EXHIBIT 25. SUMMARY OF MOST FREQUENTLY OCCURRING CHEMICALS OF POTENTIAL CONCERN BY INDUSTRY*

Compound	Industry						
	1	2	3	4	5	6	7
Acetone		X					
Aluminum							X
Ammonia		X	X		X	X	X
Ammonium Nitrate		X					
Ammonium Sulfate	X					X	
Anthracene					X		
Arsenic					X		
Benzene							X
Biphenyl					X		
Chlorine		X					
Chlorobenzene			X				
Chromium				X	X	X	
Copper					X		
Cyclohexane		X					
Dibenzofuran					X		
Dichloromethane			X	X			
Formaldehyde					X		
Freon	X						
Glycol Ethers						X	
Hydrochloric Acid			X	X			
Lead	X						
Manganese	X						
Methanol	X		X				
Methyl Ethyl Ketone		X				X	X
Naphthalene					X		
Nickel				X			
Nitric Acid		X		X			
Pentachlorophenol		X			X		
Propylene							X
Sodium Sulfate	X	X	X	X		X	X
Sodium Hydroxide	X		X	X		X	X
Sulfuric Acid	X	X		X		X	X
Trichloroethene	X			X			
Toluene			X			X	X
Titanium Tetrachloride			X				
Xylene			X			X	X
1,1,1-trichloroethane	X			X			

KEY
1 = Battery Recycling
2 = Munitions/Explosives
3 = Pesticide Manufacturing
4 = Electroplating
5 = Wood Preservatives
6 = Leather Tanning
7 = Petroleum Refining

*Summarized from Appendix II.

21-002-025

EXHIBIT 26. STEPS IN THE ASSESSMENT OF TENTATIVELY IDENTIFIED COMPOUNDS

Identification	• GC-MS analysis indicates the presence of a tentatively identified compound.
	• Incorporate retention time/retention index matching and use physical characteristics (boiling point or vapor pressure) to determine if identification is reasonable.
	• Examine historical data and industry-specific compound lists.
	• Reanalyze sample with an authentic standard.
Quantitation	• Assess known analytical response characteristics for similar compounds or similar compound classes.
	• Determine response characteristics by analysis of an authentic standard.

21-002-026

mass spectra and chromatograms can review TIC data and eliminate many false positive identifications. The use of retention indices or relative retention times can confirm TICs identified by the GC-MS computer (Eckel, *et. al.* 1989). Examination of historical data, industry-specific compound lists, compound identifications from iterative sampling episodes, and analyses performed by different laboratories may also increase confidence in the identification of a TIC. The final identification step is to reanalyze the sample after calibrating the GC-MS instrument with an authentic standard of the compound that the TIC is believed to be.

If toxic compounds are identified as TICs by this type of broad spectrum analysis, the RPM or risk assessor should request further analyses to positively identify the compound and to accurately quantitate it. The risk assessor or RPM should discuss data requirements with an analytical chemist to determine the appropriate analytical method.

Many compounds that appear as TICs during broad spectrum analyses belong to compound classes. Examples of compound classes are saturated aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs). The risk assessor may be able to make a preliminary judgment of toxicity at the compound class level without a definitive identification of each compound present. For example, in a sample contaminated by gasoline, organics analysis would indicate a series of TICs as aliphatic hydrocarbons of increasing size. These may not be carcinogenic, and more precise identification may not be required. If a similar sample were contaminated with coal tar, larger hydrocarbons and a series of PAHs would be found during the analysis. The aliphatic hydrocarbons are not especially toxic, but the PAH compound class contains carcinogens and are of greater concern.

