample matrix/phase (LNAPL vs. groundwater), collection of insufficient sample volume, or equipment failure. At the second level, incompleteness is based on the amount of valid data obtained from those samples or measurements actually collected. Incompleteness at this level is due to samples or measurement data associated with unacceptable QC analyses or a measurement system that is out of statistical control.

Completeness will be calculated by:

$$\%C = 100 \times (V/n)$$

where:

- %C = percent completeness
- V = number of measurements judged valid
- n = total number of measurements necessary to achieve an acceptable and technical level of confidence

12.2 ACCURACY

Accuracy will be assessed by evaluating the concocted QC sample measurements and surrogate and matrix spike recoveries.

For situations where concocted (synthetic) QC samples are used, accuracy will be calculated by:

$$\%R = 100 \times C_m / C_t$$

where

%R = percent recovery
C_m = measured concentration of the concocted sample
C_t = theoretical concentration of the concocted sample

For cases where surrogates and matrix spikes are employed, percent recovery will be calculated by:

$$\%R = 100 \times (S-U/C_s)$$

where

%R = percent recovery
S = measured concentration of the spiked sample
C_s = concentration of the spike added to the sample
U = measured concentration of the unspiked sample

12.3 PRECISION

The precision of each of the analytical methods employed in the analysis of the LNAPL samples will be evaluated by replicate analysis of QC samples (e.g., field and method duplicates, concocted QC samples).

The following equation will be used to calculate relative standard deviation (%RSD) of replicate (three or more) measurements of one sample type:

$$\%RSD = 100 \times (s/\text{mean of replicate results})$$

where

%RSD = percent relative standard deviation
s = standard deviation (determined with n - 1 observations)

In the case of paired analyses, such as field duplicates or matrix spike duplicates, relative percent difference may be calculated by:

$$RPD = 100(C_1 - C_2) / (C_1 + C_2)/2$$

where:

RPD = relative percent difference
C_1 = larger of the two observed values (or % recoveries)
C_2 = smaller of the two observed values (or % recoveries)

12.4 DETECTION LIMITS

Two main types of detection limits will be used in assessing data quality in this study, Method detection limits (MDLs) and instrument detection limits (IDLs). The MDL and IDL differ, not in how they are calculated, but in the way the blank samples or low-level standards (prepared at 2 to 3 times the IDL) are handled before analysis. For the MDL calculation, the blanks or standards are subjected to all the sample preparation steps the environmental (e.g., LNAPL) sample undergoes before analysis, such as extraction, digestion, filtration, or distillation. The IDL, on the other hand, is calculated from blanks or standards that a free of the above handling steps. Therefore, the main distinction between these two detection limit assessments is that the IDL estimates the detection limit of the instrument under ideal conditions, whereas the MDL estimates the detection limit in more practical terms in relation to the environmental sample.

The equation for calculating the method detection limit (MDL) is given below:

$$MDL = t_{(n-1,1-\alpha=0.99)} \times s$$

where:

MDL = method detection limit
s = standard deviation of the replicate analyses
$t_{(n-1,1-\alpha=0.99)}$ = student's t-value for a one-sided 99% confidence level

An alternate method for calculation of detection limits is by determining the standard deviation from the measurement of 7 to 10 blanks or standards analyzed on the same day.

SECTION 13.0

CORRECTIVE ACTIONS

The implementation of a sound QA program in the field and in the laboratories assists in obtaining data of the desired quality. The QA program must include mechanisms for identifying situations which are out of control with respect to the applicable QAPjP. Well-defined laboratory sample preparation and analytical procedures and associated acceptance criteria typically provide this mechanism. However, in the case of the sample matrix (LNAPL) and methods employed in this project, previously established QC criteria from standard EPA methodologies may not apply. Although the DQOs may delineate desired method performance, what may typically be indications of out-of-control situations may simply be the nature of the analyte/matrix/sample preparation/analysis method relationships. Every effort to meet QC criteria will be attempted. However, steps to correct undesired events may, in fact, simply be steps to optimize the performance of the method.

Laboratory personnel are responsible for ensuring that all project samples are analyzed according to the methods prescribed in Section 7. The analysts have the daily responsibility of meeting the acceptance criteria for operating parameters (e.g., resolution, RT stability) and analytical procedures such as instrument calibration, QC sample analysis, and data reporting. In cases of instrument malfunction, nonlinear or unstable calibrations, blank contamination, or other unacceptable situations (see Section 9), an analyst must immediately document the event and inform the laboratory supervisor who assess the need to contact the Task Leader and QA Lead. This may, but will not necessarily, cause analysis to be halted. All problems encountered during sample analysis, and all corrective actions taken must be discussed in the case narrative prepared as part of the deliverable package.

SECTION 14.0

QUALITY CONTROL REPORTS TO MANAGEMENT

14.1 CLP-LEVEL DATA PACKAGE

A complete CLP-level data package will be submitted to the WAM for all analytes by compound class (SVOCs, PCBs, Pesticides, VOCs, Metals, Cyanide). Inclusive in the data package will be:

A formal letter describing the contents of the data package, signed by the Task Leader.

Data reporting forms documenting sample analysis results, appropriate data qualifiers (definitions must be attached), MDLs, and relevant procedural information(e.g., method used for sample preparation and analysis, sample weight, analysis date/time, dilution factors).

Individual forms documenting QC results as specified by the method and/or modified, as appropriate, including IDLs for each instrument.

14.2 CASE NARRATIVE

A detailed discussion by analysis class should be written by each analyst providing observations made during sample and data processing, including all aspects of sample preparation, sample analysis, and data reduction that may be useful in future analytical work performed on LNAPL samples from this site, and in interpreting the analytical results provided. Any method/matrix-related problems and the correlating corrective actions must be discussed in the narrative.

14.3 METHOD DESCRIPTIONS

Complete, detailed, methods and/or existing SOPs used in the sample preparation and analysis of each class of analytes must be prepared. If standard methods are used (e.g., SOWs, QTM), these can be referenced and copies provided to the WAM. If any modifications to these methods are required or any specialized operating criteria are used, these procedures must be documented in exact detail. Descriptions of any innovative or specially prepared standards incorporated into the measurement system are to be provided, including the procedure by which they were prepared. Preparation of method/matrix-specific SOPs is dependant upon future requests from the WAM.

14.4 OVERALL SUMMARY STATEMENT

An overall summary of the project results (including data tables, if applicable) will be prepared, and the conclusions and any recommendations derived from the project and the performance of the analyses made. A cover letter to the WAM will accompany this statement and will also reference all

the components of the project deliverables (data package, case narrative, methods write ups, raw data, audit report).

14.5 ORIGINAL RAW DATA

All original raw analytical, QA/QC, and supporting data for the handling and analysis of each sample by analytical fraction will be provided to the WAM upon delivery of the final project deliverables (in the event that the information is subpoenaed or required by the Region for other litigatory or regulatory purposes). All raw data will be photocopied for retention in the LESAT project files.

14.6 ON-SITE SYSTEMS AUDIT REPORT

Any on-site inspection of laboratory operations will be conducted by the Project QA Lead or designee, and should consist of the evaluation of the laboratory facilities, equipment, personnel qualifications, and operations, such as sample collection and handling, record keeping, chain-of-custody/sample tracking, data reporting, and QA procedures. The results of this on-site evaluation will be summarized in an audit report that includes observations, substantive notes on interviews with personnel, problems identified and corrective actions implemented, and any recommendations. This report will be submitted to the QA Officer, project files, and the WAM.

SECTION 15.0

REFERENCES

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Laing, G., Stapanian, M., et. al. 1989. Final Report of the Multi-Laboratory Evaluation of Method 6020 CLP-M, Inductively Coupled Plasma-Mass Spectrometry, EPA Contract 68-03-3249.

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REMCOR, INC.

CHAIN-OF-CUSTODY FORMS

AND

REQUEST-FOR-ANALYSIS FORMS

FOR

THE ROCKWELL SITE LNAPL SAMPLES

FORM CS-2 REV 192

RAZ 018 - 810008A

REQUEST FOR ANALYSIS

REMCOR

REMCOR, INC. – 701 ALPHA DRIVE, P.O. BOX 38310
PITTSBURGH, PA 15238–8310 (412) 963–1106

R/A Control № 2132
C/C Control No.: 4446

Project Name: Rockwell Allegan, MI
Project No.: 9292
Project Contact: Karen Sikora
Project Manager: EPA
Send Lab Report to:

Laboratory Name: LESAT
Laboratory Contact: Dave Youngman
Laboratory Address:

Laboratory Phone No.:
Special Notes:

Turnaround Time: normal

(X – Denotes Testing Program Requested For Sample)

SAMPLE IDENTIFICATION	SAMPLE MEDIUM	TESTING PROGRAM: TCL SVOC	TCL VOC	TCL PCBs	TCL Pest					REMARKS OR SPECIAL INSTRUCTIONS
RAM-RW-03-0-0293	LNAPL	X	X	X	X					
RAM-RW-03-0-0293D	LNAPL	X	X	X	X					
RAM-MW-10-0-0293	LNAPL	X	X	X	X					
RAM-TB-04-0293	AQUEOUS	X (FB)	X							
RAM-PZ-11-0-0293	LNAPL	X	X	X	X					

DISTRIBUTION: White – Accompanies Samples
Yellow – Returned to REMCOR

POSSIBLE HAZARDS:

DISPOSAL: Lab ___ Client ___

FORM 03-1 REV 1/92

REMCOR

REMCOR, INC. – 701 ALPHA DRIVE, P.O. BOX 36310
PITTSBURGH, PA 15236-6310 (412) 963-1106

CHAIN OF CUSTODY RECORD

LARGE BOX
C/C Control No. 4446
R/A Control No.: 432

PROJECT NO.: 9292
PROJECT NAME: Rockwell Allegan, MI
SAMPLERS: ELR, JKJ, KPP

SAMPLE IDENTIFICATION	DATE	TIME	SAMPLE MEDIUM	SAMPLE LOCATION	TOTAL NUMBER OF CONTAINERS PER SAMPLE	DESCRIPTION OF CONTAINERS: 40 ml Vial	4oz Glass Jar	2oz Glass Jar				REMARKS
RAM-RW-03-0-0293	2/18/93	1000	LNAPL	RW-3	~~6~~ 8	~~6~~ 6	~~2~~	KPP				OK Bulge in lid SEP 1 #0293
RAM-RW-03-0-0293D	2/18/93	1000	LNAPL	RW-3	~~6~~ 8	6	~~2~~	KPP				OK - ALL SOLD
RAM-MW-10-0-0293	2/18/93	1430	LNAPL	MW-10	5	5						OK - NO CUSTODY
RAM-TB-~~03~~ 04-0293	2/18/93		AQUEOUS ~~LNAPL~~	TRIP BLANK	3	3						OK SEALS ON VIAL LIDS
RAM-PZ-17-0-0293	2/18/93	1700	LNAPL	PZ-17	6	6						OK NO LEAKS

B-52

RELINQUISHED BY:	DATE & TIME:	RECEIVED BY:	LABORATORY RECEIPT:	DATE:	TIME:
x [signature]	2/18/93 1900	x AIRBORNE 9988729613	x David R. Youngren	2/19/93	11:40
RELINQUISHED BY: x	DATE & TIME:	RECEIVED BY: x			
RELINQUISHED BY: x	DATE & TIME:	RECEIVED BY: x			

SAMPLE TRACKING DATA
SUBCONTRACTED LABORATORY:
DATE SHIPPED:
CARRIER/AIRBILL NO.:

DISTRIBUTION: White – Accompanies Samples ... Yellow – Returned REMCOR With Lab Signature Pink – Retained by Sa...

FORM GS-2 RE.

REQUEST FOR ANALYSIS

REMCOR

REMCOR, INC. – 701 ALPHA DRIVE, P.O. BOX 38310
PITTSBURGH, PA 15238–8310 (412) 963–1108

R/A Control No. 1960
C/C Control No.: 44477

Project Name: Rockwell Allegan, MI
Project No.: 92192
Project Contact: Karen Sikora
Project Manager: EPA
Send Lab Report to:

Laboratory Name: LEKAT
Laboratory Contact: Dave Youngman
Laboratory Address:

Laboratory Phone No.:
Special Notes:

Turnaround Time: normal

(X – Denotes Testing Program Requested For Sample)

SAMPLE IDENTIFICATION	SAMPLE MEDIUM	TESTING PROGRAM TAL Metals	TAL CN							REMARKS OR SPECIAL INSTRUCTIONS
RAM-RW-03-0-0293	LNAPL	X	X							GROSS INSPECTION: SINGLE PHASE DK BL SHIC
RAM-RW-03-0-07930	LNAPL	X	X							"
RAM-PZ-17-0-023	LNAPL	X	X							GROSS INSPECTION: 2 PHASES: CLEAR/YELL BOTTOM, BROWN TOP

DISTRIBUTION: White – Accompanies Samples
Yellow – Returned to REMCOR

POSSIBLE HAZARDS:

DISPOSAL: Lab X Client

FORM GS-1 REV 1/87

REMCOR

REMCOR, INC. – 701 ALPHA DRIVE, P.O. BOX 36310
PITTSBURGH, PA 15236-6310 (412) 963-1100

CHAIN OF CUSTODY RECORD

C/C Control № 4447 ①
R/A Control No.: 1960

PROJECT NO.: 92192
PROJECT NAME: Rockwell Allegan, MI
SAMPLERS: KPP, ELR, JKJ

SAMPLE IDENTIFICATION	DATE	TIME	SAMPLE MEDIUM	SAMPLE LOCATION	TOTAL NUMBER OF CONTAINERS PER SAMPLE	DESCRIPTION OF CONTAINERS: 40z Glass Jars						REMARKS
RAM-RW-03-0-0293	2/16/93	1000	LNAPL	RW-3	2	2						OK ALL COLD NO LEAKS
RAM-RW-03-0-0293D	2/16/93	1000	LNAPL	RW-3	2	2						OK (NO CUSTODY SEALS ON
RAM-PZ-17-0-0293	2/16/93	1700	LNAPL	~~RAM~~ PZ-17	2	2						OK BB JAR LIDS)
			~~TKR~~									

B-54

RELINQUISHED BY:	DATE & TIME:	RECEIVED BY:	LABORATORY RECEIPT:	DATE:	TIME:
x [signature]	2/17/93 1715	AIRBORNE x 9988929613	x David R. Yamamoto	2/19/93	11:34
RELINQUISHED BY: x	DATE & TIME:	RECEIVED BY: x			
RELINQUISHED BY: x	DATE & TIME:	RECEIVED BY: x			

SAMPLE TRACKING DATA

SUBCONTRACTED LABORATORY:
DATE SHIPPED:
CARRIER AIRB NO.:

DISTRIBUTION: – Accompanies Samples Yellow – Rel

COMPUCHEM LABORATORIES

Dave, can you please send box and packaging back to compu-chem labs! Thanks

CompuChem Laboratories
P.O. Box 12652
Chapel Hill/Nelson Highway
Research Triangle Park, NC 27709

2 BOXES
1 small
1 large

RETURN POSTAGE GUARANTEED

COMPUCHEM LABORATORIES CUSTODY SEAL

Signature Date

COMPUCHEM LABORATORIES CUSTODY SEAL

Signature Date

COMPUCHEM LABORATORIES CUSTODY SEAL

Signature Date

Karen Sikora, U.S. EPA
(312) 886-184

SAMPLING
S-ID#: _____ DATE: _____
ANALYZE FOR/CODE: _____

SAMPLING
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ANALYZE FOR/CODE: _____

SAMPLING
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ANALYZE FOR/CODE: _____

APPENDIX B

CALIBRATION/RETENTION TIME STANDARDS

FOR HYDROCARBON SCREENING PROCEDURE

0434-9-1

Methylene Chloride LOT # BD 803

8015 STDS

CPD	SOLV	LAL ID #	UG/ML	ALIQ ULS	VOL MLS	FINAL CONC UG/ML
N-TRIACONTANE	MECL2	434-5-1	414	10000	50	82.80
N-OCTACOSANE	MECL2		401.70	10000	50	80.34
N-HEXACOSANE	MECL2		429.60	10000	50	85.92
N-PENTACOSANE	MECL2		417.60	10000	50	83.52
N-TETRACOSANE	MECL2		402.80	10000	50	80.56
N-TRICASANE	MECL2		420.00	10000	50	84.00
N-DOCOSANE	MECL2		436.80	10000	50	87.36
N-HENEICOSANE	MECL2		430.40	10000	50	86.08
N-EICOSANE	MECL2		492.00	10000	50	98.40
N-NONADECANE	MECL2		476.00	10000	50	95.20
N-OCTADECANE	MECL2		392.40	10000	50	78.48
N-HEPTADECANE	MECL2		470.00	10000	50	94.00
N-HEXADECANE	MECL2		436.00	10000	50	87.20
N-PENTADECANE	MECL2		400.00	10000	50	80.00
N-TETRADECANE	MECL2		400.00	10000	50	80.00
N-TRIDECANE	MECL2		400.00	10000	50	80.00
N-DODECANE	MECL2		400.00	10000	50	80.00
N-UNDECANE	MECL2		400.00	10000	50	80.00
N-NONANE	MECL2		400.00	10000	50	80.00
M-OCTANE	MECL2		400.00	10000	50	80.00
N-HEPTANE	MECL2		400.00	10000	50	80.00
N-HEXANE	MECL2		400.00	10000	50	80.00

Continued on Page

Read and Understood By

Signed _____ Date _____

Signed _____ Date _____

APPENDIX C

ON-SITE LABORATORY AUDIT EVALUATION REPORT

FOR THE ANALYSIS OF LIGHT NON-AQUEOUS PHASE LIQUID SAMPLES

FROM THE ROCKWELL INTERNATIONAL CORPORATION NPL SITE

(March 12 and 15, 1993)

QA LABORATORY EVALUATION REPORT FOR RESEARCH ACTIVITIES

Laboratory: Lockheed Analytical Services / Lockheed Analytical Laboratory | EMSL-LV / QAL/CHL

Address: 975 Kelly Johnson Dr. Las Vegas, NV | 944 E. Harmon Las Vegas, NV

Task No.: 22210172

Task Title: Rockwell International NPL Site LNAPL Sample Analysi

Telephone: (702)361-1626 / (702) 798-2024

Date of Evaluation: March 12, 1993 and March 15, 1993

PERSONNEL CONTACTED

	Name	Title
3/12/93	Dolf Cardenas	Scientist
3/12/93	David Dobb	Scientific Supervisor
3/12/93	Jeffrey Jeter	Senior Scientist
3/15/93	David Youngman	Scientific Supervisor (22210172 Task Leader)

LABORATORY EVALUATION TEAM

Name	Title
Mark Silverstein	Senior Scientist / 22210172 QA Lead

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REPORT ON ON-SITE EVALUATION OF

Sample Analysis for LNAPL Samples from Rockwell Int'l NPL

Prepared by: M. E. Silverstein

Verified by:

SUMMARY OF RECOMMENDATIONS AND OBSERVATIONS

Analysts notes and logbooks appear in order and fully documented.

LNAPL samples, extracts, digestates and calibration and spiking standards stored correctly (refrigerated, if applicable) and are secured with locks, where required.

Chain-of-custody records appear in order - a transcr
error of one sample was pointed out by D. Dobb, where an "S" for spike was written as a "5." This was investigated and documented on the Chain-of-Custody form.

Technician responsible for digestate preparation, for metals not available at time of audit; all other key personnel contacted
-B results not audited as the analyses are to be redone with alternative cleanup steps.
Metals analyst (Cardenas) recommends looking at Lanthanide ratios between 2 well samples as possible "finger print" for point source of LNAPL (Said to see Tech. Support Data Evaluation Report

Attachment 1
Laboratory Evaluation Checklist

I. SAMPLE STORAGE AREA

ITEM	YES	NO	NA
I.1 Sample Storage Facilities			
1. Are adequate facilities provided for the cold storage of samples?	✓		

Comments:

Metals digestates kept locked in Supervisor's file cabinet - no need for refrigeration of these fractions.

LNAPL (raw) Samples: locked at LAL Refrigerator #418790 in Room 123. Samples kept separate from other samples in refrigerator in a sealed acrylic PLAS LABs® box.

I. SAMPLE STORAGE AREA

ITEM	YES	NO	NA
I.2 Volatile sample storage.			
1. Are VOA holding blanks present in the volatile sample storage facility?	✓	—	—

Comments:

8 VOA holding blanks available with Sample at start of project - analyzed as appropriate during analyses.

I. SAMPLE STORAGE AREA

ITEM	YES	NO	NA
I.3 Recordkeeping			
1. Is there evidence of a sample inventory/sample tracking system?	✓		
2. Is there evidence of secondary review of these documents and logbooks by someone other than the person generating the documents?	✓		

Comments:

Log book entry of sample receipt by D. Youngman and on Remcor Chain-of-Custody forms (confirmed by V. Ecker on forms at time of receipt + breakage of custody seal of shipping container).

II. SAMPLE PREPARATION AREA

Attention is given to: (a) the overall organization and neatness, (b) the proper maintenance of facilities and instrumentation, (c) the general adequacy of the facilities to accomplish the required work.

ITEM	YES	NO	NA
II.1 General Facilities			
1. Is the laboratory maintained in a clean and organized manner?	✓		
2. Does the laboratory appear to have adequate workspace (6 linear feet of unencumbered benchtop per analyst)?	✓		

Comments:

II. SAMPLE PREPARATION AREA

ITEM	YES	NO	NA
II.2 Contamination Control *(May be confirmed by examining data from blanks)*			
1. Are contamination-free areas provided for trace-level analytical work?	✓		
2. Are contamination-free work areas provided for the handling of toxic materials? (Glove box or isolated hood)	✓		
3. Are exhaust hoods provided to allow contamination-free work with volatile materials?	✓		
4. Is purity of water documented and available for the preparation of standards and blanks?	✓		
5. Are solvent storage cabinets vented or located in such a way as to prevent possible laboratory contamination?	✓		

Comments:

Blank water is Nanopure + distilled

II. SAMPLE PREPARATION AREA

ITEM	YES	NO	NA
II.3 Reagent Control			
1. Are analytical reagents dated upon receipt and used on a first-in, first-out basis?	✓	—	—
2. Are the purities and reactivities of the analytical reagents verified before use?	✓	—	—

Comments:

II. SAMPLE PREPARATION AREA

ITEM	YES	NO	NA
II.4 Balances			
1. Are the analytical balances located away from drafts and areas subject to rapid temperature changes?	✓		
2. Are the analytical balances isolated from vibration?	✓		
3. Have all balances been calibrated and checked within the last year by a certified technician?	✓		
4. Are the balances checked against class S weights at least once per month and the results recorded in a permanent notebook? (Note: Internal weights may not be recognized by NIST)	✓		

Comments:

II. SAMPLE PREPARATION AREA

ITEM	YES	NO	NA
II.5 Sample Extract Storage *(Should be protected from light and maintained at 2 to 6 °C)*			
1. Are sample extracts stored separately from standards and samples?	✓	—	—
2. Does there appear to be sufficient storage space to keep extracts for at least one year?	—	—	✓
3. Are extracts properly labeled so as to provide traceability?	✓	—	—

Comments:

Methanolic extraction in capped (Teflon-sealed tubes.

Metals fraction microwave-digested in a CEM MDS-81D

II 5.2. It is not expected that the extracts will require 1 year of storage - QAPjP (Section 5 says 60 days after delivery of data package to WAM

II. SAMPLE PREPARATION AREA

ITEM	YES	NO	NA
II.6 Recordkeeping			
1. Are data recorded in a neat and accurate manner?	✓		
2. Is there evidence of a secondary review of all documents and logbooks by someone other than the person generating the documents?	✓		

Comments:

III. STANDARDS PREPARATION AND STORAGE

ITEM	YES	NO	NA
III.1 Standards Storage *(Should be protected from light and stored at manufacturers recommended temperature)*			
1. Are measures taken to ensure that cross-contamination will not take place between volatile and non-volatile analytes which are dissolved in an organic solvent?	✓		
2. Are volatile standards stored separately from volatile samples?	✓		

Comments:

Holding blanks used to confirm no cross-contamination.

III. STANDARDS PREPARATION AND STORAGE

ITEM	YES	NO	NA
III.2 Standards Preparation			
1. Are reagent grade or higher purity chemicals used to prepare standards?	✓		
2. Are reference materials properly labeled with concentrations, date of preparation, and the identity of the person preparing the standard?	✓		
Alternatively, is a traceable reference code number used (e.g. for LIMS)?			X
3. Are fresh analytical standards prepared at a frequency consistent with GLP for:			
a. Semivolatiles (stock solutions: 12 months old)	✓		
b. Pesticides (stock solutions: 6 months)	✓		
c. Volatiles (gasses: 2 mo.; others; 6 mo., etc.)	✓		

Comments:

Standards are made more frequently than stated — they were made up fresh for this project.

III. STANDARDS PREPARATION AND STORAGE

ITEM	YES	NO	NA
III.3 Standards Recordkeeping			
1. Is the preparation of spiking/calibration standards documented in a manner that indicates traceability?	✓		

Comments:

III. STANDARDS PREPARATION AND STORAGE

ITEM	YES	NO	NA
III.4 Standards Certification			
1. Does the laboratory purchase commercially prepared standard mixes?	✓		
2. Is appropriate documentation (manufacturer's "Certificate of Analysis") available for each lot of purchased standards in use?	✓		

Comments:

Standards from Restek - certification information on file.

IV. SAMPLE ANALYSIS INSTRUMENTATION

ITEM	YES	NO	NA
IV.1 Instrument Operation and Maintenance			
1. Are manufacturer's operating manuals readily available to the operator?	✓		
2. Does the laboratory purchase a service contract for instruments?	✓		
3. Are sufficient in-house replacement parts available to ensure minimal downtime? (e.g., spare multipliers, filaments, chromatographic columns, traps)	✓		
4. Does the laboratory perform regular preventive maintenance on the instruments?	✓		
5. Is a permanent service record for each instrument maintained in a logbook?	✓		
6. Are the instruments vented to outside the facility or to appropriate traps?	✓		
7. Does the laboratory use the most recent release of the NIST spectral library for library searching?			X

Comments:

Not applicable for this project, & no TICs found. (as per Youngman)

GC/MS 5988A for SVOAs
GC/MS 5970B for VOAs (P&T)
→ HPRTEA Aquarius Rev F (data system for both MSs)
VG Plasma Quad 2 Plus for ICP-MS Metals

IV. SAMPLE ANALYSIS INSTRUMENTATION

ITEM	YES	NO	NA
IV.2 Magnetic Tape Storage of GC/MS Electronic Data			
1. Are raw data, including quantitation output files and libraries, archived on magnetic tape?	—	—	—
2. Is a log of the contents of the raw data magnetic tapes available?	—	—	—

Comments:

GC/MS Tape labeled "Allegan Michigan"

IV. SAMPLE ANALYSIS INSTRUMENTATION

ITEM	YES	NO	NA
IV.3 SOPs and Recordkeeping--Instrument Area			
1. Can the instrument operator demonstrate, using the instrument run log, that the following corrective actions have been taken when needed?			
a. Reanalyses when internal standard areas are out.	X	—	—
b. Dilutions when the calibration range is exceeded.	—	—	X
c. Blanks when the previous sample showed saturation.	—	—	X
2. Is the appropriate manual available at the instrument area?	X	—	—
3. Do the analysts accurately record all analyses in a bound or serially numbered logbook?	X	—	—
4. Are the instrument injection logbooks completed in a manner consistent with GLP?	X	—	—
5. Is there evidence of a secondary review of all documents and logbooks by someone other than the person generating the documents?	X	—	—

Comments:

V. Ecker checked GC/MS log on 3/12/93

None (ISTDs) out for GC/MS analyses

V. DATA HANDLING AND REVIEW

	ITEM	YES	NO	NA
V.1	Are data calculations spot-checked by a second person?	will be done at data package review step		
V.2	Do records indicate that appropriate corrective action has been taken when results fail to meet QC criteria?	X	—	—
V.3	Do supervisory personnel review the data and QC results prior to submission?	X	—	—

Comments:

Re ICP-MS analysis/data reporting

- Form 15 - Internal Standard Relative Intensity Summary and
- ICP-MS Indigenous Internal Standard Summary

Discussed w/ D. Dobb that, if the region agreed, it would not be necessary to supply these forms in the data package; instead they can report the ISTd for each element (minimum = 0.30), which they were well within. The supporting data (counts) will be on a spreadsheet and available on disk. Not filling out these forms would save ~10 man hours of manual data transcription and would have no affect on data documentation relative to possible litigatory issues.

Reviewed all data/logbooks w/ ICP-MS (Cardenas/Dobb), GC/MS (VOAs) (Youngman), and GC/MS (SVOAs) (Jeter). In the few instances when corrective action was needed, appropriate action was taken (e.g. "bad" 50 std on SVOAs - that is, not to our specs but OK for CLP, a CCC standard @ 50 was used)

VI. DATA MANAGEMENT

	ITEM	YES	NO	NA
VI.1	Are data and file access secured with password protection?	✓		
VI.2	Are data generated by the system checked for completeness and accuracy?	✓		
VI.3	When changes to data are required, are the changes properly documented? (rationale, review, initials)	✓		
VI.4	Are user manuals and operations/systems manuals available?	✓		
VI.5	Is a written software test and acceptance plan available for installation of system changes?		X	

Comments:

Should be done by manufactu
(as per D. Youngman)

Checked Stds log for SVOAs + VOAs analyses

VII. TASK QUALITY ASSURANCE PROJECT PLAN

ITEM	YES	NO	NA
VII.1 Is a QAPjP readily available to the scientists?	X	—	—
VII.2 Has the QAPjP been reviewed/approved by the EPA Task Monitor/ Project Officer?	X	—	—
VII.3 Has the QAPjP been reviewed/approved by a designated EPA QA Officer?	unknown		

Comments:

QAPjP submitted to WAM on 3/9/93 -

VIII. ORGANIZATION AND PERSONNEL SUMMARY

ITEM	YES	NO	NA
VIII.1 Does the Laboratory Quality Assurance Officer report to senior management levels?	✓	—	—
VIII.2 Do personnel assigned to this project have the appropriate educational background and experience to accomplish the objectives of the program?	✓	—	—
VIII.3 Is the organization adequately staffed to meet project commitments in a timely manner?	✓	—	—

Comments:

IX. LABORATORY CAPACITY

	ITEM	YES	NO	NA
IX.1	Does the laboratory have sufficient analytical instrumentation to perform the desired work in the assigned timeframe?	✓	—	—
IX.2	Are there assurances that necessary facilities and instrumentation will be available when needed to perform the work?	✓	—	—
IX.3	Does the laboratory have sufficient technical and administrative personnel to respond to EPA research needs?	✓	—	—
IX.4	Does the laboratory have an adequate sample and data tracking system to respond to a data audit?	✓	—	—

Comments:

IX.1 - The GC headspace instrument was not functioning for analysis of VOAs; however, the GC/MS purge + trap was available - this information was provided to WAM + region on 3/11/93 conference call.

IX.4 EMSL-LV uses a manual system for tracking data / LAS uses a LIMS-style bar code system.

X. VERIFICATION SUMMARY

(To be completed by Task Monitor/Project Officer and the EPA Divisional Quality Assurance Officer)

	ITEM	YES	NO	NA
X.1	Do responses to the evaluator indicate that project and supervisory personnel are aware of QA/QC procedures and their importance to the project?	✓	—	—
X.2	Do project and supervisory personnel place a positive emphasis on achieving data quality?	✓	—	—
X.3	Have responses with respect to the QA/QC aspects of the project been open and direct?	✓	—	—
X.4	Have corrective actions recommended during previous evaluations been implemented? If not, provide details below.	—	—	X

Comments:

All personnel interviewed were fully aware of project scope and objectives as they related to the particular analytical tasks at hand.

APPENDIX D

OPERATING PARAMETERS AND CALIBRATION INFORMATION FOR THE CHARACTERIZATION OF OIL SAMPLE BY GAS CHROMATOGRAPHY-FLAME IONIZATION DETECTOR

METHOD:

A Hewlett Packard Model 5890 Gas Chromatograph with flame ionization detector was used. A Hewlett Packard Model 3396 integrator was used for detector signal processing. The instrument conditions were as follows:

Column:	30 Meter RTX-5, 0.53 mm ID, 1.0 micron film (Restek Corp Catalog #10255)
Carrier Gas:	Helium @ 10.0 cc/min
Injector Temp:	290 °C
Detector Temp:	300 °C
Oven Temp:	Initial - 40 °C Initial Time - 2.5 Minutes Ramp - 4.0 °C per minute Final - 290 °C Final Time - 5 minutes

A 250 microliter aliquot of the oil sample was diluted with 25 milliliters of methylene chloride. The diluted sample (2 microliters) was directly injected into the gas chromatograph.

CALIBRATION:

A solution of straight chain hydrocarbons from C-6 to C-30 was prepared in methylene chloride. The calibration mixture, along with the boiling point and retention time for each component is presented in Table D-1. The calibration mixture was injected both before and after analysis of the LNAPL sample. A chromatogram of the standard mixture is shown in Figure D-1. A linear relationship was found between the retention time of the component hydrocarbon and its boiling point for hydrocarbons of molecular weights between nonane (C-9) and Triacontane (C-30) as shown graphically in Figure D-2. By comparing the retention times obtained from the chromatogram of the unknown oil with the retention times of the standard hydrocarbons, the boiling point range of the unknown can be obtained.

In addition to the standard solution, injections of the blank methylene chloride used for dilution were performed. Known petroleum hydrocarbon products (gasoline, diesel fuel, and motor oil) were also analyzed to present a comparison with the unknown oil.

TABLE D-1. CALIBRATION STANDARD FOR GC-FID

Compound	Concentration (μg/mL)	Boiling Point (°C)	Retention Time (minutes)
n-Hexane	80.0	68.9	1.85
n-Heptane	80.0	98.4	3.26
n-Octane	80.0	125.7	5.91
n-Nonane	80.0	150.8	9.45
n-Decane	80.0	174.1	13.29
n-Undecane	80.0	195.9	17.10
n-Dodecane	80.0	216.3	20.73
n-Tridecane	80.0	235.4	24.16
n-Tetradecane	80.0	253.7	27.40
n-Pentadecane	80.0	270.6	30.47
n-Hexadecane	87.2	287.0	33.39
n-Heptadecane	94.0	301.8	36.15
n-Octadecane	78.5	316.1	38.78
n-Nonadecane	95.2	329.7	41.29
n-Eicosane	98.4	343.0	43.70
n-Heneicosane	86.1	356.5	45.99
n-Docosane	87.4	368.6	48.19
n-Tricosane	84.0	380.2	50.31
n-Tetracosane	80.6	391.3	52.33
n-Pentacosane	83.5		54.29
n-Hexacosane	85.9	412.2	56.17
n-Octacosane	80.3	431.6	59.74
n-Triacontane	82.8	449.7	63.09

Figure D-1. Chromatogram of GC-FID calibration standard: straight-chain alkane hydrocarbons.

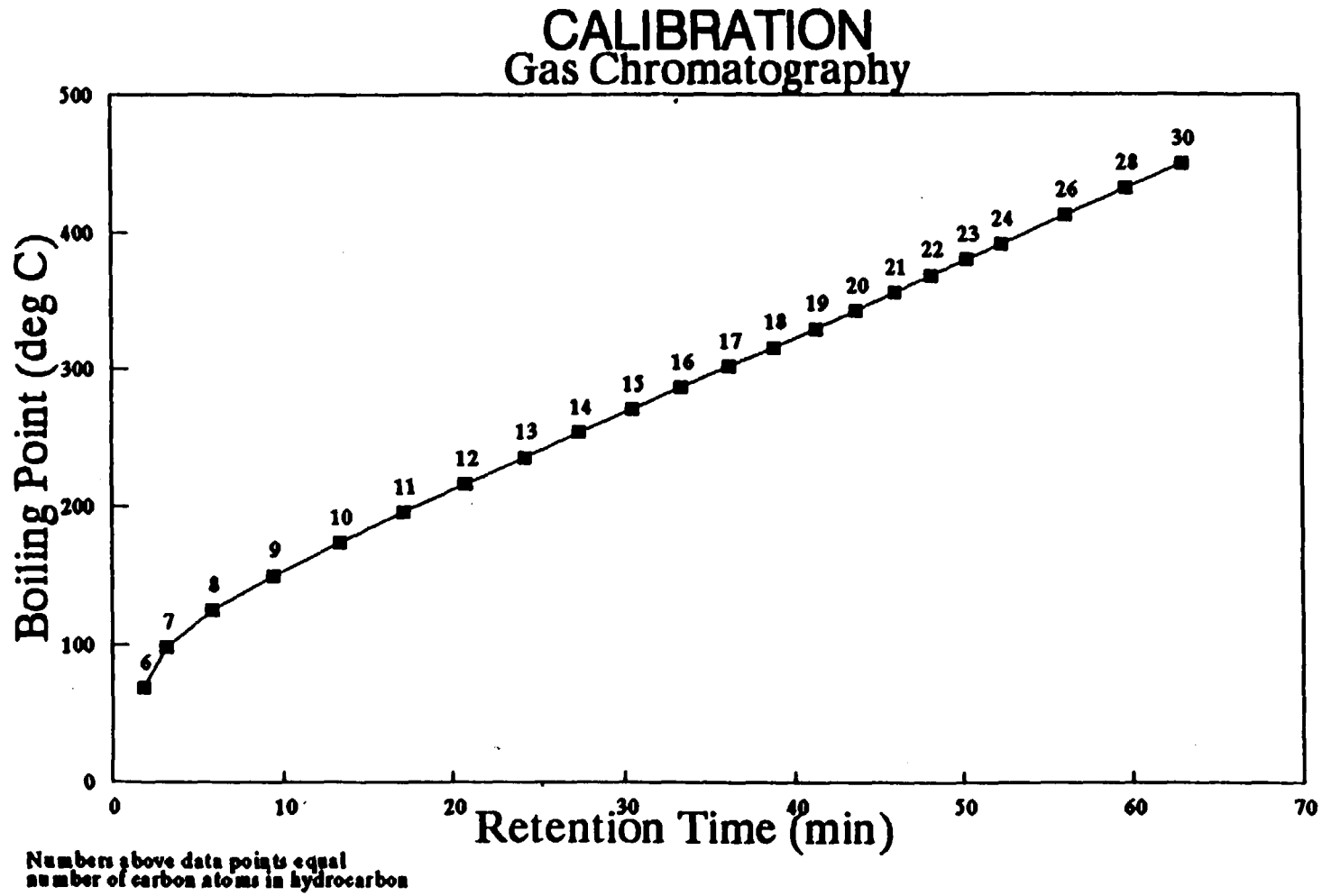


Figure D-2. Boiling points vs. retention times of calibration for straight-chain alkane hydrocarbons.

APPENDIX E

METHOD AND INSTRUMENTAL PERFORMANCE DATA FOR SEMIVOLATILE ORGANIC COMPOUND ANALYSIS OF LNAPL SAMPLES

- INSTRUMENT DETECTION LIMIT DATA
- METHOD DETECTION LIMIT DATA
- MATRIX SPIKING PRECISION AND ACCURACY DATA

TABLE E-1. INSTRUMENT DETECTION LIMITS FOR SEMIVOLATILE ORGANIC COMPOUNDS DETERMINED ON THE HP 5988 GC/MS

ANALYTE	LOW LEVEL STANDARD CONCENTRATION (µg/mL)							IDL (µg/mL)
	RUN 1	RUN 2	RUN 3	RUN 4	RUN 5	RUN 6	RUN 7	
Phenol	10.00	9.63	9.82	9.92	10.11	9.45	9.35	0.832
Bis(-2-Chloroethyl)Ether	5.20	5.39	5.13	5.64	5.33	5.61	5.30	0.562
2-Chlorophenol	9.54	9.10	9.42	9.57	8.96	9.12	9.33	0.686
1,3-Dichlorobenzene	3.83	3.59	3.95	3.86	3.82	3.71	3.76	0.337
1,4-Dichlorobenzene	4.09	3.67	3.84	3.89	3.92	3.85	3.65	0.439
Benzyl Alcohol	4.18	4.03	4.29	3.83	3.94	4.28	3.78	0.607
1,2-Dichlorobenzene	4.07	4.11	3.96	4.08	4.11	3.80	3.91	0.346
2-Methylphenol	9.83	9.61	9.86	9.45	9.99	10.01	9.76	0.586
bis(2-Chloroisopropyl)ether	5.61	5.59	5.40	5.65	5.77	5.67	5.32	0.460
4-Methylphenol	10.02	10.11	10.41	10.88	10.60	10.35	10.13	0.890
N-Nitroso-Di-n-propylamine	5.07	5.31	5.33	5.42	5.78	5.38	5.53	0.633
Hexachloroethane	4.92	4.58	4.51	4.86	5.10	4.90	5.29	0.793
Nitrobenzene	4.55	4.60	4.41	4.59	4.24	4.40	4.28	0.425
Isophorone	4.41	4.55	4.39	4.56	4.76	4.84	4.51	0.491
2-Nitrophenol	8.38	8.34	8.15	8.06	7.90	8.33	8.24	0.508
2,4-Dimethylphenol	10.32	10.21	9.70	10.15	10.22	10.01	10.47	0.715
Benzoic Acid	7.10	6.77	6.13	5.63	6.59	6.13	6.51	1.412
bis(-2-Chloroethoxy)Methane	5.00	5.26	5.01	5.04	5.08	4.72	4.81	0.517
2,4-Dichlorophenol	9.14	8.83	8.69	8.77	8.10	8.83	8.30	1.025
1,2,4-Trichlorobenzene	4.60	4.71	4.77	4.72	4.53	4.88	4.54	0.374
Naphthalene	5.18	5.14	4.92	5.05	5.12	4.86	5.01	0.344
4-Chloroaniline	4.71	5.02	4.57	4.58	5.47	4.86	4.71	0.923
Hexachlorobutadiene	4.87	4.19	3.65	4.28	4.27	4.59	3.67	1.298
4-Chloro-3-methylphenol	9.59	9.25	9.43	8.96	9.51	9.49	8.92	0.791
2-Methylnaphthalene	4.73	4.31	4.46	4.71	4.58	4.40	4.70	0.489
Hexachlorocyclopentadiene	3.44	3.30	3.38	3.42	3.03	3.23	3.32	0.409
2,4,6-Trichlorophenol	8.20	8.27	8.57	9.22	8.52	8.10	8.51	1.079
2,4,5-Trichlorophenol	8.05	7.67	8.23	9.03	8.24	9.60	8.48	1.885

2-Chloronaphthalene	4.40	4.67	4.63	4.84	4.44	4.63	4.88	0.526
2-Nitroaniline	4.32	4.58	3.82	4.83	3.92	3.83	4.17	1.137
Dimethyl Phthalate	4.63	5.01	4.82	4.67	4.53	4.79	4.57	0.487
Acenaphthylene	4.69	4.69	4.87	4.64	4.47	4.82	4.48	0.445
3-Nitroaniline	4.16	3.82	3.25	4.17	3.69	3.35	3.94	1.060
Acenaphthene	4.85	4.96	4.83	4.75	4.47	5.13	4.95	0.600
2,4-Dinitrophenol	3.77	1.98	4.15	4.34	5.12	2.26	4.81	3.535
4-Nitrophenol	4.73	4.05	1.14	4.57	6.41	5.16	3.28	4.819
Dibenzofuran	4.69	4.45	4.47	4.54	4.41	4.60	4.45	0.291
2,4-Dinitrotoluene	3.25	3.43	3.28	3.33	3.33	3.79	2.99	0.698
2,6-Dinitrotoluene	2.98	3.31	3.26	2.58	3.37	3.64	3.58	1.063
Diethylphthalate	4.17	4.38	4.32	4.51	4.46	4.33	4.32	0.321
4-Chlorophenyl-phenylether	4.14	4.72	4.23	4.67	4.33	4.72	4.42	0.706
Fluorene	4.54	4.62	4.86	4.29	4.76	4.62	4.65	0.522
4-Nitroaniline	3.48	3.57	3.43	3.50	3.65	2.99	2.91	0.845
4,6-Dinitro-2-methylphenol	6.34	6.97	6.59	6.80	6.75	7.17	6.64	0.782
N-Nitrosodiphenylamine	4.50	4.85	4.89	4.56	4.32	4.37	4.86	0.707
4-Bromophenyl-phenylether	4.62	4.46	4.66	4.33	4.20	4.20	4.78	0.672
Hexachlorobenzene	4.97	4.16	4.36	4.42	4.52	4.04	4.79	0.958
Pentachlorophenol	7.21	7.94	7.52	6.67	7.30	6.79	7.11	1.254
Phenanthrene	4.87	5.06	4.80	4.69	4.71	4.59	4.68	0.453
Anthracene	4.66	4.94	4.59	4.64	4.50	4.07	4.68	0.766
Carbazole	4.46	4.38	4.38	4.56	4.65	4.57	4.79	0.434
Di-n-Butylphthalate	4.60	4.49	4.47	4.40	4.60	4.46	4.59	0.235
Fluoranthene	4.79	4.75	4.65	4.52	4.62	4.52	4.77	0.332
Pyrene	4.79	4.38	4.81	4.57	4.84	4.86	4.18	0.773
Butylbenzylphthalate	4.03	3.72	3.95	4.22	4.30	4.56	3.75	0.886
3,3'-Dichlorobenzidine	26.47	28.39	25.20	26.23	27.97	25.66	26.69	3.373
Benzo(a)Anthracene	4.74	4.62	4.63	4.65	4.56	4.78	4.82	0.277
Bis(2-Ethylhexyl)Phthalate	3.69	3.99	3.92	4.05	4.31	4.16	3.69	0.670
Chrysene	4.70	4.62	4.58	4.72	4.98	4.47	4.79	0.476
Di-n-octyl phthalate	3.57	3.56	3.56	3.89	3.98	3.55	3.33	0.650

Benzo(b)fluoranthene	4.91	4.60	4.90	4.39	4.47	5.03	4.51	0.739
Benzo(k)fluoranthene	4.68	4.64	4.01	4.74	4.68	4.13	4.43	0.856
Benzo(a)pyrene	4.30	4.31	4.34	3.91	3.73	4.15	4.16	0.667
Indeno(1,2,3-cd)Pyrene	4.41	4.04	3.98	3.86	4.20	4.21	4.62	0.760
Dibenzo(a,h)Anthracene	3.61	3.58	3.62	3.61	4.06	3.88	3.33	0.682
Benzo(g,h,i)Perylene	3.57	3.60	3.79	3.57	3.99	4.08	4.08	0.691

TABLE E-2. METHOD DETECTION LIMITS FOR SEMIVOLATILE ORGANIC COMPOUNDS DETERMINED FROM SPIKED PENNZOIL 5W-30

ANALYTE	CONCENTRATION OF PENNZOIL SPIKE (µg/mL)							MDL (µg/Kg)
	RUN 1	RUN 2	RUN 3	RUN 4	RUN 5	RUN 6	RUN 7	
Phenol	4.35	4.17	4.13	4.78	3.80	4.46	3.95	9552.
bis(-2-Chloroethyl)ether	4.87	4.52	4.71	4.68	5.18	4.65	4.95	6452.
2-Chlorophenol	3.98	3.77	3.38	3.20	2.98	2.78	2.88	13263.
1,3-Dichlorobenzene	5.02	4.98	4.76	4.89	4.86	4.83	4.84	2617.
1,4-Dichlorobenzene	5.14	5.17	4.83	4.99	4.94	4.83	5.09	4082.
Benzyl Alcohol	3.93	2.95	3.26	3.34	2.78	1.28	1.75	27095.
1,2-Dichlorobenzene	5.14	4.96	4.79	5.21	5.03	4.94	4.92	4120.
2-Methylphenol	4.71	4.21	4.56	4.30	4.04	4.11	3.44	11944.
bis(2-Chloroisopropyl)ether	4.97	5.01	5.10	5.47	5.39	5.24	5.37	5762.
4-Methylphenol	4.20	4.23	4.41	4.20	3.87	3.96	3.61	7868.
N-Nitroso-Di-n-propylamine	4.98	4.70	5.50	5.90	4.82	4.67	5.70	14796.
Hexachloroethane	4.54	4.60	4.36	4.55	4.68	4.32	4.41	3874.
Nitrobenzene	4.20	4.09	4.18	4.18	4.09	3.86	3.87	4216.
Isophorone	4.55	4.20	4.19	4.58	4.57	4.53	4.08	6350.
2-Nitrophenol	1.15	1.05	0.59	0.26	0.19	0.00	0.00	13945.
2,4-Dimethylphenol	4.46	4.62	4.89	5.01	5.35	4.61	4.99	8885.
bis(-2-Chloroethoxy)methane	4.49	4.41	4.62	4.52	4.50	4.59	4.20	4068.
2,4-Dichlorophenol	2.28	2.65	2.33	1.40	1.50	0.00	0.00	31683.
1,2,4-Trichlorobenzene	4.24	4.35	4.16	4.25	4.15	4.39	4.26	2590.
Naphthalene	4.65	4.67	4.58	4.72	4.76	4.61	4.55	2187.
4-Chloroaniline	4.04	3.48	3.02	3.27	2.26	4.21	2.21	22863.
Hexachlorobutadiene	4.51	4.02	3.94	4.52	4.06	3.77	4.41	8754.
4-Chloro-3-methylphenol	4.14	4.05	3.99	3.32	1.28	3.28	2.81	29237.
2-Methylnaphthalene	4.64	4.39	4.29	4.61	5.62	5.56	5.41	16763.
2-Chloronaphthalene	4.46	4.24	4.49	4.10	4.25	4.28	4.53	4634.
2-Nitroaniline	3.64	3.22	4.13	2.88	2.88	2.39	3.56	16953
Dimethyl Phthalate	4.62	3.91	4.37	4.16	3.84	4.09	4.48	8487
Acenaphthylene	4.50	4.53	4.54	4.20	4.18	4.59	4.63	5370.
3-Nitroaniline	4.01	2.84	4.40	3.43	4.34	3.60	4.14	16401.