3.2.3 Identification and Quantitation

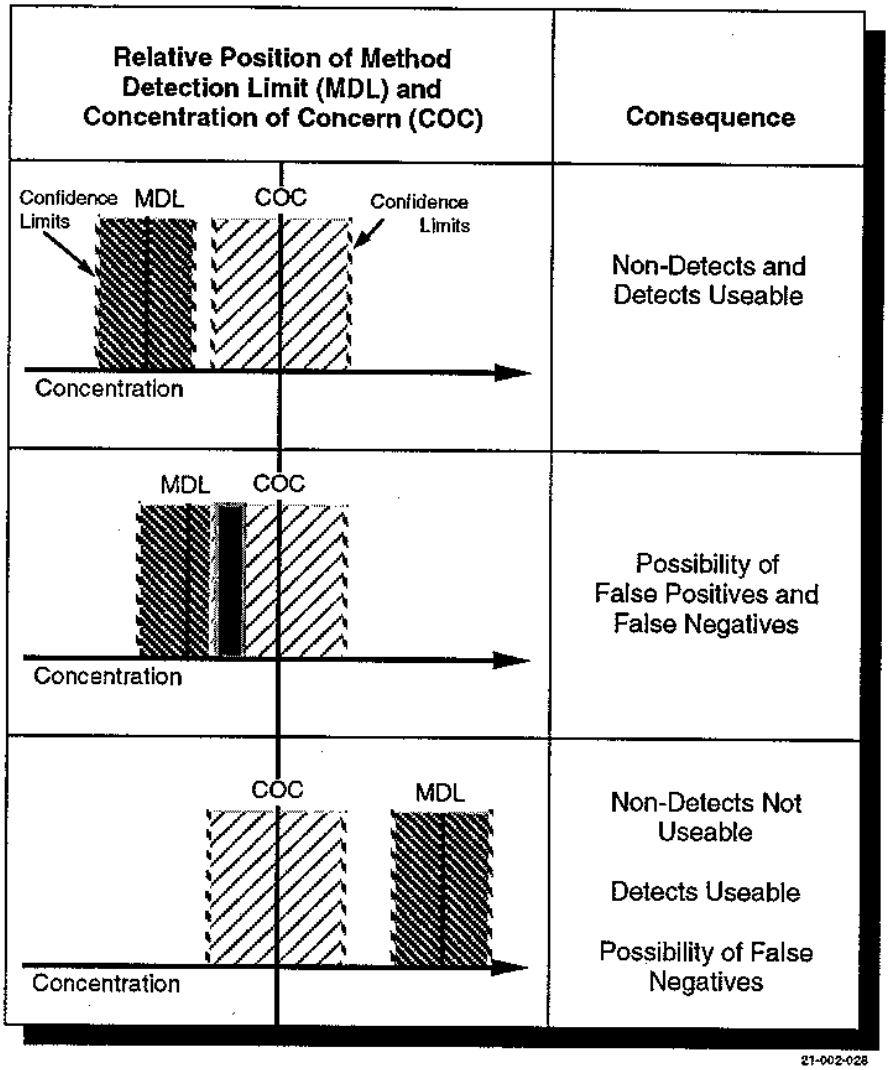
A risk assessor first confirms chemical identification, and then determines the level of contamination. This section summarizes the effects of detection limits and sample contamination considerations on the confidence in analyte identification and quantitation. Requirements for confidence are specified in Exhibit 27. When analytes have concentrations of concern approaching method detection limits, the confidence in both identification and quantitation is low. This case is illustrated in Exhibit 28. In addition, confidence in identifying and quantitating as representative of site

EXHIBIT 27. REQUIREMENTS FOR CONFIDENT IDENTIFICATION AND QUANTITATION

Identification	• Analyte present above the IDL.
	• Organic -- Retention time and/or mass spectra matches authentic standards.
	• Inorganic -- Spectral absorptions compared to authentic standards.
	• Knowledge of blank contamination (if any).
Quantitation	• Instrument response known from analysis of an authentic standard.
	• Detected concentration above the limit of quantitation and within the limit of linearity (instrument response not saturated).

21-002-027

EXHIBIT 28. RELATIVE IMPACTS OF DETECTION LIMIT AND CONCENTRATION OF CONCERN: DATA PLANNING



21-002-028

conditions is potentially diminished if the chemicals of potential concern are present as contaminants from laboratory or field procedures. This section identifies analytes and cites situations in which this is most likely to occur.

The first requirement of analysis is confidence in the identification of chemicals of potential concern. Identification means that the chemical was present in the environmental sample above the detection limit. Chemicals can be correctly identified at lower concentrations than are suitable for accurate quantitation. If lower quantitation limits are required for risk assessment purposes, a larger initial sample size may be processed, or the sample extract may be concentrated to a smaller final volume. However, concentration of an extract to a smaller volume, or increasing the sample size, may saturate the instrument in the presence of matrix interferences. The RPM should discuss these issues with an analytical chemist to determine the best approach. A further discussion of limits of quantitation is presented in Section 3.2.4. and Appendix III.