Acenaphthene	4.33	4.88	4.64	4.90	4.81	4.75	4.02	9529.
Dibenzofuran	4.26	4.29	4.24	4.13	4.14	4.26	4.43	2929.
2,4-Dinitrotoluene	2.38	2.22	2.55	2.20	3.05	2.06	1.80	11589.
2,6-Dinitrotoluene	3.57	2.83	3.08	2.99	2.84	4.43	3.04	16715.
Diethylphthalate	4.30	4.13	4.34	3.89	3.99	4.14	3.71	6536.
4-Chlorophenyl-phenylether	4.32	4.00	4.33	4.46	3.85	4.10	4.34	6409.
Fluorene	4.83	4.52	4.40	4.52	3.79	4.44	4.14	9587.
4-Nitroaniline	3.94	3.79	2.78	2.21	2.62	3.78	2.02	23432.
N-Nitrosodiphenylamine	4.26	4.51	4.27	4.71	4.69	4.65	4.07	7339.
4-Bromophenyl-phenylether	4.21	3.22	4.28	4.62	3.40	4.01	4.33	14949.
Hexachlorobenzene	3.48	3.56	3.81	4.66	3.88	4.13	4.01	11490.
Phenanthrene	4.39	4.19	3.76	4.82	4.38	4.36	4.49	9326.
Anthracene	3.78	4.05	3.81	4.37	4.17	4.75	4.46	10294.
Carbazole	4.49	4.16	3.96	4.34	3.73	4.81	4.67	11234.
Di-n-Butylphthalate	3.56	5.14	4.20	4.41	4.18	5.92	4.05	22889.
Fluoranthene	4.26	3.89	3.92	4.56	4.26	4.13	4.32	6825.
Pyrene	8.48	7.76	9.20	8.11	9.36	8.09	9.57	20845.
Butylbenzylphthalate	7.91	6.23	7.60	10.83	7.78	6.80	9.68	46803.
Benzo(a)anthracene	4.14	5.37	5.37	4.52	5.98	5.06	4.76	17857.
Bis(2-ethylhexyl)phthalate	6.89	4.73	4.62	6.56	6.54	7.17	5.06	31744.
Chrysene	4.70	4.81	6.07	5.11	5.90	4.86	5.21	15774.
Di-n-octyl phthalate	5.47	4.36	5.00	4.91	5.27	5.93	5.23	14224.
Benzo(b)fluoranthene	4.82	4.51	4.65	4.89	3.80	5.05	4.64	11781.
Benzo(k)fluoranthene	3.03	3.79	3.15	3.18	3.22	3.69	3.03	9057.
Benzo(a)pyrene	7.02	7.55	4.22	3.88	3.78	4.71	3.96	46158.
Indeno(1,2,3-cd)pyrene	5.67	5.91	4.96	4.24	4.74	6.40	5.15	21561.
Dibenzo(a,h)anthracene	3.38	5.26	4.99	4.10	4.85	5.43	4.64	20747.
Benzo(g,h,i)perylene	4.66	4.84	4.46	4.92	4.77	5.08	4.31	7752.

TABLE E-3. MATRIX SPIKE RECOVERY AND PRECISION DATA FOR SEMIVOLATILE ORGANIC COMPOUND ANALYSES

ANALYTE	MATRIX SPIKE CONC. (µg/mL)	MATRIX SPIKE DUPLICATE CONC. (µg/mL)	AVERAGE SPIKE/ SPIKE DUPLICATE (µg/mL)	ACCURACY (PERCENT RECOVERY)	PRECISION (RELATIVE PERCENT DIFF.)
2-Fluorophenol	50.74	49.32	50.0	100.06%	2.84%
Phenol-d5	53.74	52.99	53.37	106.73%	1.41%
Phenol	55.09	53.59	54.34	108.68%	2.76%
Bis(-2-Chloroethyl)ether	53.21	52.84	53.03	106.05%	0.70%
2-Chlorophenol	54.19	53.13	53.66	107.32%	1.98%
2 Chlorophenol-d4	53.96	51.92	52.94	105.88%	3.85%
1,3-Dichlorobenzene	55.44	52.20	53.82	107.64%	6.02%
1,4-Dichlorobenzene	56.28	53.41	54.85	109.69%	5.23%
1,2 Dichlorobenzene-d4	50.83	47.96	49.40	98.79%	5.81%
Benzyl Alcohol	55.46	54.54	55.00	110.00%	1.67%
1,2-Dichlorobenzene	55.79	53.49	54.64	109.28%	4.21%
2-Methylphenol	52.56	50.36	51.46	102.92%	4.28%
Bis(2-chloroisopropyl)ether	56.00	58.00	57.00	114.00%	3.51%
4-Methylphenol	53.19	50.35	51.77	103.54%	5.49%
N-Nitroso-Di-n-propylamine	53.09	52.10	52.60	105.19%	1.88%
Hexachloroethane	53.54	49.57	51.56	103.11%	7.70%
Nitrobenzene-d5	58.22	51.14	54.68	109.36%	12.95%
Nitrobenzene	60.44	55.32	57.88	115.76%	8.85%
Isophorone	54.17	51.97	53.07	106.14%	4.15%
2-Nitrophenol	59.96	53.86	56.91	113.82%	10.72%
2,4-Dimethylphenol	35.78	33.70	34.74	69.48%	5.99%
Benzoic Acid	112.04	95.98	104.01	208.02%	15.44%
Bis(-2-Chloroethoxy)methane	54.07	51.46	52.77	105.53%	4.95%
2,4-Dichlorophenol	57.08	52.95	55.02	110.03%	7.51%
1,2,4-Trichlorobenzene	52.71	49.10	50.91	101.81%	7.09%
Naphthalene	54.35	50.47	52.41	104.82%	7.40%
Hexachlorobutadiene	51.65	47.88	49.77	99.53%	7.58%
4-Chloro-3-methylphenol	58.41	51.15	54.78	109.56%	13.25%

2-Methylnaphthalene	55.99	50.48	53.24	106.47%	10.35%
Hexachlorocyclopentadiene	22.52	13.83	18.18	36.35%	47.81%
2,4,6-Trichlorophenol	58.39	53.86	56.13	112.25%	8.07%
2,4,5-Trichlorophenol	52.52	40.49	46.51	93.01%	25.87%
2-Chloronaphthalene	51.63	48.42	50.03	100.05%	6.42%
2-Fluorobiphenyl	53.36	47.42	50.39	100.78%	11.79%
2-Nitroaniline	53.05	52.79	52.92	105.84%	0.49%
Dimethyl Phthalate	51.71	48.09	49.90	99.80%	7.25%
Acenaphthylene	46.25	44.13	45.19	90.38%	4.69%
3-Nitroaniline	47.11	40.39	43.75	87.50%	15.36%
Acenaphthene	52.94	49.21	51.08	102.15%	7.30%
2,4-Dinitrophenol	28.27	24.31	26.29	52.58%	15.06%
4-Nitrophenol	44.72	28.17	36.45	72.89%	45.41%
Dibenzofuran	52.02	48.57	50.30	100.59%	6.86%
2,4-Dinitrotoluene	53.00	45.60	49.30	98.60%	15.01%
2,6-Dinitrotoluene	54.32	46.11	50.22	100.43	16.35%
Diethylphthalate	49.69	48.00	48.85	97.69%	3.46%
4-Chlorophenyl-phenylether	49.66	46.82	48.24	96.48%	5.89%
Fluorene	52.92	51.29	52.11	104.21%	3.13%
4-Nitroaniline	65.12	49.29	57.21	114.41%	27.67%
4,6-Dinitro-2-methylphenol	30.15	25.31	27.73	55.46%	17.45%
N-Nitrosodiphenylamine	63.55	61.05	62.30	124.60%	4.01%
2,4,6-Tribromophenol	70.13	68.93	69.53	139.06%	1.73%
4-Bromophenyl-phenylether	57.18	52.81	55.00	109.99%	7.95%
Hexachlorobenzene	63.68	59.89	61.79	123.57%	6.13%
Pentachlorophenol	60.83	43.42	52.13	104.25%	33.40%
Phenanthrene	58.10	50.94	54.52	109.04%	13.13%
Anthracene	39.47	26.37	32.92	65.84%	39.79%
Carbazole	49.47	43.80	46.64	93.27%	12.16%
Di-n-Butylphthalate	44.13	39.49	41.81	83.62%	11.10%
Fluoranthene	34.92	21.48	28.20	56.40%	47.66%
Pyrene	63.13	54.43	58.78	117.56	14.80%

Terphenyl-d14	54.05	49.89	51.97	103.94%	8.00%
Butylbenzylphthalate	60.74	61.39	61.07	122.13%	-1.06%
3,3'-Dichlorobenzidine	56.86	70.44	63.65	127.30%	-21.34%
Benzo(a)anthracene	55.08	53.96	54.52	109.04%	2.05%
Bis(2-Ethylhexyl)phthalate	87.01	90.74	88.88	177.75%	-4.20%
Chrysene	49.17	47.16	48.17	96.33%	4.17%
Di-n-octyl phthalate	39.22	37.42	38.32	76.64%	4.70%
Benzo(b)fluoranthene	55.16	50.76	52.96	105.92%	8.31%
Benzo(k)fluoranthene	36.74	34.30	35.52	71.04%	6.87%
Benzo(a)pyrene	42.22	40.90	41.56	83.12%	3.18%
Indeno(1,2,3-cd)pyrene	78.92	79.22	79.07	158.14%	-0.38%
Dibenzo(a,h)anthracene	64.75	60.64	62.70	125.39%	6.56%
Benzo(g,h,i)perylene	70.31	56.54	63.43	126.85%	21.71%

APPENDIX F

OPERATING PARAMETERS FOR THE SEMIVOLATILE ORGANIC COMPOUND GC/MS ANALYSIS

The operating parameters for the SVOC GC/MS analyses were as follows:

GC PARAMETERS

Gas Chromatograph:	Hewlett-Packard 5890a series II
Injection port:	Capillary splitless.
GC Column:	DB-5 30.m 0.32 mm I.D. 1.00 μm film thickness
Carrier gas:	Ultra pure Helium.
Column head pressure:	8 lbs./in^2.
Injection port temperature:	290 °C.
Transfer line temperature:	300 °C.
Initial temperature:	40 °C.
Initial time:	3.0 minutes.
Temperature ramp rate:	8.0 °C per/minute.
Final temperature:	300 °C.
Final time:	14.5 minutes.

MASS SPECTROMETER PARAMETERS

Mass spectrometer:	Hewlett-Packard 5988.
Data system:	Hewlett-Packard 1000 RTE-A Revision F.
Source temperature:	200 °C.
Ionization type:	Electron impact.
Ionizer energy:	70 Electron volts.
Emission current:	300 Micro amps.
Scan type:	Linear, full scan.
Scan range:	35 - 500 daltons.
Scan rate:	0.98 seconds/scan.

APPENDIX G

DEXSIL CORPORATION'S

CHLOR-N-OIL•

PCB SCREENING KIT

SOURCE: DEXSIL CORP.

CLOR·N·OIL™

PCB Screening Kit

DEXSIL®

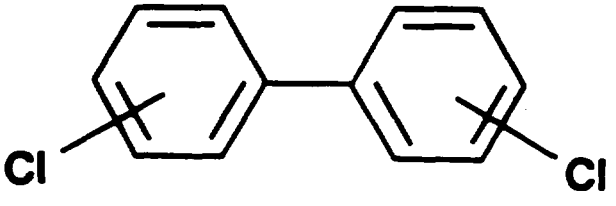
DEFINITIONS

PCB stands for "polychlorinated biphenyl" and is classified as a chlorinated hydrocarbon. PCB is made by attaching one or more chlorine atoms to a biphenyl molecule. PCB was used primarily as electrical insulating fluid in transformers, capacitors, and other electrical apparatus. PCB has a heavy oil-like consistency, is very stable, and exhibits low electrical conductivity. As well, PCB has a low water solubility, low vapor pressure, low flammability threshold, and high heat capacity, all of which made PCB an obviously stable insulating fluid in high energy electrical equipment.

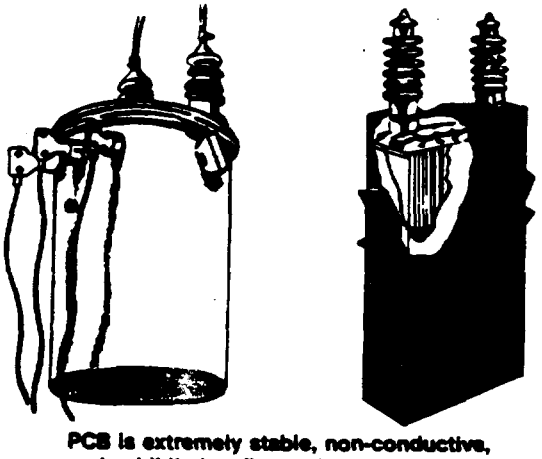
PCB was marketed under various trade names including:

Abestol	Elemex
Adkarel	Eucarel
Aroclor	Hyvol
Aroclor B	Inerteen
Askarel	No-Flamol
Chlorextol	Pyranol
Clorphen	Saf-T-Kuhl
Diaclor	Sanotherm
Dykanol	

Askarel is the most common name used to refer to PCB and is often used to mean any combination of PCB and chlorinated benzenes.



PCB is formed by joining from 1 to 10 chlorine atoms to a biphenyl molecule.



PCB is extremely stable, non-conductive, and exhibits low flammability; which made it an ideal electrical insulating and heat transfer fluid.

Dexsil® and Clor-N-Oil® are Registered Trademarks of Dexsil Corporation

EPA REGULATIONS

Environmental Protection Agency (EPA) regulations limit the concentration of PCB in electrical insulating fluid to less than 50 parts per million (ppm) wt/wt basis. Equipment containing fluid with a PCB concentration between 50 and 500 ppm is considered to be "PCB contaminated," while equipment containing fluid with a PCB concentration greater than 500 ppm is considered to be a "PCB item." Any oil or equipment containing a concentration of PCB greater than 500 ppm must have been removed from food and feed facilities by October 1985. By December 1985 all transformers containing greater than 500 ppm must have been registered with local fire personnel, and by October 1990, the use of PCB transformers with high secondary voltages ($\geq$ 480 V) was prohibited.

The EPA has determined that PCB poses a health risk to humans because of its uncommonly stable molecular structure. Once introduced into the environment, PCB will not break down into other chemicals and therefore allows any potential health hazards to persist for indefinite periods of time. The EPA has ruled that PCB is "toxic and persistent."

The most immediate health hazard to humans occurs when PCB is burned at low temperatures and creates the highly toxic chemical, dioxin. In contact with the human body, PCB also has the potential for developing chloracne, a disfiguring, though reversible, skin illness. Animal research also suggests the probability of reproductive disorders, developmental toxicity, and the formation of tumors (oncogenicity).

ABOUT THE KIT

The Clor-N-Oil PCB Screening Kit was developed by the Electric Power Research Institute (EPRI) in response to the U.S. EPA's decision to restrict the use of, and eventually remove from service, all electrical equipment containing PCB contaminated insulating fluid. Research for the kit was funded by EPRI and performed by General Electric Company of Pittsfield, Massachusetts, and Dexsil Corporation of Hamden, Connecticut. Dexsil is currently manufacturing and marketing the Clor-N-Oil kit. By using the kit as a comprehensive screening test of all suspect transformers, utilities and other users are able to eliminate up to 90% of costly laboratory analysis that is normally required.

In addition to significant cost savings, the Clor-N-Oil Kit offers immediate, on-site results in less than five minutes when equipment needs repair or when site cleanup involves fluid spills of an unknown PCB level. Although the Clor-N-Oil Kit does not eliminate the need for all laboratory analysis, it can significantly reduce the number of samples which must be sent to the lab. The kit has been used extensively throughout the U.S. and Canada, as well as in Europe, South America, and the Far East. Three different test levels for the Clor-N-Oil kit are currently available — 50 ppm, 100 ppm, and 500 ppm. Each kit is used in the same way — the end point for each has been adjusted so that it turns color at the proper level. The kit involves a "go, no-go" type of test where the result is either positive or negative — for instance, the Clor-N-Oil 50 kit will reveal whether a sample is above or below 50 ppm, but will not tell whether a sample contains 70 or 80 ppm. When the kit registers under 50 ppm, however, the darker the color, the closer the sample is to zero.

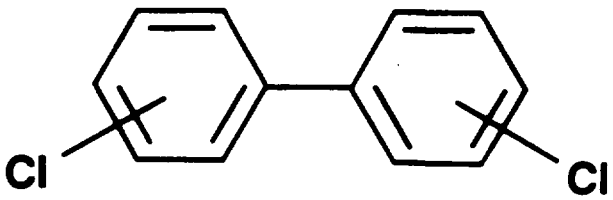
DEFINITIONS

PCB stands for "polychlorinated biphenyl" and is classified as a chlorinated hydrocarbon. PCB is made by attaching one or more chlorine atoms to a biphenyl molecule. PCB was used primarily as electrical insulating fluid in transformers, capacitors, and other electrical apparatus. PCB has a heavy oil-like consistency, is very stable, and exhibits low electrical conductivity. As well, PCB has a low water solubility, low vapor pressure, low flammability threshold, and high heat capacity, all of which made PCB an obviously stable insulating fluid in high energy electrical equipment.

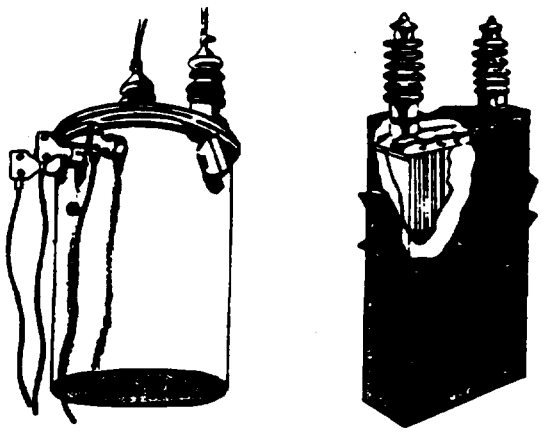
PCB was marketed under various trade names including:

Abestol	Elemex
Adkarel	Eucarel
Aroclor	Hyvol
Aroclor B	Inerteen
Askarel	No-Flamol
Chlorextol	Pyranol
Clorphen	Saf-T-Kuhl
Diaclor	Sanotherm
Dykanol	

Askarel is the most common name used to refer to PCB and is often used to mean any combination of PCB and chlorinated benzenes.



PCB is formed by joining from 1 to 10 chlorine atoms to a biphenyl molecule.



PCB is extremely stable, non-conductive, and exhibits low flammability; which made it an ideal electrical insulating and heat transfer fluid.

Dexsil® and Clor-N-Oil® are Registered Trademarks of Dexsil Corporation

CLOR-N-OIL™ ADVANTAGES

Test Samples at 50, 100 or 500 ppm:

Three different Clor-N-Oil kits are available to test at either 50, 100, or 500 parts per million.

It's Easy to Use:

The Clor-N-Oil screening kit involves a simple procedure that can be performed by anyone in the field, lab, or maintenance shop. No calibrations are required as all reagents are pre-measured in crushable glass ampules.

It's Quick:

With Clor-N-Oil, the entire testing procedure takes less than four minutes from the time the oil sample is taken from the electrical apparatus to the time results are obtained.

It's Convenient:

Since no instruments are required, tests can be performed immediately, on site. The 2 oz. kit can be stored in any lab or field vehicle for quick access on short notice when emergency testing is required.

It's Safe:

All Clor-N-Oil reagents are self-contained within the kit. After pipetting the oil sample into the pre-marked reaction tube, no measuring or pipetting of reagents is required — no reagent or other chemical ever comes into contact with the person using the kit.

It's Inexpensive:

Kits start at $7 each in boxes of ten. In quantity, prices drop to $4 per test. No initial outlay is required, so extensive savings can be realized by both small and large users.

COST ANALYSIS

Regular systematic testing of all company-owned or operated transformers can be very expensive if the testing method used is gas chromatography (GC). The Clor-N-Oil kit can save up to 70% of the total cost of GC testing, as well as alleviate downtime while waiting for GC analysis results.

One major utility has successfully used the kit to test and screen over 100,000 suspect transformers. Of all those tested to date, approximately 93% have tested negative (below 50 ppm PCB) eliminating the need for further testing. At this rate, use of the Clor-N-Oil kit will result in savings of between 1.4 and 3.7 million dollars for every 100,000 transformers tested.[1]

EPA regulations require that any PCB spill be treated as contaminated if the actual PCB concentration is not known. Clean-up costs for such leakage can run as high as $10,000 per spill. Virginia Electric and Power Company estimates a yearly savings of $124,000 by using the Clor-N-Oil kit to determine, on site, the PCB level of any leaking or damaged transformer. Such on-site testing allows for quick determination of contaminated or non-contaminated fluids resulting in carefully informed decisions regarding cleanup procedures, saving Virginia Electric considerable expense in cleanup and litigation fees.[2]

Much of the savings realized by the Clor-N-Oil kit is found in the time saved in the sampling and testing process. Because the Clor-N-Oil kit is extremely protable and inexpensive, several kits can be kept on site at service shops, substations, and in company vehicles. In the event of a spill or other emergency situation, a kit is usually in close proximity and the test can be completed within a matter of minutes. If the kit is not used, and a laboratory test must be run, a sample from the unit in question must be sent to a laboratory and then run on a gas chromatograph. This process takes at least an hour, and very often results are not reported for three or four days. During this time, the spill area must be roped off because the oil must be considered contaminated until it has been shown otherwise. This very often results in having to keep customers off line and crews on location for longer than is necessary.

[1] *"Clor-N-Oil Test Kit as a PCB Screening Tool," Proceedings: 1985 EPRI PCB Seminar, pp 4-7 to 4-14, EPRI CS/EA/EL-4480.*

[2] *"Quick and Easy Field Testing for PCBs: Clor-N-Oil," EPRI "First Use" #4ZZZF, Dec.1984.*

4

STEP BY STEP

Step 1

Unscrew black cap from the first tube. Using the plastic pipette, fill the tube with exactly 5 ml of transformer oil (to 5 ml line on tube). Replace the black cap securely.

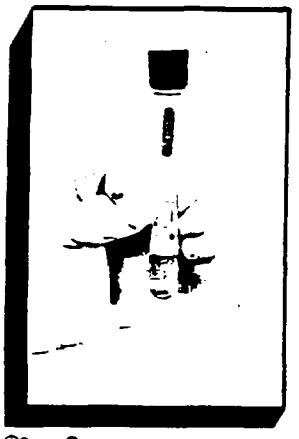
Step 2

Break the colorless ampule (lower) in the black-capped tube by compressing the sides of the tube. Shake for ten seconds. Break the gray ampule (top) and shake for ten seconds. (Be sure that the colorless ampule is broken first, the gray one second.) Allow to react for one minute, shaking intermittently. Place the tube in holder in the box.

Step 3

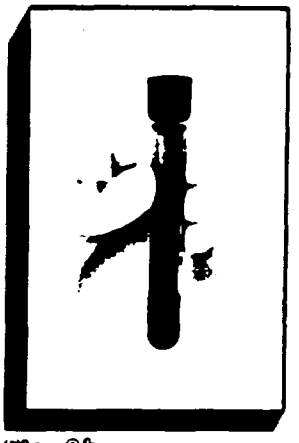
Keep black tube in holder. Remove the caps from both tubes and pour the clear solution from the white-capped tube into the black-capped tube. Replace the black cap and shake the tube for ten seconds. Vent the tube by unscrewing the black cap 1/2 turn. Tighten cap securely and shake for ten seconds more. Vent tube again and tighten cap securely. The oil should no longer appear gray.

Step 1



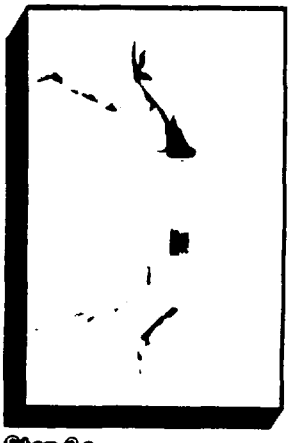
Step 2

Step 2a



Step 2b

Step 3

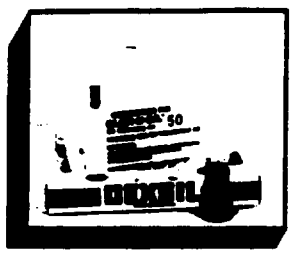


Step 3a

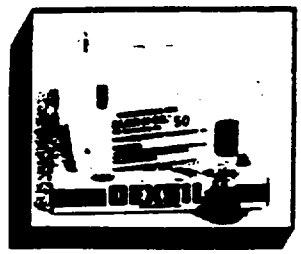
DIRECTIONS

Step 4

Turn the black-capped tube upside down, allow the solution to settle for two minutes. If the yellowish oil layer (5 ml) is below the clear buffer layer (7 ml), stop the test since the oil is primarily pure PCB. If the yellowish oil layer is on top of the clear water layer, position the black tube over the white tube, carefully flip open the black nozzle (keep nozzle pointed away from operator) and dispense exactly 5 ml of the buffer solution into the white-capped tube (to 5 ml line on the white tube). Replace the white cap securely and close the nozzle on the black cap.



Step 4 If oil layer is on bottom, STOP test.



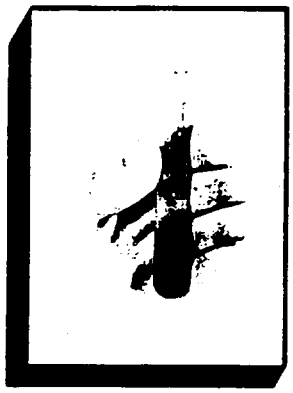
Step 4a If oil layer is on top, continue test.