To ensure maximum confidence in the identification of an organic chemical contaminant, an instrumental technique, such as mass spectrometry, that provides definitive results is necessary. Although alternative techniques are available, GC-MS determination is the best available procedure for confident identification or confirmation of volatile and extractable organic chemicals of potential concern. The application of this technique minimizes the risk of error in qualitative identification and measures chemicals of potential concern at environmental levels above the detection or quantitation limits listed in Appendix III. In cases where the target detection limit is too low to allow

but more definitive, instrumental techniques can be used.

The identification of inorganic chemicals is more certain. A reported concentration determined by atomic absorption (AA) spectroscopy or inductively coupled plasma (ICP) atomic emission spectroscopy is generally considered evidence of presence at the designated level reported, provided there is no interference. If interferences exist, the laboratory should try to characterize the type of interferences (background, spectral or chemical) and take the necessary steps to correct them.

3.2.4 Detection and Quantitation Limits and Range of Linearity

The following discussion is intended to provide the RPM and risk assessor with an understanding of the various ways that detection or quantitation limits can be reported. The term "detection limit" is frequently used without qualification. However, there are several methods for calculating detection limits. The RPM should consult with the project chemist and the risk assessor whenever analytical methods are to be selected, and specify the nature of the detection limits that must be reported; it is the laboratory's responsibility to adhere to this requirement. If no requirement has been specified, then the laboratory should be requested to explicitly describe the types of the detection limits it reports. Detection limits can be calculated for the instrument used for measurement, for the analytical method, or as a sample-specific quantitation limit. The risk assessor should request that the sample quantitation limit (SQL) be reported whenever possible. The term "detection limit" should be considered generic unless the specific type is defined. Exhibit 29 illustrates the relationship between instrument response and the quantity of analyte presented to the analytical system (i.e., a calibration curve).

> **Common Detection and Quantitation Limits**
>
> **Instrument detection limit.** The IDL includes only the instrument portion of detection, not sample preparation, concentration/dilution factors, or method-specific parameters.
>
> **Method detection limit.** The MDL is the minimum amount of an analyte that can be routinely identified using a specific method. The MDL can be calculated from the IDL by using sample size and concentration factors and assuming 100% analyte recovery.
>
> **Sample quantitation limit.** The SQL is the MDL adjusted to reflect sample-specific action such as dilution or use of a smaller sample aliquot for analysis due to matrix effects or the high concentration of some analytes.
>
> **Contract required quantitation (detection) limit.** The CRQL for organics and CRDL for inorganics are related to the SQL that has been shown through laboratory validation to be the lower limit for confident quantitation and to be routinely within the defined linear ranges of the required calibration procedures.
>
> **Practical quantitation limit.** The PQL, defined in SW846 methods, is the lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions.

> ☛ *The closer the concentration of concern is to the detection limit, the greater the possibility of false negatives and false positives.*

> ☛ *The wide range of chemical concentrations in the environment may require multiple analyses or dilutions to obtain useable data. Request results from all analyses.*