Step 4b

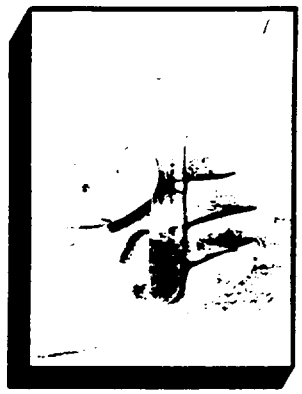
Step 4c

Step 5

Break the colorless ampule (bottom) in the white-capped tube, shake for ten seconds. Break the colored ampule (top), shake for ten seconds, and observe color.



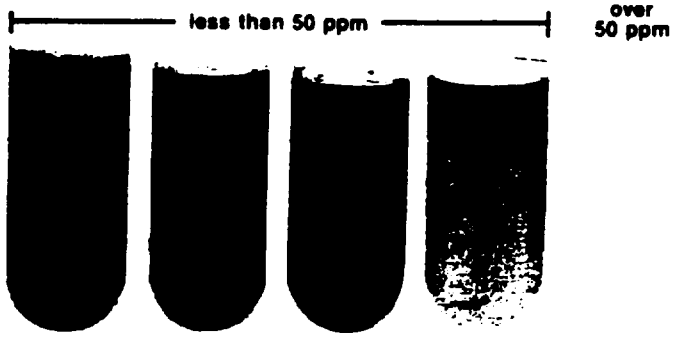
Step 5



Step 5a

Step 6

If the solution is purple, the oil sample contains less than 50 ppm PCB. If it is yellow or colorless, it may contain more than 50 ppm PCB and should be tested further by a PCB specific method. Disregard any color which may develop in a thin layer of oil on top of the solution.

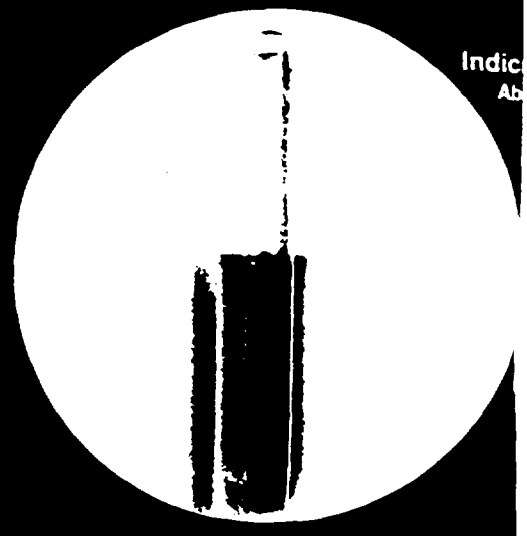


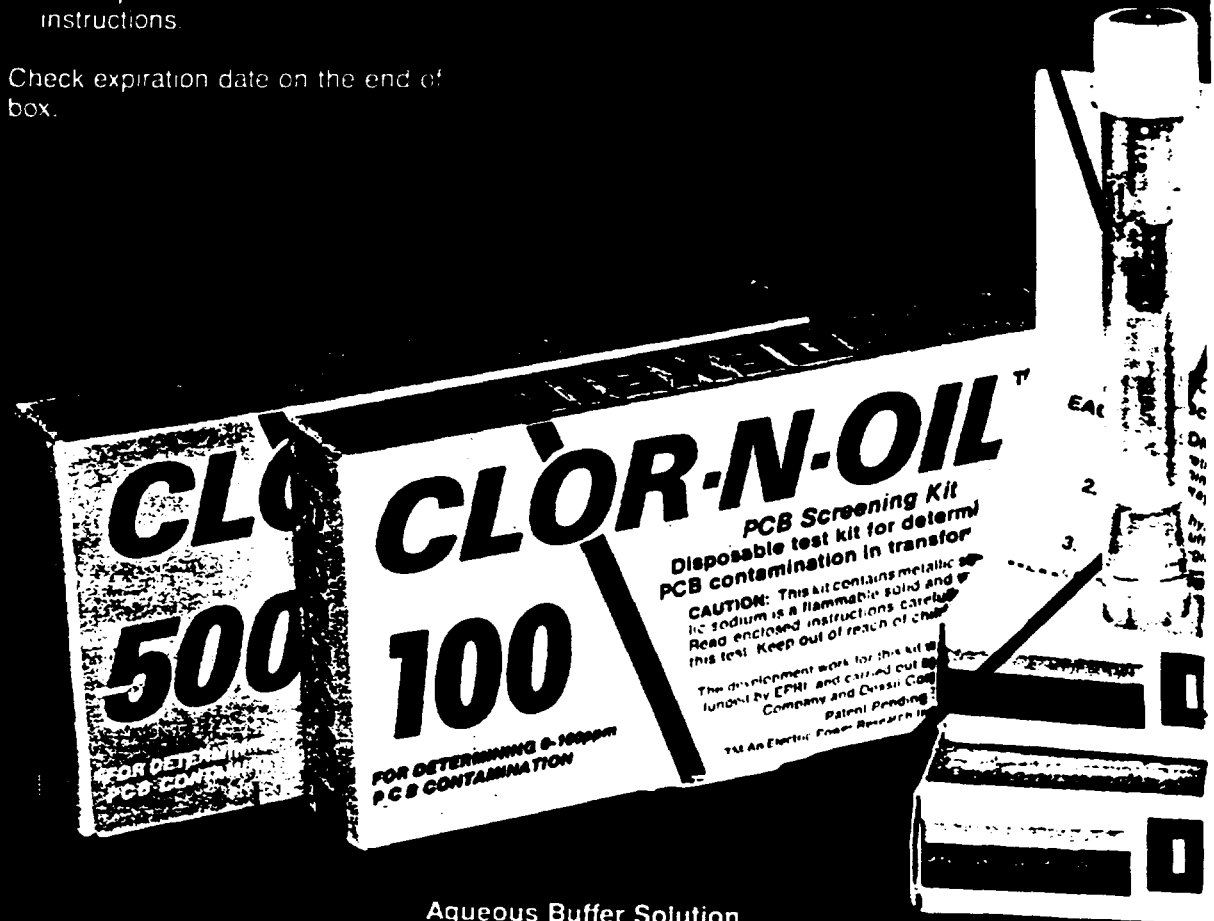
PCB SCREENING KIT

Each Kit Contains:

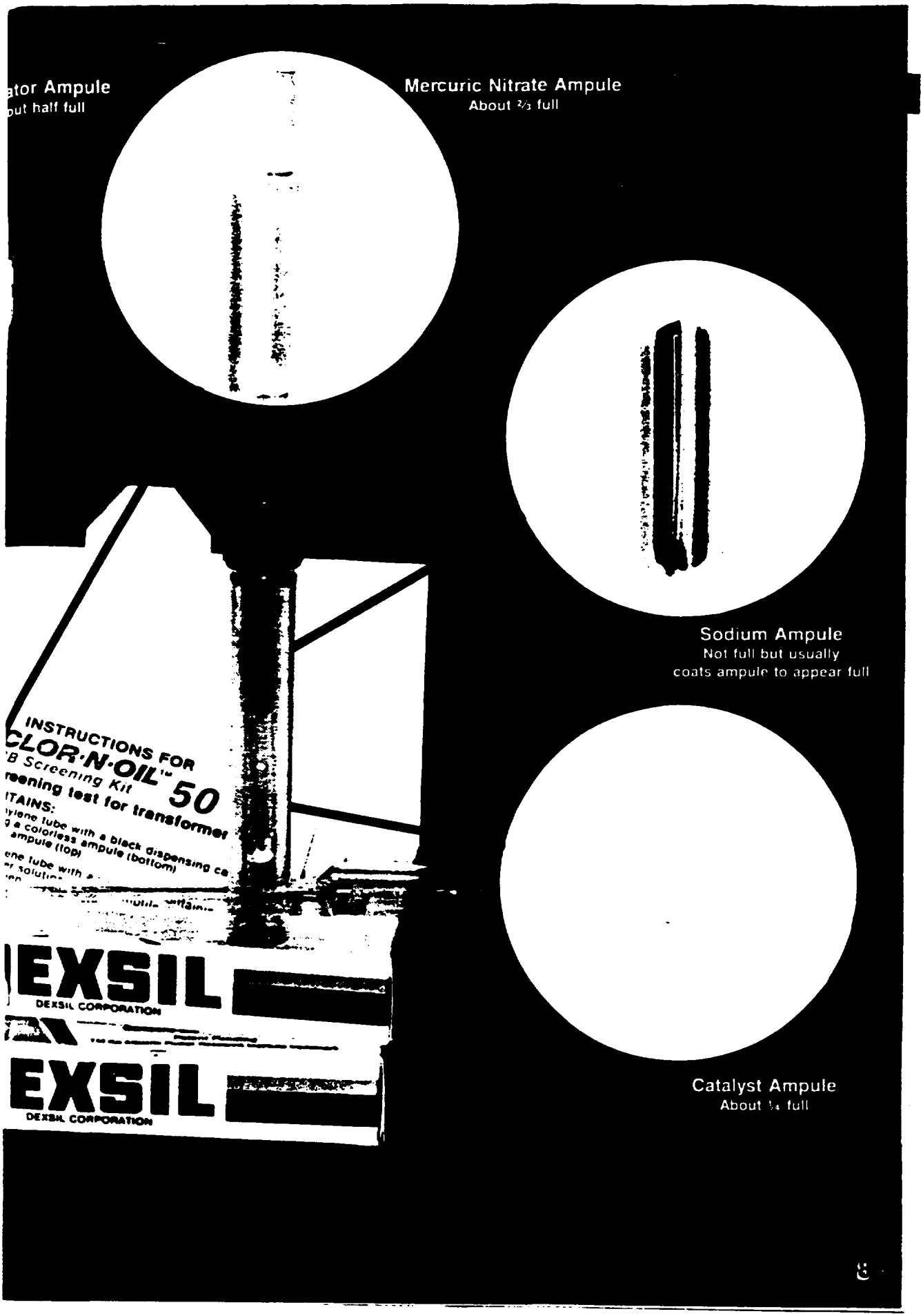
1. A polyethylene test tube with a black dispensing cap containing a colorless ampule (bottom) and a gray ampule (top).
2. A polyethylene test tube with a white cap containing 7 ml of buffer solution, a clear ampule (bottom) and a red-green ampule (top).
3. A disposable polyethylene pipette for obtaining the oil sample.
4. A comprehensive set of instructions.

Check expiration date on the end of box.





Aqueous Buffer Solution
½ inch above 5 ml. line


ator Ampule
but half full
Mercuric Nitrate Ampule
About ⅔ full
Sodium Ampule
Not full but usually
coats ampule to appear full
Catalyst Ampule
About ¼ full
INSTRUCTIONS FOR
CLOR·N·OIL™ 50
B Screening Kit
reening test for transformer
TAINS:
DEXSIL
DEXSIL CORPORATION
DEXSIL
DEXSIL CORPORATION

SUGGESTIONS FOR USING

- Wear rubber gloves and safety glasses.
- When crushing glass ampules, press firmly in the center of the ampule **once**. Never attempt to recrush broken glass in the test tube since the glass may sever the plastic and cut fingers.
- In case of accidental breakage onto skin or clothing, wash with large amounts of water. All the ampules are poisonous and should not be taken internally.
- Dispose of kits properly. Treat used kits as PCB waste. (See page 13 on PCB waste disposal.)
- The test works on the principle of chloride detection, therefore, contamination by salt (sodium chloride), sea water, perspiration, etc., will give a false positive result and require further testing in the laboratory.
- Never touch the ampules, the holder inside the tube, or the pipette tip, as salt may contaminate the test.
- The kit should be examined upon opening to see that all of the components are present and that all ampules (two in each tube) are in place and not leaking. The liquid in the white tube should be approximately 1/2 inch above the 5 ml line inscribed on the tube and the tube should not be leaking. The ampules are not supposed to be completely full.
- The Clor-N-Oil test will not work on a sample that contains water. If, in step 2, the tube loses its gray color, the sample probably contains water and the test should not be run. Another sample may be tried if the oil is dried first.
- Freezing of the buffer solution does not damage the kit, but the solution should be completely melted before running the test.

Before using a kit, make sure that the expiration date has not passed.

THE CLOR-N-OIL™ TEST KIT

- Perform the test in a warm, dry area with adequate light. In cold weather, a truck cab is sufficient. If a warm area is not available, step 4 of the directions should be performed while warming the tube in the palm of the hand.

- When drawing oil into the pipette, do not submerge tip too deeply into the oil sample. This will cause the pipette to drip.

- When inserting the pipette into the black tube, insert it all the way to the 5 ml line. This prevents oil from getting on the tube walls and reagent holder and allowing too much oil into the tube.

- Always crush the clear ampule in each tube first. If this has not been done, stop the test and start over using another complete kit. A false negative may result and allow a contaminated sample to pass without detection.

Make sure the pipette is inserted to the 5ml line so that excess oil does not accumulate on the sides of the tube.

- Check expiration date on the end of the box. If kits have expired (more critical when kits are stored at higher temperatures) you will start to notice a greater number of false positive results. For instance, a sample that actually contains about 30 ppm PCB may show greater than 50 when tested with an outdated Clor-N-Oil kit. An expired kit will not give a false negative result. As long as the kits turn purple, they are still active.

- Remember that the kit is designed to test only transformer oil of petroleum origin. It may work on other fluids, but please check with Dexsil before using the kit on anything but transformer oil.

- A video tape showing how to take a sample and use the kit in the field is available from Dexsil. Please contact Dexsil if you feel that your company could make use of this video.

TECHNICAL APPROACH

The Clor-N-Oil PCB Screening Test is based on the detection of the total concentration of chlorine in an oil sample. Since all PCB contains some chlorine and the amount of chlorine is directly proportional to the amount of PCB, then the PCB concentration in a given sample can be indirectly measured by *determining the total chlorine* concentration.

During the testing process, the chlorine atoms are stripped away from the PCB through the action of sodium and a catalyst. The chloride ions are then introduced into a water buffer solution and reacted with a carefully controlled amount of dissolved mercuric nitrate. A color indicator, sensitive to mercuric ions, is then added. If there are more mercuric ions than chloride ions, the free mercuric ions react with the indicator resulting in a purple color, indicating less than 50 ppm PCB. If the number of chloride ions is equal to or greater than the number of mercuric ions, then all the mercuric ions are associated with the chloride ions and there are no mercuric ions free to react with the color indicator, thus, no purple color can develop. The result is a pale yellow or colorless solution revealing the presence of greater than 50 ppm PCB.

Since the exact amount of mercuric nitrate is known, it is easy to determine if the concentration of chloride ions is above or below the preset endpoint dictated by the mercuric nitrate. Once the amount of chlorine is known, one has a good indication of the amount of PCB present in the sample. When a positive reading has been obtained with the Clor-N-Oil testing procedure, the oil sample should be further tested by a PCB specific method, usually gas chromatography, in order to determine the exact amount of PCB present in the sample.

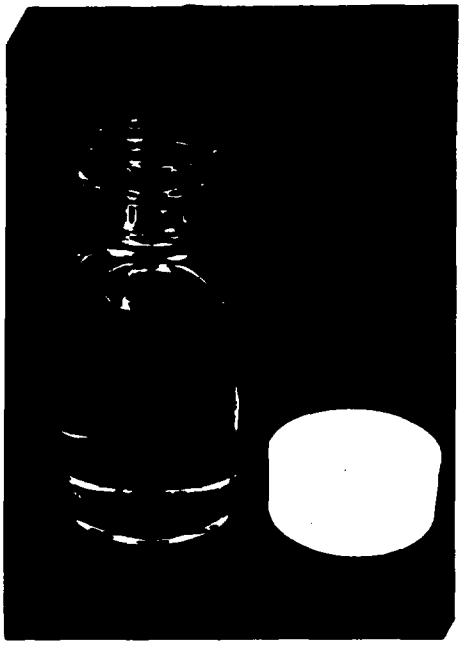
ASKAREL TYPE	% PCB IN ASKAREL			% CHLORINATED BENZENES		COMPONENT RATIOS		PCB CONCENTRATION AT 21 PPM CHLORINE (point where Clor-N-Oil gives positive result)
	1260	1254	1242 (1016)	Trichloro-benzene	Tetrachloro-benzene	PCB/ Askarel	Cl/ PCB	
1) TRANSFORMER ASKARELS (ASTM D2283)								
A	60			40		0.60	0.99	21
B	45			40	15	0.45	1.34	16
C			80	15	5	0.80	0.57	37
D		70		30		0.70	0.79	27
E			100			1.00	0.42	50
F		45		40	15	0.45	1.27	17
G		60		40		0.60	0.92	23
2) CAPACITOR ASKARELS (ASTM D2233)								
A			100			1.00	0.42	50
B		100				1.00	0.54	39
C		75		25		0.75	0.73	29
D			(100)			1.00	0.42	50

Suggested Sampling Procedures

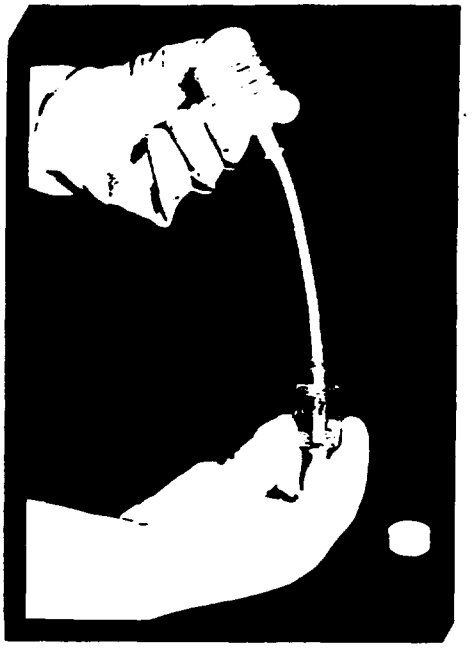
Accepted sampling p... es should be followed wher ...king an oil sample from a piece of electrical equipment or container ... use with Clor-N-Oil or GC testing ... thods.

Test samples should be taken from a spot which is representative of the entire piece of equipment. Although PCB is generally evenly dispersed throughout the oil, there may be other interfering compounds which collect either at the top or bottom of the oil container.

Because water adversely affects both the Clor-N-Oil test and the GC test, it is recommended that the sample not be taken from the bottom of the container since water is heavier and collects there. If possible, the sample should be taken a few inches below the surface of the oil. This will minimize the chances of contaminating the sample with water or other compounds that are unrepresentative of the whole. If the sample must be taken from the bottom of the unit, remove at least a quart of fluid before the sample to be tested is taken. When the sample is taken, make sure that the fluid is of consistent viscosity and color. If the oil does not appear homogenous, continue removing fluid until it does.



Samples should be stored in clean glass vials with either foil or Teflon®-lined caps.



Dexsil can provide both sample vials and a 20ml capacity pipette for taking samples from electrical equipment.

Teflon® is a registered trademark of E.I. duPont.

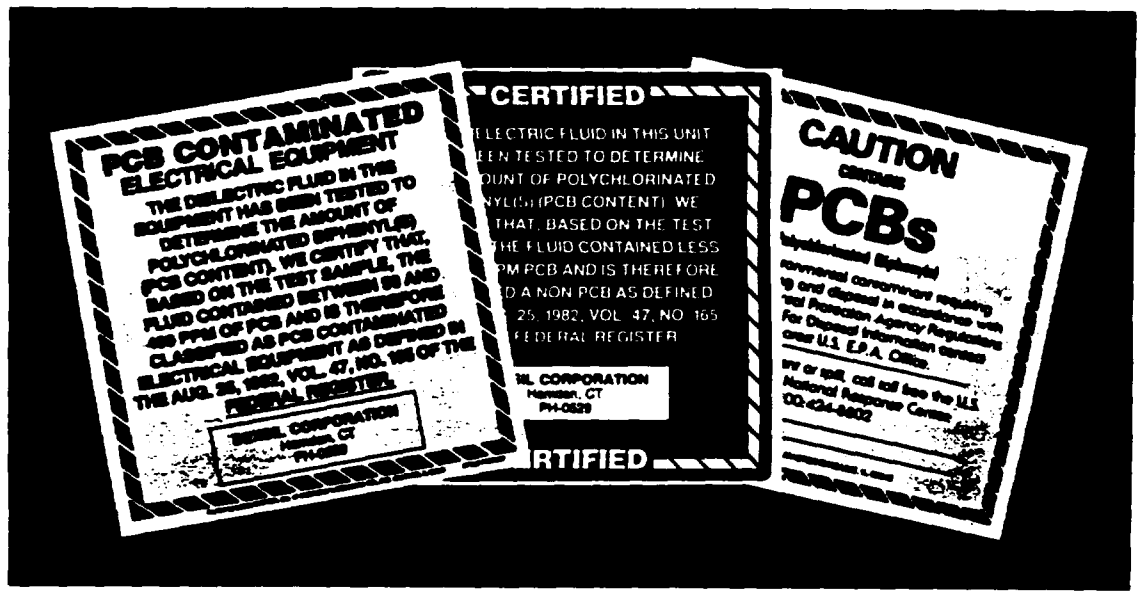
Waste Disposal

EPA regulations regarding the disposal of waste oil fall into three categories: Oils containing less than 50 ppm PCB (Non-PCB), oils containing between 50 ppm and 500 ppm PCB (PCB Contaminated), and oils containing greater than 500 ppm PCB (PCB Fluid).

1. There are no regulations governing the disposal of transformers and oils containing less than 50 ppm PCB except that such oils may not be used as a coating, sealant, dust control agent, or pesticide carrier and may not be sold for re-use.
2. Transformers and oils containing between 50 ppm and 500 ppm PCB must be packaged and stored in a certified chemical waste landfill, incinerated in high temperature boilers or incinerated in an EPA-approved high temperature incinerator.
3. Transformers and oils containing greater than 500 ppm PCB must be disposed of only by incineration in an EPA-approved high temperature incinerator.

Used Clor-N-Oil kits should be disposed of as PCB contaminated waste. Although any PCB has been broken down during the course of the chemical reaction, oil residue remaining in the extraction pipette may contain some concentration of PCB.

For additional information on PCB regulations, consult your regional EPA office or see 40 CFR Part 761.



GAS CHROMATOGRAPHIC ANALYSIS

Dexsil offers Gas Chromatographic analysis as an important follow-up to Clor-N-Oil. Once an oil sample has been screened with the Clor-N-Oil test, negative samples (less than 50 ppm) can be tagged and eliminated from concern. However, positive results (indicating greater than 50 ppm) often need to be tested by a PCB specific method, such as gas chromatography (GC), in order to determine actual PCB type and specific concentration.

Because the Clor-N-Oil kit is based on a total chlorine analysis, a positive result may occur when the sample is contaminated with chlorinated sources other than PCB. A supplementary GC analysis will verify either the presence of PCB or the presence of some other chlorinated compound.

The Dexsil laboratory is able to perform GC analysis on oil, water, soil, or wipe samples at a discount to Clor-N-Oil users. The laboratory also posesses GCMS capability for samples which may be partially degraded or which may contain compounds that are structurally similar to PCBS. Please write or call Dexsil for additional information about all our laboratory services.

Dexsil's gas chromatography laboratory performs oil, water and soil analysis at a discount to Clor-N-Oil users.

For information about ordering the Clor-N-Oil PCB Screening Kits, contact Dexsil Corporation or your nearest distributor.

Dexsil Corporation
One Hamden Park Drive
Hamden, CT 06517-3150
(203) 288-3509
Fax: (203) 248-6523

APPENDIX H

OPERATING PARAMETERS FOR THE

POLYCHLORINATED BIPHENYL AND PESTICIDES ANALYSIS BY GC/ECD;

FASP PCB EXTRACTION METHOD

PCBs and pesticides were analyzed using the following operating parameters.

GC PARAMETERS

Gas Chromatograph:	Hewlett-Packard 5880.
Injection port:	Capillary split/splitless with Y-junction.
GC Columns:	DB-5 30 m 0.53 mm I.D. 1.0 μm film thickness.
	RTX-1701 30 m 0.53 mm I.D. 1.0 μm film thickness.
Carrier gas:	Ultra pure nitrogen.
Column flow rate:	7.0 mL/minute.
Makeup gas flow rate:	55 mL/minute
Injection port temperature:	200 °C.
Detector temperature:	300 °C.
Detector:	^{63}Ni electron capture.
Initial temperature:	175 °C.
Initial time:	0.5 minutes.
Temperature ramp rate:	4.5 °C per/minute.
Final temperature:	270 °C.
Final time:	7.0 minutes.

8. EXTRACTION/ACID CLEANUP

8.1 SAMPLE EXTRACTION/ACID CLEANUP TECHNIQUE FOR PCBs IN SOIL/SEDIMENT

The sample extraction technique for PCBs in soil/sediment is as follows:

i) Discard any leaves, sticks, rocks or foreign objects from the sample and homogenize the sample. Place 2 to 3 grams of the sample to a tared and labeled 150 mm culture tube; weigh again to the nearest 0.01 gram. Record weight.

ii) Add approximately 1 gram of sodium sulfate. Mix into a slurry

iii) Add 1.0 ml of pesticide grade methanol using a repipet to the culture tube and cap.

iv) Vortex at maximum speed for 30 seconds.

v) Add 10.0 ml pesticide grade hexane using a repipet to the culture tube and recap.

vi) Vortex at maximum speed for 60 seconds.

vii) Transfer a 6 to 8 ml aliquot of the hexane layer to a labeled 100 mm culture tube using a disposable pasteur pipet.

vii) Add 1.0 ml concentrated sulfuric acid using a repipet to the aliquot and recap.

ix) Vortex at maximum speed for 60 seconds.

x) Centrifuge if needed.

xi) Transfer approximately 1 ml of the hexane extract into a Teflon-lined screw cap autosampler vial using a disposable pasteur pipet. Avoid transfer of any of the acid layer.

xii) Enhanced sensitivity may be achieved by transferring 5.00 ml of acid-treated hexane extract to a 10 ml graduated centrifuge tube and reducing the solvent volume to between 0.2 and 0.4 ml using standard low temperature N_2 blowdown techniques, and making the final sample extract concentration 0.50 ml by rinsing tube walls with hexane.

xiii) The sample extract is now ready for GC injection.