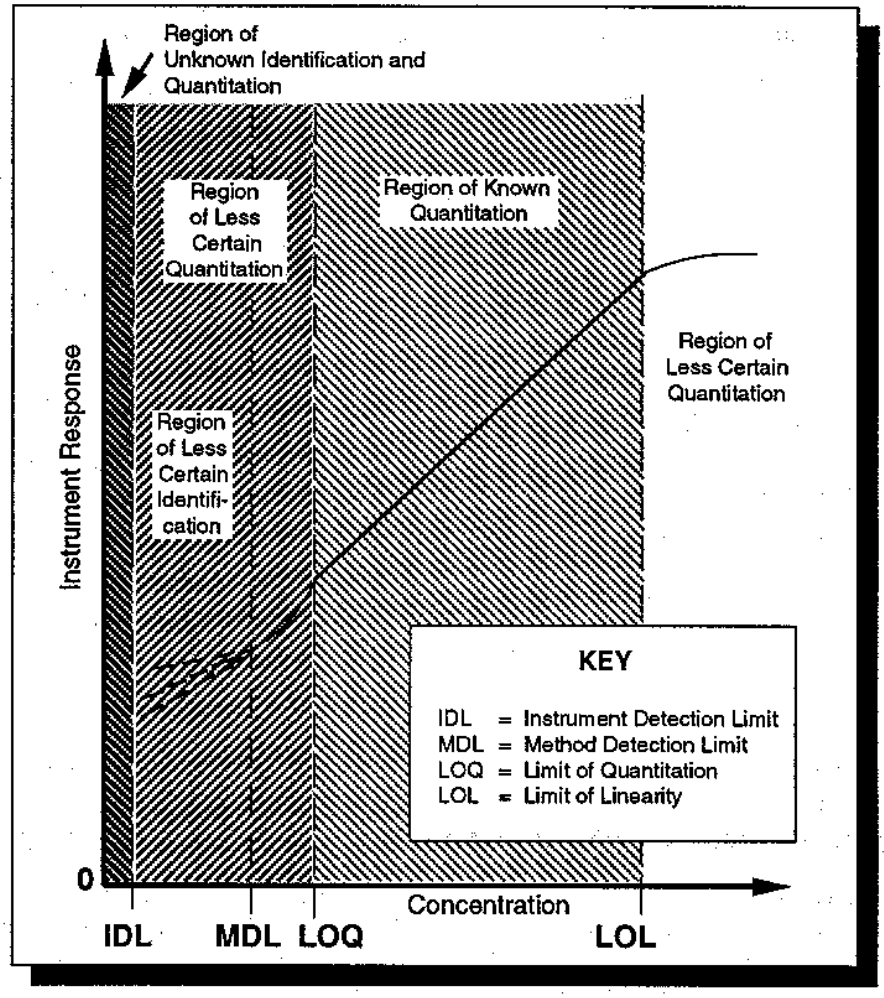
The definitions that follow are intended to provide the RPM and risk assessor with an understanding of the various methods for calculating detection limits, the terms used to describe specific detection limits, and the limitations associated with identification and quantitation of chemicals of potential concern at concentrations near specified detection limits. Understanding the different terms used to describe detection limits helps avoid reporting problems. Exhibit 30 provides examples of calculations of the three most commonly reported types of detection limits.

> ☛ *Define the type of detection or quantitation limit for reporting purposes; request the sample quantitation limit for risk assessment.*

Instrument detection limit. The instrument detection limit (IDL) includes only the instrument portion of detection, not sample preparation, concentration/dilution factors, or method-specific parameters. The IDL is operationally defined as three times the standard deviation of seven replicate analyses at the lowest concentration that is statistically different from a blank. This represents 99% confidence that the signal identified is the result of the presence of the analyte, not random noise. The IDL is not the same as the method detection limit. Use of the IDL should be avoided for risk assessment.

Method detection limit. The method detection limit

EXHIBIT 29. THE RELATIONSHIP OF INSTRUMENT CALIBRATION CURVE AND ANALYTE DETECTION



21-002-029

Method detection limit. The method detection limit (MDL) is the minimum amount of an analyte that can be routinely identified using a specific method. The MDL can be calculated from the IDL by using sample size and concentration factors and assuming 100% analyte recovery. This estimate of detection limit may be biased low because recovery is frequently less than 100%. MDLs are operationally determined as three times the standard deviation of seven replicate spiked samples run according to the complete method. Since this estimate includes sample preparation effects, the procedure is more accurate than reported IDLs. However, the evaluation is routinely completed on reagent water. As a result, potentially significant matrix interferences that decrease analyte recoveries are not addressed.

The impact of an MDL on risk assessment is illustrated in Exhibit 28. When planning to obtain analytical data, the risk assessor knows the concentration of concern or preliminary remediation goal. When the concentration of concern of an analyte is greater than the MDL, to the extent that the confidence limits of both the MDL and concentration of concern do not overlap, then both "non-detect" and "detect" results can be used with confidence. There will be a possibility of false positives and false negatives if the confidence limits of the MDL and concentration of concern overlap. When the concentration of concern is sufficiently less than the MDL that the confidence limits do not overlap, then there is a strong possibility of false negatives and only "detect" results are useable.