8.2 SAMPLE EXTRACTION/ACID CLEANUP TECHNIQUE FOR PCBs IN WATER

The sample extraction technique for PCBs in water is as follows:

i) Add 100 mL of water to a clean 100-mL volumetric flask.

ii) Add 1.0 mL of pesticide grade hexane by repipet to the flask and shake vigorously for 2 minutes.

iii) Allow the layers to separate.

iv) Transfer the hexane layer to a 10-mL graduated centrifuge tube using a disposable pasteur pipet.

v) Repeat steps 2 through 4 twice and combine the extracts.

vi) Add 1.0 Ml of concentrated sulfuric acid by repipet to the hexane extract.

vii) Vortex at maximum speed for 60 seconds.

viii) Centrifuge, if needed.

ix) Transfer approximately 1 mL of extract into a Teflon-lined screw cap autosampler vial using a disposable pasteur pipet. Avoid transfer of any of the acid layer.

x) The sample extract is now ready for GC injection.

8.3 SAMPLE EXTRACTION/ACID CLEANUP TECHNIQUE FOR PCBs IN OIL

The sample extraction technique for PCBs in oil is as follows:

i) Add 0.2 to 0.3 g of well-homogenized sample to a tared and labeled 150-mm culture tube; reweigh to the nearest 0.01 g. Record weight.

ii) Add 10.0 ml of pesticide grade hexane by repipet to the culture tube and recap.

iii) Vortex at maximum speed for 60 seconds.

iv) Transfer a 6 to 8 ml aliquot of the hexane layer to a labeled 100-mm culture tube using a disposable pasteur pipet.

v) Add 1.0 ml of concentrated sulfuric acid by repipet to the aliquot and recap.

vi) Vortex at maximum speed for 60 seconds.

vii) Centrifuge, if needed.

viii) Transfer approximately 1 ml of extract into a Teflon-lined screw cap autosampler vial using a disposable pasteur pipet.Avoid transfer of any of the acid layer.

ix) Enhanced sensitivity may be achieved by transferring 5.00 ml of acid-treated hexane extract to a 10-ml graduated centrifuge tube and reducing the solvent volume to between 0.2 and 0.4 ml by standard low-temperature N_2 blowdown techniques and making the final sample extract volume 0.50 ml by rinsing tube walls with hexane.

x) The sample extract is now ready for GC injection.

8.4 SAMPLE EXTRACTION/ACID CLEANUP TECHNIQUE FOR PCB WIPES

The sample extraction techniques for PCB wipes is as follows:

i) Transfer the wipe to a 10ml centrifuge tube. Add 10ml of hexane by repipet. Cap the tube and mix on a vortex mixer for 60 seconds.

ii) Transfer the hexane layer to another 10ml centrifuge tube. Add 1.0ml of concentrated sulfuric acid by repipet to the hexane extract. Mix on the vortex mixer for 60 seconds. Centrifuge, if needed.

iii) Transfer approximately 1ml of the hexane extract by disposable pasteur pipet to a screw capped autosampler vial. Extract is now ready for GC injection.

9. CLEANUP

9.1 GENERAL EXTRACT CLEANUP

Use of sulfuric acid as a routine cleanup procedure (Section 8) may not be necessary in all cases but is required for all samples as a general precaution. Clean extracts extend both column and detector life and provide more accurate and precise data.

Interferences resulting from extracts containing elevated levels of hydrocarbons are not completely eliminated by this technique. High levels of hydrocarbons may cause suppression of detector response leading to quantitative underestimates (generally by ≤10 percent, based on experience) of PCB concentrations. Small shifts in retention times, which the analyst must be aware of, may also be caused by hydrocarbons in the extract.

9.2 SULFUR REMOVAL

9.2.1 Sulfur Interference

Elemental sulfur may be encountered in many sediment samples, marine algae, and some industrial wastes. The solubility of sulfur in various solvents is very similar to that of PCBs; therefore, the sulfur interference follows along with the PCBs through the normal extraction and cleanup techniques. Sulfur will be quite evident in gas chromatograms obtained from ECDs. If the GC is operated at the normal conditions for PCB analysis, the sulfur interference can completely mask a large region of the chromatogram. The recommended technique for the elimination of sulfur follows.

9.2.2 Summary of Method

The sample extract is combined with clean copper turnings. The mixture is shaken and the extract is removed from the sulfur cleanup reagent.

9.2.3 Procedure for Sulfur Cleanup

i) The copper used must be reactive; therefore, all oxides of copper must be removed so that the copper has a shiny, bright appearance.

ii) Transfer 1ml of final extract described in Section 8.1.ix, 8.2.ix, 8.3.viii or 8.4.iii to a 16 mm x 100 mm screw cap culture tube with a Teflon-lined cap.

iii) Add approximately 2 g of cleaned copper to the tube. Mix for at least 1 minute on the vortex mixer. If the copper is blackened, then transfer the extract to another culture tube. Add 2 g more of

cleaned copper and vortex. Repeat this step until the copper no longer blackens.

iv) Resume the procedure described in Section 8 at Step 11.

v) The effect of copper on PCB recovery is shown in Table 9-2.

9.3 CLP RAS/SAS ANALYSES

FASP methodologies, including cleanup, may not be sufficient to continue acceptable analyses. In such cases, CLP RAS/SAS analyses may be the only acceptable alternatives.

APPENDIX I

OPERATING PARAMETERS FOR THE VOLATILE ORGANIC COMPOUND ANALYSIS BY GC/MS

The operating parameters for the VOC GC/MS analyses were as follows:

PURGE AND TRAP PARAMETERS

Purge and Trap device:	O.I. Corporation 4460A.
Trapping material:	Tenax/Silica Gel.
Purge gas:	Helium.
Purge time:	11.0 minutes.
Purge flow rate:	35.0 mL per minute.
Purge temperature:	30 °C.
Desorb time:	4.0 minutes.
Desorb flow rate:	Same as GC flow rate.
Desorb temperature:	180 °C.
Reconditioning temperature:	210 °C.
Reconditioning time:	12.0 minutes.

GC PARAMETERS

Gas Chromatograph:	Hewlett-Packard 5890a series II.
Injection port:	Packed.
GC Column:	DB-624 30 m 0.53 mm I.D. 3.0 μm film thickness.
Carrier gas:	Ultra pure Helium.
Column head pressure:	20 lbs./in^2.
Injection port temperature:	220 °C.
Transfer line temperature:	250 °C.
Initial temperature:	10 °C.
Initial time:	5.0 minutes.
Temperature ramp rate:	6.0 °C per/minute.
Final temperature:	160 °C.
Final time:	6.0 minutes.
Separator type:	Glass jet.
Subambient cooling:	Liquid nitrogen.

MASS SPECTROMETER PARAMETERS

Mass spectrometer:	Hewlett-Packard 5970B.
Data system:	Hewlett-Packard 1000 RTE-A Revision F.
Source temperature:	Radiantly heated from transfer line.
Ionization type:	Electron impact.
Ionizer energy:	70 Electron volts.
Emission current:	200 Micro amps.
Scan type:	Linear, full scan.
Scan range:	35 - 260 daltons.
Scan rate:	1.17 seconds/scan.

APPENDIX J

PROCEDURE FOR THE METHANOLIC EXTRACTION AND ANALYSIS OF VOLATILES IN OIL

The procedure for the methanolic extraction and analysis of volatiles in oil is as follows:

1. Weigh 6.0 grams (to the nearest 0.01 g) of the oil matrix into a 15-mL conical screw-cap (Teflon-lined) centrifuge tube.

2. Add 5.7 mL of reagent grade (purge-and-trap) methanol to the centrifuge tube.

3. Add 0.3 mL of surrogate solution at a concentration of 50 μg/mL to the lower oil layer. The needle should be placed through the methanol layer and the surrogate solution injected into the oil and not the methanol.

4. Place the screw cap securely on the tube and vortex for 45 seconds at high speed.

5. Centrifuge the tube at 2000 rpm for 5.0 minutes.

6. After removing the centrifuge tube, add 0.1 mL of the methanolic extract to a gas-tight Luer lock 5-mL syringe containing 4.9 mL of reagent-grade distilled water.

7. Analyze using purge and trap as per CLP 3/90 medium level procedure for soil.

APPENDIX K

METHOD AND INSTRUMENTAL PERFORMANCE DATA FOR VOLATILE ORGANIC COMPOUND ANALYSIS OF LNAPL SAMPLES

- INSTRUMENT DETECTION LIMIT DATA
- METHOD DETECTION LIMIT DATA
- MATRIX SPIKING PRECISION AND ACCURACY DATA

TABLE K-1. INSTRUMENT DETECTION LIMITS FOR VOLATILE ORGANIC COMPOUNDS ANALYZED BY INSTRUMENT GC/MS HP-5970 B.

ANALYTE	LOW-LEVEL STANDARD CONCENTRATION (µg/L)							IDL µg/L
	RUN 1	RUN 2	RUN 3	RUN 4	RUN 5	RUN 6	RUN 7	
Chloromethane	9.57	12.59	10.58	10.12	9.25	10.51	9.17	3.42
Bromomethane	10.90	10.42	10.28	9.26	9.76	11.00	9.24	2.11
Vinyl Chloride	9.79	11.09	10.55	10.56	11.04	11.07	10.77	1.34
Chloroethane	6.25	10.96	8.90	10.14	8.31	9.21	8.75	4.33
Methylene Chloride	12.39	12.50	11.54	12.38	11.84	13.32	12.58	1.65
Acetone	14.00	13.53	13.24	16.74	16.36	13.05	14.13	4.36
Carbon Disulfide	10.83	11.38	10.22	10.83	10.70	10.50	10.40	1.10
1,1-Dichloroethene	11.18	10.64	10.07	8.44	10.09	10.79	10.29	2.56
1,1-Dichloroethane	11.27	11.16	10.54	10.84	11.50	12.10	11.66	1.51
trans-1,2-Dichloroethene	10.63	9.32	9.92	9.50	10.70	9.73	10.14	1.55
cis-1,2-Dichloroethene	11.02	11.05	10.37	11.20	10.64	11.91	11.73	1.60
Chloroform	11.03	11.18	10.16	10.96	11.21	11.88	11.58	1.57
1,2-Dichloroethane-d4	11.18	11.15	10.99	11.73	11.25	12.47	12.10	1.63
1,2-Dichloroethane	11.00	11.43	10.44	10.93	11.74	12.19	12.16	1.92
2-Butanone	11.16	10.32	8.63	14.65	11.36	9.15	11.07	5.69
1,1,1-Trichloroethane	9.94	10.71	9.63	10.82	10.80	11.30	11.58	2.02
Carbon Tetrachloride	10.42	10.85	10.25	10.96	10.85	11.56	11.24	1.31
Vinyl Acetate	11.37	11.64	9.76	11.90	12.10	11.78	11.63	2.27
Bromodichloromethane	10.43	10.30	10.01	10.46	10.57	11.63	11.51	1.80
1,2-Dichloropropane	10.31	10.70	10.05	10.80	10.99	12.15	11.49	2.07
Trans-1,3-Dichloropropene	9.27	9.84	9.28	9.42	9.69	10.79	10.38	1.69
Trichloroethene	10.53	10.42	9.72	10.16	10.40	11.24	10.25	1.34
Dibromochloromethane	9.58	9.79	9.70	9.98	10.18	11.36	10.68	1.85
1,1,2-Trichloroethane	10.92	10.58	10.37	10.98	11.35	12.37	11.79	2.04

Benzene	10.46	10.66	10.16	10.77	10.71	11.87	11.23	1.63
cis-1,3-Dichloropropene	10.96	10.89	10.57	10.57	10.91	12.47	11.25	1.90
Bromoform	9.75	9.68	9.22	9.81	10.43	10.93	9.97	1.62
2-Hexanone	11.27	11.41	11.88	13.48	13.38	12.56	12.08	2.58
4-Methyl-2-Pentanone	11.10	11.25	12.12	13.26	13.45	12.63	11.80	2.69
Tetrachloroethene	10.42	10.20	9.79	9.44	9.81	11.15	10.69	1.72
1,1,2,2-Tetrachloroethane	10.89	11.24	11.13	11.93	12.04	12.75	11.93	1.88
Toluene	10.60	11.05	9.83	10.43	10.11	11.67	11.08	1.84
Toluene d-8	10.57	10.98	10.49	10.86	10.78	11.92	11.52	1.52
Chlorobenzene	10.52	10.71	10.12	10.60	10.46	11.70	11.20	1.53
Ethylbenzene	10.28	10.59	10.14	10.20	10.28	12.01	11.29	2.05
Styrene	10.08	10.25	9.44	9.85	10.08	11.25	10.88	1.79
m,p-Xylenes	21.47	20.76	19.91	20.27	20.93	23.36	21.42	3.27
o-Xylene	10.51	10.47	10.29	10.45	10.37	11.88	11.36	1.77
Bromofluorobenzene	10.19	10.58	9.81	10.20	10.42	11.26	10.97	1.44

TABLE K-2. METHOD DETECTION LIMITS FOR VOLATILE ORGANIC COMPOUNDS DETERMINED FROM SPIKED PENNZOIL 5W-30

ANALYTE	CONCENTRATION (μg/L)							MDL (μg/Kg)
	RUN 1	RUN 2	RUN 3	RUN 4	RUN 5	RUN 6	RUN 7	
Chloromethane	21.24	19.50	19.77	18.52	20.29	18.02	18.29	170.
Bromomethane	10.33	9.62	11.04	9.35	9.27	9.10	9.12	106.
Vinyl Chloride	10.84	14.05	14.24	13.64	13.35	12.15	13.48	175.
Chloroethane	9.94	13.29	12.71	10.44	9.53	10.10	14.26	277.
Methylene Chloride	184.69	86.15	74.93	68.90	68.45	72.98	97.30	6052.
Acetone	21.92	16.83	16.30	16.17	16.80	15.55	17.76	311.
Carbon Disulfide	4.04	4.58	4.99	4.01	4.44	3.87	5.11	71.3
1,1-Dichloroethene	6.93	6.97	6.86	6.25	7.08	6.31	7.89	79.5
1,1-Dichloroethane	7.95	9.24	8.94	8.24	8.82	8.34	9.05	69.6
trans-1,2-Dichloroethene	7.23	8.30	6.47	7.09	7.66	6.98	7.72	86.6
cis-1,2-Dichloroethene	8.84	9.58	9.74	8.78	9.55	9.29	9.84	61.4
Chloroform	9.62	10.07	10.63	9.38	9.93	9.70	10.53	67.8
1,2-Dichloroethane	7.42	8.22	8.27	7.51	8.11	7.92	8.62	62.3
2-Butanone	5.09	5.05	6.23	5.37	6.20	1.82	5.07	215.9
1,1,1-Trichloroethane	6.39	7.43	7.69	6.52	7.45	6.62	8.01	93.1
Carbon Tetrachloride	4.65	5.58	5.50	4.44	5.17	4.78	5.72	73.2
Vinyl Acetate	9.96	10.76	11.02	9.79	10.93	10.35	10.68	69.6
Bromodichloromethane	8.56	8.83	9.11	8.51	9.15	8.46	9.58	60.4
1,2-Dichloropropane	7.85	8.91	8.96	8.23	9.41	8.12	9.37	90.9
Trans-1,3-Dichloropropene	7.29	7.63	7.91	7.66	8.19	7.74	7.92	41.2
Trichloroethene	5.78	6.44	6.88	5.79	6.90	5.67	6.52	77.2
Dibromochloromethane	6.76	7.72	7.37	7.10	7.64	7.28	7.90	57.1
1,1,2-Trichloroethane	7.95	8.80	8.37	8.77	9.51	8.64	9.43	80.4
Benzene	6.67	7.73	7.76	6.53	7.66	6.85	8.06	89.9

cis-1,3-Dichloropropene	7.86	8.88	8.62	8.10	8.52	8.33	9.11	63.1
Bromoform	6.20	7.46	6.79	6.56	7.15	6.87	7.35	65.0
2-Hexanone	7.89	7.78	8.23	8.08	8.01	8.35	8.00	28.2
4-Methyl-2-Pentanone	5.15	5.24	5.07	5.29	5.41	6.19	4.89	60.8
Tetrachloroethene	3.19	3.87	4.37	3.42	3.91	3.71	4.39	65.2
1,1,2,2-Tetrachloroethane	9.57	10.03	10.76	10.69	10.47	10.20	11.23	79.0
Toluene	86.13	86.76	87.16	91.36	88.33	87.42	88.70	252.
Chlorobenzene	5.56	6.37	6.72	5.79	6.56	5.87	6.42	64.0
Ethylbenzene	5.03	6.02	6.12	5.38	5.92	5.57	6.42	69.5
Styrene	24.48	25.34	26.29	26.19	26.74	25.81	26.17	109.
m,p-Xylenes	14.33	16.24	16.00	15.06	16.09	15.12	17.00	131.
o-Xylene	609.92	625.38	636.35	645.23	648.96	658.19	642.27	2337.

TABLE K-3. VOLATILE ORGANIC COMPOUNDS MATRIX SPIKE RECOVERY AND PRECISION DATA FOR VOLATILE ORGANIC COMPOUNDS

ANALYTE	MATRIX SPIKE CONC. (µg/L)[a]	MATRIX SPIKE DUPLICATE CONC. (µg/L)[a]	AVERAGE PERCENT RECOVERY	RELATIVE PERCENT DIFF.
Chloromethane	51.87	50.61	102.48%	2.45%
Bromomethane	40.91	35.12	76.02%	15.23%
Vinyl Chloride	43.08	41.96	85.04%	2.65%
Chloroethane	46.58	38.24	84.82%	19.67%
Methylene Chloride	58.30	52.09	110.39%	11.24%
Acetone	55.65	50.72	106.37%	9.26%
Carbon Disulfide	15.62	15.63	31.25%	-0.06%
1,1-Dichloroethene	26.49	26.50	52.99%	-0.06%
1,1-Dichloroethane	40.25	40.03	80.28%	0.55%
trans-1,2-Dichloroethene	35.35	32.13	67.48%	9.53%
cis-1,2-Dichloroethene	45.72	44.81	90.53%	2.02%
Chloroform	45.36	43.67	89.03%	3.79%
1,2-Dichloroethane-d4	45.42	44.43	89.85%	2.20%
1,2-Dichloroethane	44.00	41.31	85.31%	6.32%
2-Butanone	63.64	56.98	120.62%	11.05%
1,1,1-Trichloroethane	30.82	30.12	60.93%	2.30%
Carbon Tetrachloride	24.37	23.68	48.05%	2.87%
Vinyl Acetate	55.99	53.26	109.25%	5.00%
Bromodichloromethane	42.96	41.46	84.42%	3.55%
1,2-Dichloropropane	43.09	43.03	86.12%	0.15%
Trans-1,3-Dichloropropene	38.75	37.60	76.35%	3.01%
Trichloroethene	30.10	29.83	59.92%	0.90%
Dibromochloromethane	42.99	43.54	86.53%	-1.26%
1,1,2-Trichloroethane	49.82	49.70	99.52%	0.23%

Benzene	35.19	35.15	70.34%	0.10
cis-1,3-Dichloropropene	43.88	42.08	85.96%	4.20%
Bromoform	39.17	39.42	78.59%	-0.62%
2-Hexanone	58.69	55.44	114.12%	5.70%
4-Methyl-2-Pentanone	56.75	51.62	108.37%	9.47%
Tetrachloroethene	16.99	16.16	33.15%	4.98%
1,1,2,2-Tetrachloroethane	50.93	48.81	99.73%	4.25%
Toluene	27.26	26.09	53.34%	4.39%
Toluene d-8	28.30	26.80	55.10%	5.44%
Chlorobenzene	30.53	28.93	59.46%	5.40%
Ethylbenzene	24.01	23.13	47.14%	3.73%
Styrene	27.65	26.45	54.09%	4.44%
m,p-Xylenes	50.11	48.60	98.70%	3.06%
o-Xylene	29.16	26.72	55.87%	8.73%
Bromofluorobenzene	31.81	30.58	62.39%	3.96%

[a] μg/L in sample extract

APPENDIX L

EVALUATION AND IMPROVEMENT OF PREPARATION PROCEDURES USED IN THE HIGH CONCENTRATION INORGANIC STATEMENT OF WORK

(SUAREZ ET. AL., 1993)

WORK ASSIGNMENT 2.4

EVALUATION AND IMPROVEMENT OF PREPARATION PROCEDURES USED IN THE HIGH CONCENTRATION INORGANIC STATEMENT OF WORK, INCLUDING EVALUATION OF NEW PREPARATION METHODS

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APPENDIX B

Method 200.XX-A-CLP
DISSOLUTION OF INDUSTRIAL WASTE MATERIALS FOR ELEMENTAL ANALYSES BY CLOSED VESSEL MICROWAVE DIGESTION USING HYDROFLUORIC ACID

TABLE OF CONTENTS

Method 200.XX-A-CLP

DISSOLUTION OF INDUSTRIAL WASTE MATERIALS FOR ELEMENTAL ANALYSES BY CLOSED VESSEL MICROWAVE DIGESTION USING HYDROFLUORIC ACID

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure offers an alternative sample preparation method to the potassium hydroxide fusion method specified in the High Concentration Inorganic Statement of Work (HCIN SOW). Microwave digestion using hydrofluoric acid has been successfully used to prepare solutions for metal analysis of oils, oily soils, soils, and aqueous phase materials which are expected to be analyzed under the HCIN SOW.

2.0 SUMMARY OF METHOD

2.1 A 0.25 g aliquot of sample is digested in 5 mL of concentrated nitric acid (HNO_3), 2 mL of concentrated hydrochloric acid (HCl), and 3 mL of concentrated hydrofluoric acid (HF) for 1 hour using microwave heating with a suitable laboratory microwave unit. The weighed aliquot sample is placed in a teflon (PFA) vessel with the 10 mL of the acid mixture. The vessel is capped and heated in the microwave unit. After cooling, the vessels are opened, and a boric acid solution is added to the vessel to neutralize un-reacted HF. The solution is diluted to volume and analyzed by the appropriate instrumental method.

2.2 The spike sample is prepared by adding 0.0125 g of solid spiking material mixture to a 0.25 g aliquot sample which is then carried through the sample preparation procedure.

2.3 All samples shall be carried through the sample preparation procedure and then run undiluted. When an analyte concentration exceeds the calibrated or linear range, appropriate dilution and reanalysis of the prepared sample is required. The dilution factor shall not bring the concentration below the CRQL. All dilutions shall be taken from the original sample, diluting previously diluted samples are not acceptable.

3.0 INTERFERENCES

3.1 The complete decomposition of either carbonates or carbon based samples, may cause enough pressure to build causing the vessels to vent.

4.0 APPARATUS AND MATERIALS

4.1 Microwave Apparatus Requirements

4.1.1 The microwave unit provides programmable power with a minimum of 574 watts an can be programmed to within ± 10 W of the required power.

4.1.2 The microwave unit cavity is corrosion resistant as well as ventilated.

4.1.3 All electronic components are protected against corrosion for safe operation.

4.1.4 The microwave system vessels should have a minimum capacity of 120 mL. The vessels should be capable of withstanding pressures of 200 psi.

4.1.5 The microwave system should have a rotating turn table to ensure even distribution of microwave radiation within the oven.

4.2 Polymeric volumetric ware (teflon or polypropolyene) in 50 mL or 100 mL capacities.

4.3 Analytical balance, 300 g capacity, and minimum ± 0.001 g.

4.4 Hotplate capable of maintaining a solution at 40°C

4.5 Exhaust hood or suitable venting system.

4.6 Disposable plastic 125 mL (4 oz) bottles with lids

4.7 1 liter teflon bottle which can fit into the microwave cavity for microwave system calibration.

5.0 REAGENTS

All reagents should be trace metal grade or equivalent to minimize the blank levels due to metallic contamination.

5.1 ASTM Type II water

5.2 Concentrated nitric acid, trace metal grade

5.3 Concentrated hydrochloric acid, trace metal grade

5.4 Concentrated hydrofluoric acid, trace metal grade

5.5 6% Boric acid solution: prepared by dissolving 6 grams of ultra pure boric acid per 100 mL of warm (50°C) water. The solution should be maintained at 40°C to prevent precipitation of the boric acid.

6.0 SAMPLE PREPARATION AND HANDLING

6.1 Samples are processed through the phase separation procedure (Method 50.60-CLP). Waste samples are not generally dried; results will be reported on a wet basis. Phases of a sample will be prepared and analyzed individually.

7.0 MICROWAVE CALIBRATION PROCEDURE

7.1 Calibration of Microwave Equipment

7.1.1 The calibration procedure is a critical step prior to the use of any microwave unit. The microwave system must be calibrated every six months. The calibration data for each calibration be available for review during on-site audits. In order that absolute power settings may be interchanged form one microwave unit to another the actual delivered power must be determined.