EXHIBIT 30. EXAMPLE OF DETECTION LIMIT CALCULATION

IDL = 3 x SD* of replicate injections

Example: 100 ppb pentachlorophenol standard

If: SD = 5 ppb

Then: IDL = 3 x 5 ppb = 15 ppb

MDL = 3 x SD of replicate analyses (extraction and injection)

Example: 100 ppb pentachlorophenol spiked in sample producing average measured concentration of 50 ppb (not all analyte is recovered or measured)

If: SD = 18 ppb

Then: MDL = 3 x 18 ppb = 54 ppb

Incorporate calculation of MDL from IDL

SQL = MDL corrected for sample parameters

Example: 100 ppb pentachlorophenol with MDL of 57 ppb

If: Dilution factor = 10 (sample is diluted due to matrix interference or high concentrations of other analytes)

Then: SQL = 10 x 57 ppb = 570 ppb

* SD = Standard Deviation

21-002-030

Sample quantitation limit. The SQL is the MDL adjusted to reflect sample-specific action such as dilution or use of smaller aliquot sizes than prescribed in the method. These adjustments may be due to matrix effects or the high concentration of some analytes. The SQL is the most useful limit for the risk assessor and should always be requested.

For the same chemical, the SQL in one sample may be higher than, lower than, or equal to SQL values for other samples. In addition, preparation or analytical adjustments, such as dilution of the sample for quantitation of an extremely high level of one chemical, could result in non-detects for other chemicals included in the analysis, even though these chemicals may have been present at trace quantities in the undiluted sample. The risk assessor should request results of both original and dilution analyses in this case. Since the reported SQLs take into account sample characteristics, sample preparation, and analytical adjustments, they are the most relevant quantitation limits for evaluating non-detected chemicals.

Contract required quantitation (detection) limit. The CLP specifies a contract required quantitation limit (CRQL) for organics and a contract required detection limit (CRDL) for inorganics. Each of these quantities is related to the SQL that has been shown through laboratory validation to be the lower limit for confident quantitation and to be routinely within the defined linear ranges of the required calibration procedures.

The use of CRQLs and CRDLs attempts to maintain the analytical requirements within performance limits (which are based upon laboratory variability using a variety of instruments). CRQLs are typically two to five times the reported MDLs and they generally correspond to the limit of quantitation.

Practical quantitation limit. The practical quantitation limit (PQL), defined in SW846 methods, is the lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. It is important to note that the SQL and PQL are not equivalent. Use of PQL values as measures of quantitation limits should be avoided wherever possible in risk assessment.

Other quantitation measurements. The limit of quantitation (LOQ) is the level above which quantitative

results may be obtained with a specified degree of confidence. At analyte concentrations close to, but above the MDL, the uncertainty in quantitation is relatively high. Although the presence of the analyte is accepted at 99% confidence, the reported quantity may be in the range of ±30%. Ten times the standard deviation measured for instrument detection is recommended to demonstrate a level at which confidence is maximized (Borgman 1988).

The limit of linearity (LOL) is the point at or above the upper end of the calibration curve at which the relationship between the quantity present and the instrument response ceases to be linear (Taylor 1987). Instrument response usually decreases at the LOL, and the concentration reported is less than the amount actually present in the sample because of instrument saturation. Dilution is necessary to analyze samples in which analyte concentrations are above the LOQ. However, dilutions correspondingly increase SQLs. Data should be requested from both diluted and undiluted analyses.

3.2.5 Sampling and Analytical Variability Versus Measurement Error

Sampling and analytical variability and measurement error are two key concepts in data collection. Each is discussed in the context of evaluating strategies for the collection and analysis of both site and background samples.

Exhibit 21 defines sampling variability and measurement error. Most SAPs are a necessary compromise between cost and confidence level. Basically, two types of decisions must be made in planning:

- What statistical performance is necessary to produce the quality of data appropriate to meet the risk assessor's sampling variability performance objectives and
- What types and numbers of QC samples are required to detect and estimate measurement error.