Calibration of a laboratory microwave unit depends on the type of electronic system used by the manufacture. If the unit has a precise and accurate linear relationship between the output power and the scale used in controlling the microwave unit, then the calibration can be a two-point calibration at maximum and 40 % power. If the unit is not accurate or precise for some portion of the controlling scale, then a multi-point calibration is necessary. If the unit power calibration needs a multiple point calibration, then the point of linearity must be identified. For example: a calibration at 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% power settings can be applied and the data plotted. The non-linear portion of the calibration can be excluded or restricted in use.

The power available for heating is evaluated so that the absolute power setting (watts) may be compared from one microwave to another. This is accomplished by measuring the temperature rise in 1 kg of water exposed to microwaves for a fixed time period. Measurements are made on a weighed replicates (3 replicates) of one kilogram samples of room temperature distilled water in thick-walled microwave transparent (Teflon) vessels. The containers must be circulated continuously thorough the microwave field for at least 2 minutes at full power. The vessel(s) are removed from the microwave, the water is stirred vigorously, and the final temperature is recorded. The final reading is the maximum temperature reading after each exposure. If more measurements are needed, do not use the same water until it has cooled down to room temperature. Otherwise, use a fresh water sample.

7.1.2 Calibration Formula - Weigh replicates of 1 Kilogram distilled room-temperature water in a microwave transparent vessel:

7.1.2.1 Measure initial temperature of water, (T_i), to within 0.1°C. The starting temperature should be between 21 and 25°C.

7.1.2.2 Irradiate 1 Kilogram of water at full power, 100% (99, 98, 97, 95, 90, 80, 70, 60, 50, or 40%) for 2 minutes. The container must be circulated through the cavity at a rate of at least on revolution every 30 sec. during the irradiation.

7.1.2.3 Measure the final temperature of water, (T_f), to within 0.1°C with stirring (an electronic stirrer using a large stir bar works best) within 30 sec of the ending of microwave irradiation. Take the maximum reading.

7.1.2.4 Repeat for a new sample, for a total of three replicates per microwave setting, of distilled room temperature in the cooled vessel, (this can be done by running cold water on the outside of the vessel).

7.1.2.5 Calculate microwave power according to the following formula:

$$P = \frac{(K)(C_p)(m)(DT)}{t}$$

Where:

P = The apparent power absorbed by the sample in watts (W=joules per s^2)

K = The conversion factor for thermochemical calories per second to watts (= 4.184)

Cp = The heat capacity, thermal capacity, or specific heat (calories per gram per °C = 1.0 for water).

m = The mass of the water sample in grams (g)

DT = (T_f - T_i) in °C.

t = The time in seconds (s)

Using 2 minutes and 1 Kg of distilled water, the calibration equation simplifies to:

$$P = (DT) \cdot 34.87$$

Following this procedure the power in watts can be related to the percent power settings of the microwave.

8.0 MICROWAVE DIGESTION VESSEL CLEANING PROCEDURE

8.1 Initial cleaning procedure for microwave vessels.

8.1.1 The vessels are rinsed with distilled water and immersed in 1:1 HCl for a minimum of three hours after the cleaning bath has reached a temperature just below boiling.

8.1.2 Rinse with ASTM Type I water.

8.1.3 The vessels are immersed in 1:1 HNO_3 for a minimum of three hours after the cleaning bath has reached a temperature just below boiling.

8.1.4 Rinse with ASTM Type I water. The vessels are now ready for use.

8.2 Digestion Vessel cleaning procedure between sample digestions.

8.2.1 Wash the entire vessel in hot water using laboratory grade non-phosphate detergent.

8.2.2 Rinse with 1:1 nitric acid.

8.2.3 Followed by three rinsing using distilled water. If contaminants are found in the preparation blank, follow steps 8.1.1 through 8.1.4.

8.2.4 Due to the digestion of sample that contain organics, it might be necessary to clean the vessel with acetone before step 8.2.1.

9.0 MICROWAVE DIGESTION PROCEDURE

9.1 Weigh a 0.25 g sample to the nearest 0.001 g into a teflon PFA sample vessel equipped with a single ported cap and pressure relief valve.

9.2 In a fume hood to each digestion vessel, add 5 ± 0.1 mL concentrated nitric acid, 2 ± 0.1 mL concentrated hydrochloric acid, and 3 ± 0.1 mL concentrated hydrofluoric acid, place the samples on an orbital shaker and shake for one hour at approximately 200 rpm, to allow any effervesce to subside before capping the digestion vessel. Cap the vessels and weigh them to the nearest 0.1 g.

9.3 Microwave Digestion Procedures

9.3.1 Digestion Using Pressure Control

9.3.1.1 For microwave systems having pressure control set systems to the following program:

40 psi for 2 min
60 psi for 2 min
80 psi for 2 min
100 psi for 54 min

9.3.2 Digestion Using Temperature Control

9.3.2.1 For microwave systems having temperature control set system to digest samples at 180°C for 1 hour.

9.3.3 Digestion Using Power Program

9.3.3.1 For microwave systems not cable of pressure or temperature control choose the appropriate program from one of the following power control programs:

Place eight sample vessels in the microwave evenly distributed.

For oily soil, soil, and waters use the following program:

	Time	Power
1	6 min 15 sec	563 watts
2	20 min	282 watts
3	20 min	235 watts
4	15 min	266 watts

For oils use the following program:

	Time	Power
1	6 min 15 sec	563 watts
2	3 min 30 sec	282 watts
3	5 min 30 sec	196 watts
4	51 min	118 watts

At the end of any of the microwave programs, allow the vessels to cool down for at least 15 minutes, or in the case of the pressure control program allow the pressure to drop to 25 psi for the oily soil, soils, and waters, and for the oils the pressure only drops to about 45 psi, due to the build up of gases, before removing the vessels from the microwave. Allow the vessels to cool to room temperature. Weigh the vessel assemblies. If the weight of the acid plus the samples varies by more than 10 percent from the original weight, discard the sample digests. Losses are typically attributed to large a sample, improper heating conditions, or digestion time that is too long for the samples. Once the source has been determined and corrected, prepare a new set of samples for digestion.

9.5 Shake the sample vessel well and open each vessel under a fume hood. Inspect each sample to ensure that sample decomposition and dissolution was complete. The digestion procedures described in section 9.3 are for total decomposition and dissolution of the samples matrix. Due to the variety of sample types involved in environmental analysis, some silicates may not have completely dissolved. In the oil and oily soil samples an organic residue is left on the sides of the vessels. To each sample vessel add 20 mL of a 6% boric acid solution to neutralize the un-reacted hydrofluoric acid.

9.6 Transfer the digested sample solution into a acid-cleaned, polyethylene volumetric flask. Bring the solution to volume with deionized water. Alternately if plastic volumetric flasks are not available transfer the sample solutions into acid-cleaned previously weighed polyethylene bottles. Add ASTM Type II water to the samples bottles to achieve a total weight of 100 g plus the weight of the bottle.

9.7 If the digested sample contains particulates which may clog the nebulizers of interfere with the injection of the sample into the instrument, the sample may be centrifuged, filtered, or allowed to settle.

9.7.1 Centrifugation: Centrifugation at 2,000 to 3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

9.7.2 Settling: Allow the sample to stand until the supernatant is clear. Allowing a sample to stand over night will usually accomplish this. If settling does not work, centrifuge or filter the sample.

9.7.3 Filtering: Filter the sample into a second acid cleaned container using quantitative filter paper.

9.8 The diluted digest has an approximate concentration of 5% HNO_3, 3% HF, 2% HCl and 20% Boric Acid, 6% wt/v). The samples are ready for analysis by ICP or GFAA.

9.9 Calculation : The concentration for each sample phase is reported individually. The concentrations determined are reported on the basis of the actual weight of the original sample.

$$\text{Concentration (mg/Kg)} = \frac{C \cdot V}{W}$$

where:

C = concentration in mg/L

V = Final volume in liters

W = Weight in Kg of wet sample

APPENDIX C

NOTES FOR GFAA OF MICROWAVE DIGESTION SOLUTIONS CONTAINING HYDROFLUORIC ACID

Method 202.62-D-CLP states "the composition of the sample phase can have major effects on the analysis. By modifying the sample phase, either to remove interferences or to stabilize the analyte, interferences can be minimized." The method also states that "interferences from a smoke producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the present air. Care must be taken to prevent the loss of analyte."

During the GFAA analyses some interferences with the analytical spikes occurred with Antimony and Selenium in the microwave digested samples which contained 5%HNO3; 3%HF; 2%HCL; and 20% of a 6% Boric Acid solution. The analytical spike for Sb was enhanced on the external reference material sample (BCSS1) due to a matrix effect. The problem was corrected when a longer char temperature (25 sec.) was applied. Selenium had very low analytical spike recovery using 1000 ppm Ni as the matrix modifier. Switching to the Pd mix gave slightly higher recoveries for some samples. The Method of Standard Addition was used for those whose recovery was still low.

The total solid content of microwave digestion using hydrofluoric acid solutions are nearly the same for the sample solutions prepared using the KOH sample preparation method. From GFAA, the analysis of MWHF solutions containing hydrofluoric, result in better analytical recovery and is more accurate than in the later. This probably due to a different mechanisms for losses of major analyte constituents. For the KOH digest the majority of the residue will be a mixture of potassium chloride, which sublimes at 1500°C, and potassium nitrate, which sublimes at 400°C. For the microwave-hydrofluoric acid digest the boric acid is added in slight excess to from boro-fluor species that are volatile (decomposition sequence beginning at 130°C) and the excess boric acid will decompose to form very refractory boron carbide (melting point > 3500°C) on the furnace wall. This explains why there are fewer matrix interferences in the microwave hydrofluoric-boric acid matrix as the boron species are in effect is removed (temporally separated) from the atomization step. With the potassium species this is apparently not the case and hence the matrix interference.

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APPENDIX M

ICP-MS ANALYSIS

METHOD 6020 CLP-M VERSION 8.1

FOR TAL METALS

Inductively Coupled Plasma - Mass Spectrometry

NOTICE

This document is a preliminary draft. It has not been formally released by the U.S. Environmental Protection Agency and should not at this stage be construed to represent Agency policy. It is being circulated for comments on its technical merit and policy implications. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

1 SCOPE AND APPLICATION

1.1 Inductively coupled plasma mass spectrometry (ICP-MS) is a technique which determines most elements in solution [1,2]. The method is applicable to a large number of elements in water and wastes after appropriate sample preparation steps are taken. When dissolved constituents are required, samples must be filtered and acid preserved prior to analysis. No further digestion is required prior to analysis for dissolved elements. Acid digestion prior to analysis is required for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are required.

1.2 Elements for which Method 6020 is applicable are listed in Table 1. In time, other elements may be added as more information becomes available and as required. Instrument detection limits, sensitivities, and linear ranges for these elements will vary with the matrices, instrumentation, and operating conditions. The data shown in Table 1 are typical for dilute aqueous solutions using commercially available instrumentation with pneumatic nebulizers.

1.3 Use of this method is restricted to spectroscopists who are knowledgeable in the recognition and the correction of spectral, chemical, and physical interferences in ICP-MS. Experience requirements are 6 months on a commercially available ICP-MS.

2 SUMMARY OF METHOD

2.1 Prior to analysis, samples which require total values must be solubilized or digested using appropriate Sample Preparation Methods outlined in sections 8.2 - 8.3.

2.2 Method 6020 describes the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the neutral plasma gas and introduced, by means of a water-cooled interface, into a mass spectrometer, capable of providing a resolution, better than or equal to 1 amu peak width at 10 % of the peak height. The water-cooled interface consisting of tandem skimmers is differentially pumped and leads into the high vacuum chamber of the mass spectrometer. The ions and ion clusters produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a detector. Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix. The recommended elemental equations which correct for many of these interferences are listed in Table 2. Use of the internal standard technique is required to compensate for suppressions and enhancements caused by sample matrices [3-4].

3 DEFINITIONS

3.1 Dissolved - Those elements which will pass through a 0.45 μm membrane filter.

3.2 Suspended - Those elements which are retained by a 0.45 μm membrane filter.

3.3 Total - The concentration determined on an unfiltered sample following vigorous digestion.

3.4 Instrumental Detection Limits - (See Section 10.1)

3.5 Sensitivity - The slope of the analytical curve (i.e., functional relationship between instrument readout and concentration).

3.6 Instrument check standard - A multi-element standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis. Also known as the Continuing Calibration Verification Solution (See Section 6.6).

3.7 Interference check sample - A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors (See Table 7).

3.8 Quality control sample - A solution obtained from an outside source having known concentration values to be used to verify the calibration standards (See Section 6.8).

3.9 Calibration standards - A series of known standard solutions used by the analyst for calibration of the instrument (i.e. preparation of the analytical curve) (See Section 9.6).

3.10 Linear dynamic range - The concentration range over which the analytical curve remains linear as determined by the analysis of a standard analyzed during an analytical run for which the standard is ± 5% of the true value.

3.11 Reagent blank - A volume of ASTM Type I water containing the same acid matrix as the calibration standards carried through the entire analytical scheme (See Section 6.5.2).

3.12 Calibration blank - A volume of ASTM Type I water acidified with the same acid concentrations as is present in the samples after digestion (See Section 6.5.1).

4 INTERFERENCES

4.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting out the appropriate signal from the isotope of interest. Data that is corrected must be noted in the report along with the exact calculations used. Commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height. High ion currents at adjacent masses may also contribute to ion signals at the mass of interest. Table 3 shows the analyte concentration measured when an interferant is present at 100 mg/L. Note that the information described in Table 3 was experimentally derived and the interferences which are described occur from several different sources. One interference is the effect of resolution on adjacent peaks. In a quadrupole mass spectrometer, this has a larger effect 1 amu less than the interferant, than 1 amu greater than the interferant's mass, because of its trapezoidal peak shape. Another interference which would be observed is the formation of a hydride ion. Hydride ion interferences only cause an interference at 1 amu greater than the interferant's mass. It should also be remembered that these interferences are not necessarily linear, and attempts must not be made to extrapolate the values in Table 3 to a particular data set. The table has been included for its guidance purposes only and does not contain absolute values which would be applicable to any particular laboratory.

4.2 Isobaric molecular and doubly charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge. Table 4 lists isobaric molecular-ion interferences which could affect the analytes. Note that many of these interferences are extremely rare, but adverse effects on data quality could occur if the individual constituents occurred in the sample at sufficiently high concentrations. When these interferences cannot be avoided by the use of another isotope with sufficient natural abundance, corrections to the data must be applied or the data flagged to indicate the presence of interferences. Instrumental plasma conditions and matrix components affect the production of these ion clusters and the effects must be minimized and measured before corrections are applied. Corrections for molecular-ion interferences must be applied with caution to avoid introducing errors. Corrections for molecular-ion interferences may either be based upon the natural isotope ratios of the molecular ion or a determination of the actual amount of interference which occurs when the interferant is present. The first type of interference correction can be demonstrated by the use of a simultaneous equation which examines the molecular and elemental interferences of molybdenum oxide, for example, on cadmium as listed below.

	species involved			
masses affected	Cd	MoO	Sn	Pd
105	.0000	.0000	.0000	.2233
108	.0089	.1480	.0000	.2546
114	.2873	.2411	.0070	.0000
118	.0000	.0000	.2430	.0000

The values listed are the natural abundances for the elemental and molecular species listed at the mass observed.

Table 2 lists the recommended elemental equations which may be used for the analysis of the elements specified by this method. Note that the equations in Table 2 have been derived with various simplifying assumptions and that a more rigorous equation may occasionally be required, such as that described by the above matrix components. A more rigorous equation could very well provide superior corrections for molecular interferences. The equations detailed in Table 2 were tested in the multi-laboratory study performed by the EPA. Other equations may be used by the laboratory but a description of the rationale for their use must be included in the case narrative. The description must include which molecular isotopes are included, and the assumptions being made for the equation. For example, the Cadmium equation in Table 2, is derived to compensate for the interferences described above, after simplifying by assuming that the Palladium concentration is near zero and constant. This allows the model to be reduced to three equations and three unknowns, resulting in the cadmium equation listed in Table 2.

In the case for which the interferant level is determined when applying corrections the following example may be used. If a correction for an oxide ion is based upon the ratio of parent to oxide ion intensities, the correction may be adjusted for the effects of the sample matrix by the use of an appropriate internal standard previously demonstrated to form a similar level of oxide as the interferant. This second type of correction has been reported for oxide ion corrections using ThO/Th [5] for the determination of rare earth elements. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature [6,7], and the extent of their interferences is shown in Table 5 under three sets of plasma conditions. Note that the information described in Table 5 was experimentally derived, and attempts must not be made to extrapolate the values to a particular data set. The table has been included for its guidance purposes only and does not contain absolute values which could be expected by any given laboratory.

4.3 Physical interferences are effects associated with the sample nebulization and transport processes as well as ion-transmission efficiencies. Nebulization and transport processes are those in which the matrix component causes a change in surface tension or viscosity in a manner different from the standards used in performing calibration. Internal standards have been used to correct for these interferences in the past [3]. The interferences are primarily suppressions and lighter elements are suppressed more than the heavier elements. Matrix effects are greater for matrix components with heavier atomic mass than for matrix

components with lighter atomic mass. Changes in matrix composition therefore can cause significant suppressions and enhancements [8]. Dissolved solids can also deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total dissolved solid levels below 0.2% (2,000 ppm) have been recommended [9] to minimize solid deposition. Internal standards must be affected to the same degree as the analyte to demonstrate that they compensate for these interferences. Table 6 lists the internal standards which may be used in performance of this method. A minimum of three internal standards must be used during data acquisition for any samples analyzed under this contract. When the intensity level of an internal standard is less than 30 percent of the intensity of the first standard used during calibration, the sample must be reanalyzed for the affected analytes after performing a fivefold (1+4) dilution.

4.4 Memory interferences are effects which are dependant upon the relative concentration differences between samples or standards which are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer used, affect the extent of the memory interferences which are present. The memory test solution is used to identify the maximum concentration of an analyte which does not cause a memory effect in excess of the CRDL in the next sequential sample with the instrument configuration used. To verify that memory effects do not have an adverse impact on data quality, the memory test must be performed on the tuned and calibrated instrument before any analyses are performed. A multielement memory test solution (Table 12) containing levels of analytes at approximately 10X the upper end of the linear dynamic range is aspirated into the system for a normal sample exposure period. A blank solution is then introduced, noting the time when the uptake tube is switched to the blank solution. After the normal routine rinse time has elapsed, begin a routine analysis of the blank solution. Inspect the resulting data to see if any analytes are in excess of the Contract Required Detection Limit (CRDL). The memory test must be passed before any samples are analyzed under this contract. Any samples analyzed under an out-of-control situation, must be reanalyzed at no additional cost to the government. If a memory problem does exist for a given analyte, either increase the rinse time, change the instrument hardware, or change the concentration of the element which is failing the memory test until the memory test is passed. The concentration of the element may be reduced provided that the element is on the Target Analyte List. An apparent memory problem may in fact be blank contamination. This may be determined by evaluating a second blank analysis and noting the values obtained.

5 APPARATUS AND MATERIALS

5.1 Inductively coupled plasma - mass spectrometer:

5.1.1 System capable of providing resolution, less than or equal to 1 amu, at 10% peak height from 6 - 253 amu with a data system that allows corrections for isobaric interferences and the application of the internal standard technique. Use of a mass-flow controller for the nebulizer argon and a peristaltic pump for the sample solution are recommended.

5.1.2 Argon gas supply: high-purity grade (99.99%)

5.2 Operating conditions: The analyst must follow the instructions provided by the instrument manufacturer. In general, operating conditions will vary depending upon the instrument manufacturer. The following is a suggested listing of operating conditions which may be useful.

	Perkin-Elmer Sciex Model 500	VG Plasmaquad
Plasma Gas (lpm)	12.	13.
Aux. Gas (lpm)	1.2	0.65
Neb. Gas (lpm)	0.95	0.69
Forward power (kW)	1.2	1.30
Reflected power (W)	< 5.	< 5.
Meinhard nebulizer	Type 3C	Type 3C
Sampling Height (mm above load coil)	18	12

Sensitivity, Instrumental Detection Limits (IDL's), precision, linear dynamic range and interference effects must be established for each analyte on a particular instrument. The analyst must maintain quality control data confirming instrument performance and analytical results.

5.3 Precautions must be taken to protect the channel electron multiplier from high ion currents. The channel electron multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this time period, response factors are constantly changing. This invalidates the calibration curve, causes instability, and invalidates sample analyses. Samples run during such periods are required reruns at no additional cost to the government under this contract.

6 REAGENTS

6.1 Acids used in the preparation of standards and for sample processing must be below the CRDL's for the analytes of interest for the purpose of a study. Redistilled acids are recommended because of the high sensitivity of ICP-MS. Nitric acid at less than 2 per cent (v/v) is required for ICP-MS to minimize damage to the interface and to minimize isobaric molecular-ion interferences with the analytes. Many more molecular-ion interferences are observed on the analytes when hydrochloric and sulfuric acids are used, as demonstrated in Table 4 [6,7]. Concentrations of antimony and silver above 300 μg/L require 1% (v/v) HCl for stability. If HCl is added as a stabilizer then corrections for the chloride molecular- ion interferences must be applied to all data generated.

6.2 ASTM Type I water (ASTM D1193) is required: Water must be monitored for analytes by the use of reagent blanks.

6.3 Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hour at 105 C, unless otherwise specified.

(CAUTION: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.)

Typical stock solution preparation procedures follow. Concentrations are calculated based upon the weight of pure element added, or with the use of the gravimetric factor and the weight of the metal salt added.

Metal

$$\text{Concentration (mg/L)} = \frac{\text{weight of metal (mg)}}{\text{volume (L)}}$$

Metal salts

$$\text{Concentration (mg/L)} = \frac{\text{weight of salt (mg) x gravimetric factor}}{\text{volume (L)}}$$

Note: The recommended amounts of the starting materials specified for the following stock solutions are dependant upon the stoichiometry of the materials used as starting materials. Actual assay values of the starting materials must be used and the actual amounts corrected accordingly.

6.3.1 Aluminum Solution, stock, 1 mL = 100 μg Al: Dissolve 1.3903 g $Al(NO_3)_3 9H_2O$ in 10 mL ASTM Type I water with 10 mL HNO_3. Dilute to 1000 mL with ASTM Type I water.

6.3.2 Antimony solution, stock, 1 mL = 100 μg Sb: Dissolve 0.1197 g Sb_2O_3 in 5 mL ASTM Type I water containing 0.1233 g $C_4O_6H_6$ (tartaric acid). Add 500 mL ASTM Type I water, add 1 mL conc. HNO_3 and dilute to 1000 mL with ASTM Type I water.

6.3.3 Arsenic solution, stock, 1 mL = 100 μg As: Dissolve 0.1320 g of As_2O_3 in 100 mL of ASTM Type I water containing 0.45 g NH_4OH. Acidify the solution with 12 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

6.3.4 Barium solution, stock, 1 mL = 100 μg Ba: Dissolve 0.1437 g $BaCO_3$ in 10 mL ASTM Type I water with 10 mL conc. HNO_3. After dissolution is complete, warm the solution to degas. Dilute to 1,000 mL with ASTM Type I water.

6.3.5 Beryllium solution, stock, 1 mL = 100 μg Be: Do not dry salt. Dissolve 4.5086 g $BeO(C_2H_3O_2)_6$ in ASTM Type I water, add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

6.3.6 Cadmium solution, stock, 1 mL = 100 μg Cd: Dissolve 0.1142 g CdO in a minimum amount of (1+1) HNO_3. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

6.3.7 Calcium solution, stock, 1 mL = 100 μg Ca: Suspend 0.2498 g $CaCO_3$ dried at 180 C for 1 h before weighing in ASTM Type I water and dissolve cautiously with a minimum amount of (1+1) HNO_3. After dissolution is complete, warm the solution to degas. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with ASTM Type I water.

6.3.8 Chromium solution, stock, 1 mL = 100 μg Cr: Dissolve 0.2424 g of $(NH_4)_2Cr_2O_7$ in ASTM Type I water. Reduce the chromium with a few drops of hydrazine (NH_2NH_2), exhibited by the color change of the solution from orange to green. When solution is complete, acidify with 10 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

6.3.9 Cobalt solution, stock, 1 mL = 100 μg Co: Dissolve 0.1000 g of cobalt metal in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

6.3.10 Copper solution, stock, 1 mL = 100 µg Cu: Dissolve 0.1000 g Cu in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

6.3.11 Iron solution, stock, 1 mL = 100 µg Fe: Dissolve 0.1000 g Fe in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

6.3.12 Lead solution, stock, 1 mL = 100 µg Pb: Dissolve 0.1599 g $Pb(NO_3)_2$ in a minimum amount of (1+1) HNO_3. Add 10.0 mL of conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

6.3.13 Magnesium solution, stock, 1 mL = 100 µg Mg: Dissolve 0.1658 g MgO in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

6.3.14 Manganese solution, stock, 1 mL = 100 µg Mn: Dissolve 0.3149 g of manganese acetate $Mn(C_2H_3O_2)_2$ in ASTM Type I water. Add 10.0 mL of conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

6.3.15 Mercury solution, stock, 1 mL = 100 µg Hg: Dissolve 0.1708 g mercury (II) nitrate $Hg(NO_3)_2 \cdot H_2O$ in 75 mL of ASTM Type I water. Add 10 mL of conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

6.3.16 Nickel solution, stock, 1 mL = 100 µg Ni: Dissolve 0.1000 g of nickel metal in 10 mL hot conc. HNO_3, cool and dilute to 1,000 mL with ASTM Type I water.

6.3.17 Potassium solution, stock, 1 mL = 100 µg K: Dissolve 0.1767 g K_2CO_3 in a minimum amount of (1+1) HNO_3. After dissolution is complete, warm the solution to degas. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

6.3.18 Selenium solution, stock, 1 mL = 100 µg Se: Do not dry. Dissolve 0.1727 g H_2SeO_3 (actual assay 94.6%) in ASTM Type I water and dilute to 1,000 mL.

6.3.19 Silver solution, stock, 1 mL = 100 µg Ag: Dissolve 0.1575 g $AgNO_3$ in 100 mL of ASTM Type I water and 10 mL conc. HNO_3. Dilute to 1,000 mL with ASTM Type I water.

6.3.20 Sodium solution, stock, 1 mL = 100 µg Na: Dissolve 0.2305 g Na_2CO_3 in a minimum amount of (1+1) HNO_3. After dissolution is complete, warm the solution to degas. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

6.3.21 Thallium solution, stock, 1 mL = 100 µg Tl: Dissolve 0.1303 g $TlNO_3$ in ASTM Type I water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

6.3.22 Vanadium solution, stock, 1 mL = 100 µg V: Dissolve 0.2296 g NH_4VO_3 in a minimum amount of conc. HNO_3. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

6.3.23 Zinc solution, stock, 1 mL = 100 µg Zn: Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

6.3.24 Bismuth internal standard solution, stock, 1 mL = 100 µg Bi: Dissolve 0.1115 g Bi_2O_3 in a minimum amount of dilute HNO_3. Add 10 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

6.3.25 Holmium internal standard solution, stock, 1 mL = 100 µg Ho: Dissolve 0.1757 g $Ho_2(CO_3)_2 \cdot 5H_2O$ in 10 mL ASTM Type I water and 10 mL HNO_3. After dissolution is complete, warm the solution to degas. Add 10 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

6.3.26 Indium internal standard solution, stock, 1 mL = 100 μg In: Dissolve 0.1000 g indium metal in 10 mL conc. HNO_3. Dilute to 1,000 mL with ASTM Type I water.

6.3.27 Lithium internal standard solution, stock, 1 mL = 100 μg ^6Li: Dissolve 0.6312 g 95 atom % enriched ^6Li, Li_2CO_3 in 10 mL of ASTM Type I water and 10 mL HNO_3. After dissolution is complete, warm the solution to degas. Add 10 mL conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

6.3.28 Rhodium internal standard solution, stock, 1 mL = 100 μg Rh: Dissolve 0.3593 g ammonium hexachlororhodate (III) $(NH_4)_3RhCl_6$ in 10 mL ASTM Type I water. Add 100 mL conc. HCl and dilute to 1,000 mL with ASTM Type I water.

6.3.29 Scandium internal standard solution, stock, 1 mL = 100 μg Sc: Dissolve 0.15343 g Sc_2O_3 in 10 mL (1+1) hot HNO_3. Add 5 ml conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

6.3.30 Terbium internal standard solution, stock, 1 mL = 100 μg Tb: Dissolve 0.1828 g $Tb_2(CO_3)_3 \cdot 5H_2O$ in 10 mL (1+1) HNO_3. After dissolution is complete, warm the solution to degas. Add 5 ml conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

6.3.31 Yttrium internal standard solution, stock, 1 mL = 100 μg Y: Dissolve 0.2316 g $Y_2(CO_3)_3 3H_2O$ in 10 mL (1+1) HNO_3. Add 5 ml conc. HNO_3 and dilute to 1,000 mL with ASTM Type I water.

6.3.32 Titanium solution, stock, 1 mL = 100 μg Ti: Dissolve 0.4133 g $(NH_4)_2TiF_6$ in ASTM Type I water. Add 2 drops of conc. HF and dilute to 1,000 mL with ASTM Type I water.

6.3.33 Molybdenum solution, stock, 1 mL = 100 μg Mo: Dissolve 0.2043 g $(NH_4)_2MoO_4$ in ASTM type I water. Dilute to 1,000 mL with ASTM type I water.

6.4 Mixed calibration standard solutions -- Dilute the stock-standard solutions to levels in the linear range for the instrument in a solvent consisting of 1 percent (v/v) HNO_3 in ASTM Type I water along with the selected concentration of internal standards (see Table 6) such that there is an appropriate internal standard element for each of the analytes (See Section 6.4.6). Prior to preparing the mixed standards, each stock solution must be analyzed separately to determine possible spectral interferences or the presence of impurities. Care must be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to freshly acid-cleaned FEP fluorocarbon bottles for storage. Fresh mixed standards must be prepared as needed with the realization that concentrations can change on aging. Calibration standards must be initially verified using a quality control sample (see Section 6.8) and monitored weekly for stability. Although not specifically required, some typical calibration standard combinations follow.

6.4.1 Mixed standard solution I -- Manganese, beryllium, cadmium, lead, silver, barium, copper, cobalt, nickel and zinc.

6.4.2 Mixed standard solution II -- Arsenic, selenium, chromium, thallium, aluminum, calcium, magnesium, potassium, sodium, and mercury.

6.4.3 Mixed standard solution III -- Antimony, vanadium, iron.

6.4.4 Mixed standard solution IV -- Bismuth, holmium, indium, lithium, scandium, yttrium, and terbium.

6.4.5 Mixed standard solution V -- Rhodium.

6.4.6 Internal standards must be used to monitor and correct for changes that occur from differences between standards and samples. The changes for which internal standards correct are primarily physical interferences. A minimum of three internal standards must be present in all standards and samples at identical levels by mixing the internal standard into the solution being nebulized prior to the nebulizer. The three internal standards used must be selected to bracket the mass range, and must include one internal standard from each of the following mass ranges (1-70), (71-125), and (126-250). This may be accomplished by using a second channel of the peristaltic pump to add the internal standard to the uptake tube. If adding the solution to the uptake tube is not used, then the internal standards must be added in a separate aliquot to the samples and standards. Internal standard spiking may occur either by adding a constant volume of internal standard concentrate to identical volumes of the standards and prepared samples, or by diluting the internal standard to the appropriate level for its use in the analyses. One typical example is to measure out 10.0 mL of all standards and samples into individual containers, then add 0.100 mL of a 10 mg/L solution of the internal standard is added to each of the containers. This adds identical amounts of the internal standard to each solution for analysis. The concentrations of the analyte levels in the standards do not have to be corrected for the dilution which occurs because the dilution of the samples and standards are identical.

6.4.7 In the determination of trace elements, containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) depleting concentrations through adsorption. Thus the collection and treatment of the samples prior to analysis require particular attention. The following cleaning treatment sequence has been determined to be adequate to minimize contamination in the sample bottles, whether borosilicate glass, linear polyethylene, or Teflon: detergent, Type II water, 1+1 hydrochloric acid, ASTM Type I water , 1+1 nitric acid, and Type I water.

NOTE: Chromic acid must not be used because chromium is one of the contract required analytes, and its use may lead to contamination.

6.5 Three types of blanks are required for the analysis. The calibration blank is used in establishing the calibration curve. The reagent blank is used to monitor for possible contamination resulting from the sample preparation procedure. The rinse blank is used to flush the system between all samples and standards.

6.5.1 The calibration blank consists of 1 percent HNO_3 (v/v) in ASTM Type I water along with the selected concentrations of internal standards (see Table 6) such that there is an appropriate internal standard element for each of the analytes.

6.5.2 The reagent blank must contain all the reagents in the same volumes as used in processing the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solutions used for analysis.

6.5.3 The rinse blank consists of 1-2 percent HNO_3 (v/v) in ASTM Type I water. Prepare a sufficient quantity to flush the system between standards and samples.

6.6 The instrument check standard is the Continuing Calibration Verification (CCV) solution which is prepared by the analyst by combining compatible elements at concentrations equivalent to the midpoint of their respective calibration ranges (see Section 10.12.2 for use).

6.7 The interference check solution(s) (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. The ICS solutions are detailed in Table 7. The chloride concentration provides a means to evaluate software corrections for chloride-related interferences such as $^{35}Cl^{16}O^+$ on $^{51}V^+$ and $^{40}Ar^{35}Cl^+$ on $^{75}As^+$. Since the natural abundance of ^{35}Cl of 75.8 percent is 3.13 times the ^{37}Cl abundance of 24.2 percent, the ion corrections can be calculated with adjustments for isobaric contributions. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate

oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement scheme to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

6.7.1 Mixed ICS solution I may be prepared by adding 2.781 g $Al(NO_3)_3 9H_2O$, 1.499 g $CaCO_3$ dried at 180 C for 1 h before weighing, 0.500 g Fe, 0.332 g MgO, 1.153 g Na_2CO_3, and 0.353 g K_2CO_3 to 25 mL of ASTM Type I water. Slowly add 40 mL of (1+1) HNO_3. After dissolution is complete, warm the solution to degas. Cool and dilute to 1,000.0 mL with ASTM Type I water.

6.7.2 Mixed ICS solution II may be prepared by slowly adding 1.489 g 85 % H_3PO_4, 1.275 g 96% H_2SO_4, 20.012 g 37% HCl, and 2.133 g citric acid $C_6O_7H_8$ to 100 mL of ASTM Type I water. Dilute to 1,000.0 mL with ASTM Type I water.

6.7.3 Mixed ICS solution III may be prepared by adding 5.000 mL each of arsenic stock solution (6.3.3), cadmium stock solution (6.3.6), selenium stock solution (6.3.18), and zinc stock solution (6.3.23); 10.000 mL each of chromium stock solution (6.3.8), cobalt stock solution (6.3.9), copper stock solution (6.3.10), manganese stock solution (6.3.14), nickel stock solution (6.3.16), silver stock solution (6.3.19), and vanadium stock solution (6.3.22). Dilute to 100.000 mL with 2% HNO_3.

6.7.4 ICS A may be prepared by adding 50.00 mL of mixed ICS solution I (6.7.1), 2.00 mL each of titanium stock solution (6.3.32) and molybdenum stock solution (6.3.33), and 25.00 mL of mixed ICS solution II (6.7.2). Dilute to 100.00 mL with ASTM Type I water. ICS solution A must be prepared fresh weekly.

6.7.5 ICS AB may be prepared by adding 50.00 mL of mixed ICS solution I (6.7.1), 2.00 mL each of titanium stock solution (6.3.32) and molybdenum stock solution (6.3.33), 25.00 mL of mixed ICS solution II (6.7.2), and 2.00 mL of Mixed ICS solution III (6.7.3). Dilute to 100.00 mL with ASTM Type I water. ICS solution AB must be prepared fresh weekly.

6.8 The quality control sample is the Initial Calibration Verification (ICV) solution which must be prepared in the same acid matrix as the calibration standards in accordance with the instructions provided by the supplier. If the ICV is not available from the EPA, or where a certified solution of an analyte is not available from any source, an analyses shall be conducted on an independent standard at a concentration other than that used for instrument calibration and near the midpoint of the linear range. An independent standard is defined as a standard composed of the analytes from a different source than those used in the standards for instrument calibration. EPA will supply either a quality control sample or information where one of equal quality can be procured.

7 Safety

The Contract Laboratory assumes full responsibility for the safety of its employees. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Therefore, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available. They are:

1. "Carcinogens - Working with Carcinogens", Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77- 206, August 1977.

2. "OSHA Safety and Health Standards, General Industry", (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, revised January 1976.

3. "Proposed OSHA Safety and Health Standards, Laboratories", Occupational Safety and Health Administration, Federal Register, July 24, 1986, p. 26660.

4. "Safety in Academic Chemistry Laboratories", American Chemical Society Publication, Committee on Chemical Safety, 3rd edition, 1979.

8 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 See Table 8, Sample Preservation and Holding Times for the criteria to be used in sample collection, preservation, and handling.

8.2 Aqueous Sample Preparation

8.2.1 This procedure is used to determine the total (acid leachabel) amount of the element in the sample. This digestion procedure is used for the preparation of aqueous samples and wastes that contain suspended solids for analysis by inductively coupled plasma mass spectrometry (ICP-MS) for the following elements:

Aluminum	Lead
Antimony	Magnesium
Arsenic	Manganese
Barium	Nickel
Beryllium	Potassium
Cadmium	Selenium
Calcium	Silver
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc

8.2.2 Shake sample and transfer a 100 mL aliquot of well-mixed sample to a 250 mL beaker, add 1 mL of (1+1) HNO_3 and 2 mL of 30% H_2O_2 to the sample. Cover with a watch glass or similar cover and heat on a steam bath or hot plate for 2 hours at 95 C or until sample volume is reduced to between 25 and 50 mL, making certain that the sample does not boil. Cool the sample and filter to remove insoluble material. Adjust the sample volume to 100 mL with ASTM Type I water. The sample is now saved for analysis. Prior to analysis the sample must be spiked with internal standards (Section 6.4.6).

NOTE: The water sample preparation procedure for ICP-AES analysis must be used for quantitation, if this digestate contains more than 30 μg/L of silver, or more than 100 μg/L of antimony.

8.3 Soil/Sediment/Sludge Sample Preparation

8.3.1 This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by ICP-MS for the following elements:

Aluminum	Lead
Antimony	Magnesium
Arsenic	Manganese
Barium	Nickel
Beryllium	Potassium
Cadmium	Silver
Calcium	Sodium
Chromium	Thallium
Cobalt	Vanadium
Copper	Zinc
Iron	

NOTE: The recovery of antimony from these matrices is known to be lower than the recovery which would be provided by a modified aqua regia digestion. Similarly, the recovery of silver may be reduced in some cases. The soil/sediment sample preparation procedure for ICP-AES analysis must be used for quantitation if this digestate contains more than 30 μg/L of silver, or more than 100 μg/L of antimony.

8.3.2 Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh (to the nearest 0.01 g) a 1.0 to 1.5 g portion of the sample and transfer to a beaker.

8.3.3 Add 10 mL of (1+1) HNO_3, mix the slurry, and cover with a watch glass. Heat the sample and reflux for 10 minutes without boiling at 95 C. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the watch glass, and reflux for 30 minutes. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the beaker.

8.3.4 After the second reflux step has been completed and the sample has cooled, add 2 mL of ASTM Type I water and 3 mL of 30% hydrogen peroxide (H_2O_2). Return the beaker to the hot plate for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the beaker.

8.3.5 Continue to add 30% H_2O_2 in 1 mL aliquots with warming until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 10 mL 30% H_2O_2.)

8.3.6 Continue heating the acid-peroxide digestate until the volume has been reduced to approximately 2 mL, add 10 mL of ASTM Type I water, and warm the mixture. After cooling, filter and dilute to 200 mL with Type I water. The sample is now saved for analysis. Prior to analysis the sample must be spiked with internal standards (Section 6.4.6).

8.3.7 Calculations

(1) A separate determination of percent solids must be performed.

(2) The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry weight)(mg/kg)} = \frac{C \times V}{W \times S}$$

Where,

C = Concentration (mg/L)
V = Final volume in liters after sample preparation
W = Weight in kg of wet sample

$$S = \frac{\% \text{ Solids}}{100}$$

9 PROCEDURE

9.1 Solubilization and digestion procedures are presented in the Sample Preparation Methods (Sections 8.2 - 8.3).

9.2 Initiate appropriate operating configuration of instrument computer.

9.3 Set up the instrument with the proper operating parameters established in Section 5.2. Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. This must be verified by running the tuning solution (Table 10) at least four times with relative standard deviations of less than 10% for the analytes contained in the tuning solution.

9.4 Conduct mass calibration and resolution checks using the tuning solution (100 ppb of the elements Li, Co, In, and Tl). The recommended intensities and isotope ratios of these elements are listed on Form XI-IN. The response factor criteria found in Table 11 and on Form XI-IN are only recommendations which might be helpful when setting up the instrument, but are not required criteria. EPA will collect the reported information to assess their effect on data quality and possibly set windows at a future date. The mass calibration and resolution parameters are required criteria which must be met prior to any samples being analyzed under this contract. If the mass calibration exceeds a difference of more than 0.1 amu from the actual value, then the mass calibration must be adjusted to the correct values. The resolution must also be verified to be less than 1.0 amu full width at 10 percent peak height. The tuning solution must be analyzed at the beginning of each run prior to calibration and after the mass calibration and resolution checks are performed. The tuning solution must also be run at the end of the analytical run or twice per 8 hour working shift, whichever is more frequent.

9.5 Prior to analyzing any samples under this contract, all of the samples must be screened for the presence of internal standards which might be indigenous to the samples. This screen is performed by calibrating the instrument for each of the internal standards using a single point calibration curve at the same level which will be used during the normal analytical run. After the screening calibration has been performed, then each sample to be analyzed during the normal analytical run will be introduced to the instrument without any internal standard added, and all of the masses associated with the internal standards will be scanned. The internal standard calibration standard must be analyzed at the end of the screening run. There is no additional

quality assurance criteria associated with the screening run. The data from the screening run must be included in the raw data package and no further reporting requirements are needed.

9.6 Calibrate the instrument for the analytes of interest using the calibration blank and at least a single standard (described in Section 6.4) according to the manufacturer's recommended procedure for each detector configuration which will be used in analysis. Flush the system with the rinse blank (6.5.3) between each standard solution. Report each integration during the calibration and sample analysis and use the average of the multiple integrations for both standardization and sample analysis. A minimum of two replicate integrations are required for both calibration and sample analysis. The raw data must include the concentrations of elements in each integration as well as the average. Additionally, if different detector configurations are used, the raw data must indicate which detector configuration is being used.

9.7 Some elements (such as Hg, W, and Mo) require extended flushing times which need to be determined for each instrumental system. Run the Memory Test (described in Section 4.4) on the solution in Table 12 to verify that memory problems will not affect the data quality.

9.8 As a minimum, all masses which would affect data quality must be monitored to determine potential effects from matrix components on the analyte peaks. These masses must be monitored simultaneously for the purpose of post-analysis data validation by the EPA. This information will be used to assess data quality and as a minimum must include the masses which are boldfaced and underlined in Table 9 for each element. These masses must all be monitored either in a separate scan or at the same time quantification occurs. Failure to provide a scan which includes all of the required masses will result in non-acceptance of the data package and the samples associated with the incomplete data must be rerun at no cost to the government.

9.9 Immediately after the calibration has been established, the calibration must be verified and documented for every analyte by the analysis of the Initial Calibration Verification solution (ICV). When measurements exceed ± 10% of the accepted value the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified. Any samples analyzed under an out-of-control calibration must be rerun at no cost to the government.

Note: During the course of an analytical run, the instrument may be "resloped" or recalibrated to correct for instrument drift. The recalibration may only be performed after the successful analysis of a CCV and CCB. The recalibration then must be followed immediately by a new analysis of a CCV and CCB before any further samples may be analyzed. Any samples analyzed under an out-of-control CCV and CCB must be rerun at no cost to the government.

9.10 Flush the system with the rinse blank solution (6.5.3) for at least 30 seconds before the analysis of each sample (see NOTE to Section 9.7). Aspirate each sample for at least 30 seconds before collecting data. Analyze the Continuing Calibration Verification (CCV) (Section 6.6) and the Continuing Calibration Blank (CCB) (Section 6.5.1) at a frequency of 10%. A frequency of 10% means once every 10 analytical samples.

Note: Calibration blanks (ICB/CCB) and calibration verification (ICV/CCV) solutions are not counted as analytical samples when determining the 10% frequency.

9.11 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte (or species needed for a correction) or measure an alternate less-abundant isotope for which quality control data has already been established and exhibits linear response at the concentration involved. No analyte may be reported from an analysis of a diluted sample, in which the analyte concentration is less than 5 % of the linear dynamic range or less than 5 times the IDL, whichever is lower. For practical purposes the analysis of solutions which contain concentrations of analytes at levels higher than the linear range standard may be analyzed by either dilution, or adjustment of the mass spectrometer to reduce sensitivity for the analytes. If

the sensitivity of the mass spectrometer is reduced, then all QA/QC criteria must be met under the new instrument operating conditions.

9.12 Calculations: Appropriate concentration units must be specified on the required forms. The quantitative values shall be reported in units of micrograms per liter (μg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. No other units are acceptable. Results for solid samples must be reported on a dry weight basis. If dilutions were performed, the appropriate corrections must be applied to the sample values. Analytical results must be reported to two significant figures if the resulting value is less than 10 and to three significant figures if the value is greater than or equal to 10. Results for percent solids must be reported to one decimal place.

10 QUALITY CONTROL - All quality control (QC) data must be submitted with each data package. These tests, as outlined in 10.6 through 10.10, will enable the analyst to detect positive or negative interferences that distort the accuracy of the reported values.

10.1 Instrument Detection Limits (IDL's) (in μg/L) must be determined by multiplying by three the average of the standard deviations obtained on three nonconsecutive days (example Mon., Wed., Fri.) from the analysis of a standard solution (each analyte in reagent water) at a concentration 3x-25x IDL, with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDL's must be determined and reported for each equation and each detector configuration used in the analysis of the samples. An IDL must exist, which at a minimum meets the CRDL's listed in Table 1 for each analyte. Other equations may be used for quantitation, provided that an explanation regarding the use of the equation is stipulated by the laboratory. For example, if quantitation for arsenic is normally performed using one equation, but that equation cannot provide correction for an interferant which occurs in a given sample, an alternate equation may be used which does correct for the interferant, provided that the CCB and CCV criteria have been met.

10.2 The results of the reagent blank are to be less than the CRDL stated in Table 1. If it is not, all samples associated with the blank with an analyte concentration less than 10 times the blank concentration and above the IDL, must be redigested and reanalyzed for that analyte at no additional cost to the government. The sample concentration is not to be corrected for the reagent blank value.

10.3 The intensities of all internal standards must be monitored for every analysis. When the intensity of an internal standard fails to exceed 30% of the intensity of the initial calibration standard intensity, the following procedure is followed. The sample must be diluted fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standard. This procedure must be repeated until the internal standard intensity exceeds the prescribed criteria. Alternately, if the reason for the internal stadard intensity falling below 30% of the intensity of the initial calibration statndard is instrumental drift, then the analysis must be stopped, the problem corrected, the instrument recalibrated, and the affected samples rerun at no additional cost to the government.

10.3.1 The results of monitoring the internal standards must be reported on FORM XV(PART 1) and FORM XV(PART 2). FORM XV(PART 1) is used to monitor the the overall internal standard intensities of each sample by comparing the sample internal standard intensity to the internal standard intensity when calibration was performed. This is determined by calculating the percent relative internal standard intensity (%RI) as follows:

$$\%RI = \left(\frac{I_n}{I_0}\right) * 100$$

where,

I_n = internal standard intensity of the sample
I_0 = internal standard intensity of the calibration blank.

10.3.2 To determine when an internal standard is indigenous to the sample, the indigenous internal standard (IS_i) is determined as follows:

$$IS_i = \frac{\dfrac{I_{x_n}}{I_{x_{n-1}}} + \dfrac{I_{x_n}}{I_{x_{n+1}}}}{\dfrac{I_{\bar{y}_n}}{I_{\bar{y}_{n-1}}} + \dfrac{I_{\bar{y}_n}}{I_{\bar{y}_{n+1}}}}$$

where,

I = internal standard intensity
x = the internal standard of interest
$\bar{y}$ = the mean of all internal standards except x
n = the n^{th} sample
n-1 = the sample preceeding the n^{th} sample
n+1 = the sample following the n^{th} sample

10.3.2.1 Specific acceptance criteria for determining the indigenous internal standard will the set by EPA in the future. In the interim, the analysis must be reported on FORM XV(PART 2)-IN.

10.4 The results of the duplicate sample analyses must be reported on Form VI-IN, in $\mu g/L$ for aqueous samples and mg/Kg dry weight basis for solid samples.

10.5 To obtain analyte data of known quality, it is necessary to measure for more than the analytes of interest in order to know the required interference corrections. If the concentrations of interference sources (such as C, Cl, Mo, Zr, W) are below the levels that show an effect on the analyte level, uncorrected equations may be used provided all QC criteria are met. Note that monitoring the interference sources does not necessarily require monitoring the interferant itself, but that a molecular species may be monitored to indicate the presence of the interference. When corrected equations are used all QC criteria must also be met. Extensive QC for interference corrections are required at all times. The monitored masses must include those elements whose oxygen, hydroxyl, chlorine, nitrogen, carbon and sulfur molecular ions which could impact the analytes of interest. When an interference source is present, the sample elements impacted must be flagged to indicate (a) the percentage interference correction applied to the data or (b) an uncorrected interference by virtue of the elemental equation used for quantitation. The isotope proportions for an element or molecular-ion cluster provide information useful for quality assurance.

10.6 Serial dilution: If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of 20 above the CRDL), an analysis of a fivefold dilution must agree

within ± 10% of the original determination. If not, an interference effect must be suspected. One serial dilution must be analyzed for each twenty samples or less of each matrix in a batch. Samples identified as Field Blanks cannot be used for serial dilution analysis.