☛ *When contaminant levels in a medium vary widely, increase the number of samples or stratify the medium to reduce variability.*

Sampling plans attempt to estimate and minimize both sampling variability and measurement error. Sampling variability affects the degree of confidence and power the risk assessor can expect from the results. Confidence is the ability to detect a false positive hypothesis, and power is the ability to detect a false negative. Power is more important for risk assessment. An estimate of the sampling variability that is a function of the spatial variation in the concentrations of chemicals of potential concern is obtained by calculating the coefficient of variation for each chemical. When the coefficient of variation is less than 20% and a substantial quantity of data are available, the effect of spatial and temporal variation on concentrations of chemicals of potential concern is minimal, and the power and certainty of statistical tests is high (EPA 1989c).

Spatial variability can be analyzed after an initial sampling effort through simple statistical summation or through the use of variogram analysis, a part of the geostatistics. EPA has developed software to assist a risk assessor in this analysis: Geostatistical Environmental Assessment Software (GEOEAS) (EPA 1988c) and Geostatistics for Waste Management (GEOPACK) (EPA 1990b) .

Measurement error is estimated using the results of QC samples and represents the difference between the true sample value and the reported value. This difference has five basic sources: the contaminant being measured, sample collection procedures, sample handling procedures, analytical procedures, and data production procedures. Measurement error due to analytical procedures is discussed in Section 3.2 under analytical issues. Measurement error due to sampling is estimated by examining the precision of results from field duplicates. The minimum recommended number of field duplicates is 1 for every 20 environmental samples (5%). A minimum of one set of duplicates should be taken per medium sampled unless many strata are involved; five sets are recommended. Exhibit 31 summarizes the types and uses of QC samples in defining variation and bias in measurement.

☛ *Sampling variability typically contributes much more to total error than analytical variability.*

In summarizing the discussion of sampling variability and measurement error, one finding puts the concepts in perspective: "An analysis of the components of total error from soils data from an NPL site sampled for PCBs indicated that 92% of the total variation came from the location of the sample and 8% from the measurement process" (EPA 1989f). Of the 8%, less than 1% could be attributed to the analytical process. The rest of the 8% is attributable to sample collection, sample handling, data processing and pollutant characteristics. Sampling variability is often three to four times that introduced by measurement error. Exceptions to this observation on the components of variation or sources of error occur in instances of poor method performance for specific analytes.

EXHIBIT 31. MEASUREMENT OF VARIATION AND BIAS USING FIELD QUALITY CONTROL SAMPLES

Quality Control Sample Types	Variation or Bias Measured
Field duplicate	Provides data required to estimate the sum of subsampling and analytical variances.
Field blank	Provides data required to estimate the bias due to contamination introduced during field sampling or cleaning procedures. Also measures contamination at laboratory. Compare with laboratory method blank to determine source of contamination.
Field rinsate	Provides data required to estimate the sum of the bias caused by contamination at the time of sampling from sampling equipment and by analysis and data handling. Indicates cross-contamination and potential contamination due to sampling devices.
Trip blank	Provides data required to estimate the bias due to contamination from migration of volatile organics into the sample during sample shipping from the field and sample storage at the laboratory.

Source: EPA 1990c.

21-002-031

Media or matrix variability. Appropriate samples must be collected from each medium of concern and, for heterogeneous media, from designated strata. Stratification reduces variability in results from individual strata, which can be different layers or surface areas. Media to be sampled should include those currently uncontaminated but of concern, as well as those currently contaminated. For media of a heterogeneous nature (e.g., soil, surface water, or hazardous waste), strata should be established and samples specified by stratum to reduce variability, the coefficient of variation and the required number of samples.

Sampling considerations vary according to media. The sampling concern may involve contaminant occurrence, temporal variation, spatial variation, sample collection, or sample preservation. Exhibit 32 indicates potential sampling problem areas for each medium. Problem areas are classified relative to other media. RPMs can use this exhibit to plan for possible sampling problems in the data collection design. Sampling designs must be structured to identify and characterize hot spots. Information needed for fate and transport modeling should be obtained during a site sampling investigation. This information also differs by the medium of concern (EPA 1989a).