10.7 Matrix spike addition: An analyte spike added to a portion of an undigested sample of each matrix, must be recovered to within 75% to 125% of the EPA established value. Spiking levels must be performed at the levels indicated in Table 13 for the relevant matrix analyzed. One matrix spike addition must be performed for each twenty samples or less of a matrix in a batch. If the spike is not recovered within the specified limits, of 75-125%, the data of all samples associated with that spike sample must be flagged with the letter "N" on forms I-IN and V-IN. An exception to this rule is granted in situations where the sample concentration exceeds the spike concentration by a factor of four or more. In such and event, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

10.7.1 The spike recovery is calculated as follows:

$$\%\text{Recovery} = \left(\frac{SSR}{(SA + SR)}\right) * 100$$

where,

SSR = Spiked Sample Result
SR = Sample Result
SA = Spike Added

10.7.2 When the pre-digestion spike recovery falls outside the control limits and the sample result does not exceed 4 times the spike added, a post-digestion spike must be performed for those elements that do not meet the criteria (exception Ag). Spike the original digested sample at the level specified in Table 13. Results of the post-digestion spike must be reported on FORM V(PART 2)-IN.

10.8 Post digest spike addition: When the pre-digestion spike recovery falls outside the control limits and the sample result does not exceed 4 times the spike added, a post-digestion spike must be performed for those elements that do not meet the specified criteria (exception; Ag). Spike the unspiked aliquot of the sample at 2 times the indigenous level or 2 times the CRDL, whichever is greater. Results of the post-digestion spike must be reported on Form 5B.

10.9 CRDL standard: To verify linearity near the CRDL for ICP-MS analysis, a standard at two times the CRDL must be analyzed, at the beginning and end of each sample analysis run, or a minimum of twice every 8 hours, whichever is more frequent, but not before Initial Calibration Verification. This standard must be run using every elemental equation used during analysis. A CRDL standard does not have to be run for Al, Ba, Ca, Fe, Mg, Na, and K.

10.9.1 The CRDL standard must be recovered within 50% to 150% of the true value. If the CRDL standard at the beginning of the analytical run is not recovered within 50% to 150% of the true value, then the analysis must be terminated, the problem corrected, the instrument recalibrated, and a new analytical run started, before any analytical samples are analyzed under this contract. If the CRDL standard is not recovered within 50% to 150% of the true value at the end of the run, then all sample results between the CRDL standards must be flagged with a "C" on FORM I-IN in the Q qualifier column. The analysis must be reported on Form III-IN.

10.10 Laboratory Control Sample Analysis

10.10.1 A Laboratory Control Sample (LCS) analysis must be prepared for each analyte using the same sample preparations, analytical methods and QA/QC procedures employed for the EPA samples received. The aqueous LCS solution must be obtained from EPA (if unavailable, the Initial Calibration

Verification solutions may be used). One aqueous LCS must be prepared for each batch at a frequency of one LCS for each 20 samples or less.

10.10.2 The EPA provided solid LCS must be prepared and analyzed using each of the procedures applied to the solid samples received (the percent solids determination is not required). If the EPA solid LCS is unavailable, other EPA quality assurance check samples or other certified materials may be used. One solid LCS must be prepared for each 20 samples or less in a batch.

10.11 Each analytical run must specify the concentration beyond which results cannot be reported under this contract without dilution of the analytical sample. These values are reported on FORM XII-IN, the linear ranges form. The reported concentration may either be the most concentrated standard used during calibration or a linear range verification check standard which was analyzed during the course of the analytical run. If a linear range verification check standard is used, the analytically determined concentration of the standard must be within ± 10% of the true value.

10.12 Check the instrument standardization by analyzing appropriate quality control solutions as follows:

10.12.1 Check instrument calibration using a calibration blank (6.5.1) and the Initial Calibration Verification (ICV) solution (See Sections 6.8 and 9.9).

10.12.2 Verify calibration at a frequency of 10% which means once every 10 analytical samples with the Continuing Calibration Verification (CCV) solution (Section 6.6) and the continuing calibration blank Section (6.5.1). These solutions must also be analyzed for each analyte at the beginning of the run and after the last analytical sample.

10.12.2.1 The results of the ICV and CCV solutions must agree within ± 10% of the expected value. If not, terminate the analysis, correct the problem, and recalibrate the instrument. Any sample analyzed under an out-of-control calibration must be reanalyzed at no additional cost to the government.

10.12.2.2 The results of the calibration blank must be less than the CRDL listed in Table 1. If they are not, terminate the analysis, correct the problem, recalibrate, and reanalyze the samples analyzed under an out-of-control condition at no additional cost to the government.

10.13 Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every 8 hours, whichever is more frequent. Do this by analyzing the A and AB interference check solutions (Table 7). The results of the A interference check solution must not exceed the CRDL. The results of the AB interference check solution must not exceed the true value ± 20%.

NOTE: Analytical values are not required for the analytes present in ICS solution A.

10.14 ICP-MS Memory Test and Recovery Blanks

10.14.1 The memory test solution is used in this contract to identify the maximum concentration of an analyte which does not cause a memory effect in excess of the CRDL in the next sequential sample with the instrument configuration used. To perform the memory test, a solution containing elements at the concentrations specified in Table 12, except where analyst discretion is allowed, is evaluated. If the memory test solution is changed from the specified concentrations listed in Table 12, then the composition of the memory test solution must be identified on the Comments Page, associated with the Sample Delivery Group. Note that changes in the composition of the memory test solution affect operational aspects of the analytical run by changing the maximum concentration of an analyte which may occur in a sample without running a blank prior to reporting subsequent analyte concentrations. If the memory test

solution has different concentrations from those specified in Table 12, then the composition of the memory test solution must be reported on the Comments Page in the data package.

10.14.2 To verify that memory effects do not have an adverse effect on data quality, the memory test must be performed on the tuned and calibrated instrument before any analyses are performed. The memory test solution is aspirated into the system for a normal sample exposure period and the time is documented. This is followed by the rinse time associated with the analytical run. Then a calibration blank solution is introduced, the time is documented, and the solution analyzed. The difference between the two times is the minimum allowable elapsed time between two samples. The results of the calibration blank solution must not exceed the CRDL for any of the analytes. If any analyte exceeds the CRDL in the blank solution, then either increase the rinse time, change the instrument hardware, or change the concentration of the element which is failing the memory test until the memory test is passed. The raw data must contain a memory test for which the rinse/washout times used have passed the CRDL criteria.

10.14.3 During the analytical run, if a sample contains an element whose concentration exceeds the level used in the memory test solution, then a recovery blank must be analyzed until the analyte concentration is less than the CRDL. All affected analyses for the analyte must be rerun after a recovery blank has been reported below the CRDL.

10.15 Analyze one duplicate sample for every matrix in a batch at a frequency of one matrix duplicate for every 20 samples.

10.15.1 The relative percent difference between duplicate determinations must be calculated as follows:

$$RPD = \left(\frac{|D_1 - D_2|}{\frac{(D_1 + D_2)}{2}} \right) * 100$$

where:

RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (duplicate)

A control limit of 20% RPD must not be exceeded for sample values greater than or equal to 5 times the CRDL. The results of the duplicate sample analyses must be reported on FORM VI-IN, in $\mu g/L$ for aqueous samples and mg/Kg dry weight basis for solid samples.

10.16 When considering all of the aforementioned quality assurance requirements, the following run sequence becomes apparent from an operational point of view.

Instrument initialization
Warm up
Perform mass calibration
Perform resolution check
Validate tuning criteria
Calibration blank
Calibration standard 1
.
.
Calibration standard n
Initial calibration verification 1
Initial calibration verification 2

Initial calibration verification 3
Initial calibration verification 4
Initial calibration blank
Exposure to memory test solution
Memory blank
CCV1
CCB1
ICS A
ICS AB
CRDL
Aqueous or soil preparation blank
Aqueous or soil LCS
sample n
sample n duplicate
sample n serial dilution
sample n spike
sample n+1
CCV2
CCB2
sample n+2
sample n+3
sample n+4
sample n+5
sample n+6
sample n+7
sample n+8
sample n+9
sample n+10
sample n+11
CCV3
CCB3

Recalibration sequence
CCV4
CCB4

Optional - May be omitted if recalibration not required.

return to running samples (see sample n+2)
CRDL (completion of run sequence)
CCV n
CCB n

11 METHOD PERFORMANCE

11.1 Precision and accuracy data are available in Laing, G., Stapanian, M., Aleckson, K., Dobb, D.,Rowan, J., and Garner, F., Final Report of the Multi-Laboratory Evaluation of Method 6020 CLP-M, Inductively Coupled Plasma - Mass Spectrometry, EPA Contract No. 68-03-3249, December 1989.

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Table 1 - Contract Required Detection Limits and Estimated Detection Limits of the Elements Approved for ICP-MS Method 6020 CLP-M

Element	CRDL	Estimated Detection Limit (µg/L)
Aluminum	200	0.1
Antimony	60	0.02
Arsenic	10	0.4
Barium	200	0.02
Beryllium	5	0.1
Cadmium	5	0.07
Calcium	5000	10.0
Chromium	10	0.02
Cobalt	50	0.01
Copper	25	0.03
Iron	100	0.2
Lead	3	0.02
Magnesium	5000	0.10
Manganese	15	0.04
Nickel	40	0.03
Potassium	5000	1000.0
Selenium*	5	1.0
Silver	10	0.04
Sodium	5000	0.06
Thallium	10	0.05
Vanadium	50	0.03
Zinc	20	0.08

* Analysis for Selenium may only be performed on aqueous samples.

Table 2 - Recommended Elemental Equations for use in Method 6020

Element	Isobaric Correction	Mathematical Equation
Al	none	$(1.0000)(^{27}M)$
Sb	none	$(1.0000)(^{121}M)$
As	ArCl, Se	$(1.0000)(^{75}M)-(3.1278)(^{77}M)+(1.0177)(^{78}M)$
Ba	none	$(1.0000)(^{135}M)$
Be	none	$(1.0000)(^{9}M)$
Cd	MoO, Sn	$(1.0000)(^{114}M)-(0.0149)(^{118}M)-(1.6285)(^{108}M)$
Ca	none	$(1.0000)(^{44}M)$
Cr	none	$(1.0000)(^{52}M)$
Co	none	$(1.0000)(^{59}M)$
Cu	none	$(1.0000)(^{65}M)$
Fe	none	$(1.0000)(^{57}M)$
Pb	none	$(1.0000)(^{208}M)+(1.0000)(^{207}M)+(1.0000)(^{206}M)$
Mg	none	$(1.0000)(^{25}M)$
Mn	none	$(1.0000)(^{55}M)$
Ni	none	$(1.0000)(^{60}M)$
K	none	$(1.0000)(^{39}M)$
Se	Ar_2	$(1.0000)(^{78}M)-(0.1869)(^{76}M)$
Ag	none	$(1.0000)(^{107}M)$
Na	none	$(1.0000)(^{23}M)$
Tl	none	$(1.0000)(^{205}M)$
V	ClO, Cr	$(1.0000)(^{51}M)-(3.1081)(^{53}M)+(0.3524)(^{52}M)$
Zn	none	$(1.0000)(^{66}M)$
^{6}Li	Li(natural)	$(1.0000)(^{6}M)-(0.0813)(^{7}M)$
Sc	none	$(1.0000)(^{45}M)$

Table 2 Continued

Element	Isobaric Correction	Mathematical Equation
Y	none	(1.0000)(^{89}M)
Rh	none	(1.0000)(^{103}M)
In	Sn	(1.0000)(^{115}M)-(0.0149)(^{118}M)
Tb	none	(1.0000)(^{159}M)
Ho	none	(1.0000)(^{165}M)
Bi	none	(1.0000)(^{209}M)

M = the total ion count rate at the specified mass.

Table 3 - Contributions of Concomitant Elements to Nearby Analytes when Resolution and Measurement Schemes Vary. Concentrations listed are the approximate level (μg/L) measured when the interferant is present at 100 mg/L.

		Peak Width at 10% of the Peak Height			
		1.0 amu		0.8 amu	
	Interferant	Integration Width		Integration Width	
Analyte	Element	0.9 amu	0.3 amu	0.9 amu	0.3 amu
^{121}Sb	^{120}Sn	820	5	10	1
^{121}Sb	^{122}Te	77	none	1	none
^{75}As	^{74}Se, ^{76}Se	910	4	3	none
^{9}Be	^{10}B	1,200	12	9	1
^{112}Cd	^{113}In	1,700	8	10	none
^{114}Cd	^{115}In	>5,000	150	180	18
^{116}Cd	^{115}In	30	none	5	none
^{52}Cr	^{51}V	1.4	1.5	none	none
^{53}Cr	^{54}Fe	650	7	1	none
^{59}Co	^{58}Ni, ^{60}Ni	>1,500	6	2	none
^{63}Cu	^{62}Ni, ^{64}Ni	190	1	none	none
^{63}Cu	^{64}Zn	4,000	14	9	none
^{65}Cu	^{64}Ni	1	1	none	none
^{65}Cu	^{64}Zn, ^{66}Zn	>4,400	22	15	none
^{208}Pb	^{209}Bi	140	14	57	none
^{55}Mn	^{54}Fe, ^{56}Fe	900	8	4	none
^{58}Ni	^{59}Co	>3,000	96	75	7
^{60}Ni	^{59}Co	9	4	10	5
^{62}Ni	^{63}Cu	>8,500	690	4,500	16
^{107}Ag	^{106}Pd, ^{108}Pd	>2,400	22	80	4
^{107}Ag	^{106}Cd, ^{108}Cd	130	3	5	2
^{109}Ag	^{108}Pd, ^{110}Pd	1,800	12	36	3

Table 3 Continued

Analyte	Interferant Element	Peak Width at 10% of the Peak Height: 1.0 amu Integration Width, 0.9 amu	1.0 amu Integration Width, 0.3 amu	0.8 amu Integration Width, 0.9 amu	0.8 amu Integration Width, 0.3 amu
^{109}Ag	^{108}Cd, ^{110}Cd	1,600	10	37	3
^{51}V	^{52}Cr	>2,100	45	410	1
^{64}Zn	^{65}Cu, ^{63}Cu	>7,800	57	410	2
^{66}Zn	^{65}Cu	2	none	3	2

Table 4 - Isobaric molecular-ion interferences which could affect the analytes.

Analyte	Oxygen Inter.	Hydroxyl Inter.	Nitrogen Inter.	Chlorine Inter.	Sulfur Inter.	Carbon Inter.	Other
^{121}Sb	PdO		AgN			AgC	
^{123}Sb	AgO		AgN	SrCl	ZrS	CdC	
^{75}As	CoO	NiOH	NiN	ArCl	CaS	CuC	
^{138}Ba	SnO	SbOH					
^{137}Ba	SbO	SnOH		MoCl			
^{136}Ba	SnO	SnOH				SnC	
^{135}Ba	SnO	SnOH		MoCl			
^{134}Ba	SnO	SnOH	SnN	MoCl		SnC	
^{132}Ba	SnO, CdO	InOH	SnN	MoCl	MoS	SnC	
^{130}Ba	CdO	CdOH	SnN, CdN	MoCl	MoS	SnC	
^{9}Be							
^{114}Cd	MoO	MoOH	MoN	SeCl	SeS		
^{112}Cd	MoO, ZrO	MoOH	MoN	SeCl, AsCl	SeS	MoC	
^{111}Cd	MoO	MoOH	MoN	GeCl			
^{110}Cd	MoO, ZrO		MoN, ZrN	GeCl, AsCl	SeS	MoC	
^{113}Cd	MoO	MoOH		SeCl, AsCl			
^{116}Cd	MoO						
^{106}Cd	ZrO		MoN, ZrN		GeS	MoC, ZrC	
^{108}Cd	MoO, ZrO	ZrOH	MoN, ZrN	GeCl	SeS, GeS	MoC, ZrC	
^{52}Cr	ArO	ClOH				ArC	
^{53}Cr	ClO	ArOH	KN	NCl, OCl		KC	
^{50}Cr	SO		ArN		SO	ArC	Mo^{++}
^{54}Cr		ClOH	ArN, CaN			CaC	
^{59}Co	CaO	CaOH	ScN	MgCl	AlS	TiC	Sn^{++}

Table 4. Continued

Analyte	Oxygen Inter.	Hydroxyl Inter.	Nitrogen Inter.	Chlorine Inter.	Sulfur Inter.	Carbon Inter.	Other
^{63}Cu	TiO, PO_2	TiOH	TiN	SiCl, MgCl	PS	VC	ArNa
^{65}Cu	TiO	TiOH	VN	SiCl	SS, SO_2H	CrC	
^{208}Pb							
^{206}Pb							
^{207}Pb							
^{204}Pb							
^{55}Mn	KO	ArOH	KN		NaS	CaC	Cd^{++}
^{202}Hg	WO						
^{200}Hg	WO	WOH	WN				
^{199}Hg	WO	WOH					
^{201}Hg		WOH					
^{198}Hg	WO	TaOH	WN			WC	
^{204}Hg							
^{196}Hg			WN			WC	
^{58}Ni	CaO	KOH	CaN	NaCl	MgS	TiC	Cd^{++},Sn^{++}
^{60}Ni	CaO	CaOH	TiN	MgCl, NaCl	SiS	TiC	Sn^{++}
^{62}Ni	TiO	ScOH	TiN	AlCl, MgCl	SiS	TiC, CrC	Sn^{++}
^{61}Ni	ScO	CaOH	TiN	MgCl	SiS	TiC	Sn^{++}
^{64}Ni	TiO	TiOH	TiN, CrN	SiCl, AlCl	SS	CrC	
^{80}Se	ZnO	CuOH	ZnN	ScCl, CaCl	TiS	ZnC	
^{78}Se	NiO	NiOH	ZnN	CaCl, KCl	TiS	ZnC	
^{82}Se	ZnO	CuOH	ZnN	TiCl, ScCl	TiS, CrS		
^{76}Se	NiO	CoOH	NiN	KCl	CaS	ZnC	
^{77}Se	NiO	NiOH	CuN	CaCl, ArCl	ScS	CuC	

Table 4. Continued

Analyte	Oxygen Inter.	Hydroxyl Inter.	Nitrogen Inter.	Chlorine Inter.	Sulfur Inter.	Carbon Inter.	Other
^{74}Se	NiO	FeOH	NiN	ClCl, KCl	CaS	NiC	
^{107}Ag	ZrO	ZrOH		GeCl	AsS	MoC	
^{109}Ag		MoOH	MoN	GeCl	SeS	MoC	
^{205}Tl							
^{203}Tl		WOH					
^{51}V	ClO	SOH	ClN	ClO, ClN	FS	KC	
^{50}V	SO		ArN			ArC	Mo^{++}
^{64}Zn	TiO	TiOH	TiN, CrN	SiCl, AlCl	SS	CrC	
^{66}Zn	TiO	TiOH	CrN	PCl, SiCl	SS	FeC	
^{68}Zn	CrO	VOH	FeN	PCl	ArS	FeC	Ba^{++}
^{67}Zn	VO	TiOH, Cr	CrN	SCl	ClS	MnC	Ba^{++}
^{70}Zn	FeO	CrOH	GeN	ClCl	ArS	NiC	

Note: The information provided in this table does not indicate that all of the described interferences need to be tested. However, the table can be consulted for informational purposes if unusual samples are encountered.

Table 5 - Changes in Isobaric molecular-ion interferences with changing plasma conditions.**

	Molecular Interference	Nebulizer Flow Rate High	Average	Low
Oxides				
	ScO/Sc	0.00326	0.00055	0.00116
	YO/Y	0.00568	0.00395	0.00353
	TbO/Tb	0.0156	0.00648	0.00614
	ClO/Cl	0.00725	0.00227	0.00233
Hydroxides				
	ScOH/Sc	0.00040	0.00011	0.00000
	YOH/Y	0.00078	0.00044	0.00048
	TbOH/Tb	0.00034	0.00008	0.00011
	ClOH/Cl	0.00048	0.00031	0.00029
Chlorine				
	ClO/Cl	0.00725	0.00227	0.00233
	ClOH/Cl	0.00048	0.00031	0.00029
	ArCl/Cl	0.00605	0.00091	0.00477

** Information for this table is being determined by the EPA.

Table 6 - Internal Standards which may be used in Method 6020 CLP-M.

Internal Standard
^{6}Li
Sc
Y
Rh
In
Tb
Ho
Bi

Table 7 - Interference check sample components and concentrations.

Interference component	Solution A Concentration (mg/L)	Solution AB Concentration (mg/L)
Al	100.0	100.0
Ca	300.0	300.0
Fe	250.0	250.0
Mg	100.0	100.0
Na	250.0	250.0
P	100.0	100.0
K	100.0	100.0
S	100.0	100.0
C	200.0	200.0
Cl	1,800.0	1,800.0
Mo	2.0	2.0
Ti	2.0	2.0
As	0.0	0.100
Cd	0.0	0.100
Cr	0.0	0.200
Co	0.0	0.200
Cu	0.0	0.200
Mn	0.0	0.200
Ni	0.0	0.200
Se	0.0	0.100
Ag	0.0	0.200
V	0.0	0.200
Zn	0.0	0.100

Table 8 - Sample Preservation and Holding Times.

Measurement Parameter	Container (1)	Preservative (2)	Maximum Holding Time (3)
Waters			
Metals (4)	P,G	HNO_3 to pH < 2	6 months

Soils/Sediments/Wastes

The preservation required for soil/sediment/waste samples is maintenance at 4 C (±2 C) until digestion.

FOOTNOTES

(1) Polyethylene (P) or glass (G).
(2) Sample preservation is performed by the sampler immediately upon sample collection.
(3) Samples must be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still considered valid. Holding times are calculated from the date when the sample was collected.
(4) Samples are filtered immediately on-site by the sampler before adding preservative for dissolved elements.

Table 9 - Suggested mass choices for elements which may be monitored either during the analytical run or in a separate scan. Boldface and underlined masses indicate the masses which must have the most impact on data quality and the elemental equations used to collect the data. Boldface and underlined masses must be monitored.

Mass	Element of interest
27	Aluminum
121, 123	Antimony
75	Arsenic
138, 137, 136, **135**, 134, 132, 130	Barium
9	Beryllium
114, 112, 111, 110, 113, 116, 106, **108**	Cadmium
42, 43, **44**, 46, 48	Calcium
52, **53**, **50**, 54	Chromium
59	Cobalt
63, **65**	Copper
56, **54**, **57**, 58	Iron
208, **207**, **206**, 204	Lead
24, **25**, **26**	Magnesium
55	Manganese
202, **200**, 199, 201	Mercury
58, **60**, 62, **61**, 64	Nickel
39	Potassium
80, **78**, **82**, **76**, **77**, 74	Selenium
107, **109**	Silver
23	Sodium
205, 203	Thallium
51, **50**	Vanadium
64, **66**, **68**, **67**, 70	Zinc
83	Krypton
72	Germanium
139	Lanthanum
140	Cerium
129	Xenon
118	Tin
105	Palladium
47, **49**	Titanium
125	Tellurium
69	Gallium
35, 37	Chlorine
98, 96, 92, **97**, 94	Molybdenum

NOTE: Although the only masses which must be monitored are indicated in bold face, it is strongly recommended that the other elements be monitored to indicate other potential molecular interferences which could affect the data quality.

Table 10 - Tuning Solution - The tuning solution must consist of the following elements at the concentrations described.

Element	Concentration (µg/L)
^{7}Li	100
Co	100
In	100
Tl	100

Table 11 - Tuning and Response Factor Criteria

Minimum Response from Tuning Solution	
^{7}Li	>2,000
^{59}Co	>20,000
^{115}In	>10,000
^{205}Tl	>1,000
^{102}Ru	<25
Ion Abundance Criteria	
$^{7}Li/^{59}Co$	0.20 - 1.00
$^{59}Co/^{59}Co$	1.00
$^{115}In/^{59}Co$	0.75 - 2.00
$^{205}Tl/^{59}Co$	0.50 - 1.20
Required Mass Calibration	
^{7}Li	7.016 ± 0.1
^{59}Co	58.9332 ± 0.1
^{115}In	114.904 ±0.1
^{205}Tl	204.9744 ± 0.1

Table 12 - Memory Check Solution - The recommended concentrations of the memory test solution are listed below. The stated concentrations must be used for elements which are not on the Target Analyte List. For elements on the Target Analyte List, the concentrations may be modified at the discretion of the analyst but must be reported on the Comments Page.

Element	Concentration (mg/L)
Al	500.0
Ca	500.0
Fe	500.0
Mg	500.0
Na	500.0
K	500.0
C	1000.0
Cl	3600.0
Mo	10.0
P	500.0
S	500.0
Ti	10.0
Sb	10.0
As	10.0
Ba	10.0
Be	10.0
Cd	10.0
Cr	10.0
Co	10.0
Cu	10.0
Pb	10.0
Mn	10.0
Ni	10.0
Se	10.0
Ag	10.0
Tl	10.0
V	10.0
Zn	10.0

Table 13 Spiking Levels For ICP-MS Analysis (μg/L)

Element	Water	Soil
Aluminum	*	*
Antimony	200	200
Arsenic	100	100
Barium	500	500
Beryllium	50	50
Cadmium	50	100
Calcium	*	*
Chromium	200	500
Cobalt	200	200
Copper	200	500
Iron	1,000	*
Lead	100	200
Magnesium	*	*
Manganese	200	*
Nickel	200	250
Potassium	*	*
Selenium	50	50
Silver	50	100
Sodium	*	*
Thallium	50	50
Vanadium	200	300
Zinc	500	500

NOTE: Elements without spike levels and not designated with an asterisk, must be spiked at appropriate levels.

(1) The levels shown indicate concentrations in the final digestate of the spiked sample (200 mL final volume).

*No spike required.