The type of medium in which a chemical is present affects the potential sensitivity, precision, and accuracy of the measurement. Sharp distinctions occur in applying a single method to media such as water, oil, sludge, soil, or tissue. Medium or matrix problems are indicated by the presence of analytical interferences, poor recovery of analytes from the matrix, physical problems such as viscosity (flow parameters), and particulate content that affect sample processing. Exhibit 33 shows the sources of uncertainty across media. Spiked environmental samples monitor the effect of these sources of uncertainty on the accuracy of recovery of target compounds from the matrix. Duplicates quantify the effect of these parameters on precision. The method must be chosen carefully if a difficult medium such as oily waste or soil is to be analyzed. Routine methods usually specify the medium or media for which they are applicable.

Method detection and general confidence in analytical determinations are also often affected by specific media types and by analytical interference. The impact of matrix interference on detection limits, identification,

EXHIBIT 32. SAMPLING ISSUES AFFECTING CONFIDENCE IN ANALYTICAL RESULTS

Major Sampling Issues	Problem Likelihood by Medium					
	Soil	Ground Water	Surface Water	Air	Biota	Hazardous Waste
Contaminant Migration	√√		√	√		√√
Temporal Variation			√√	√		
Spatial Variation	√√	√√	√√	√	√	√√
Topographic/ Geological Properties	√√			√		
Hot Spots	√√	√√				√√
Sample Collection	√		√√	√√		√
Sample Preparation/ Handling	√√	√	√√	√√	√	√
Sample Storage		√√	√√	√√	√√	
Sample Preservation		√√	√√		√√	

Key: √√ = Likely source of significant sampling problem.
√ = Potential source of sampling problem.

Source: Modified from Keith 1990b.

21-002-032

and quantitation is illustrated by the following discussions (which are not meant to be comprehensive).

- Oil and hydrocarbons affecting GC-MS analyses,
- Phthalates and non-pesticide chlorinated compounds that can interfere with pesticide analyses, and
- Iron spectral interference affecting ICP sample results.

Oil and hydrocarbons. The presence of appreciable concentrations of oil and other hydrocarbons may interfere with the extraction or concentration process. Also, even at low concentrations, oil in a sample usually produces a large series of chromatographic peaks that interfere with the detection of other chemicals of potential concern during gas chromatography. Any chemicals of potential concern that may elute concurrently from the GC column are obscured by the hydrocarbon response and may not present a distinct spectrum. Also, hydrocarbons that are present in significant quantity are often identified as TICs, potentially adding a large number of compounds for consideration by the risk assessor.

During RI planning, the risk assessor should determine if there is a potential for hydrocarbon contamination, through knowledge of historical site use and examination of historical data. The laboratory can be instructed to add cleanup protocols to the analysis, or to use a supplemental analysis for which the hydrocarbons are not interferences (e.g., electron capture detection for halogenated compounds).

Phthalates and non-pesticide chlorinated compounds. Phthalates interfere with pesticide analyses by providing a detector response similar to that for chlorinated compounds. Phthalates and non-pesticide

EXHIBIT 33. SOURCES OF UNCERTAINTY THAT FREQUENTLY AFFECT CONFIDENCE IN ANALYTICAL RESULTS

Source of Uncertainty	Degree of Significance by Medium				
	Soil	Water	Air	Biota	Hazardous Waste
SAMPLING					
Design	√√	√	√√		√
Contamination	√√	√	√		
Collection	√	√√	√√		√
Preparation	√√				
Storage		√√	√√		
Preservation		√√			
LABORATORY					
Storage	√√	√√	√√		
Preparation	√√√	√√√		√√	√√
Analysis	√√		√	√	√√
Reporting			√	√√	√√
ANALYTE-SPECIFIC					
Volatility	√√	√	√		
Photodegradation		√	√		
Chemical Degradation	√	√√			
Microbial Degradation	√√	√√			
Contamination	√√		√√		

KEY:
√√ = Likely source of significant error or uncertainty.
√ = Potentially source of significant error or uncertainty.
√√√ = Magnitude of effect determined by examination of data.

21-002-033

chlorinated compounds are often present in greater concentrations than the pesticides of concern. Pesticide data are often required at low detection limits and, therefore, GC-MS analyses are not used for quantitation. In these cases, a gas chromatographic analysis using electron capture detection is more sensitive, providing a wider useful range of detection. The phthalates and chlorinated compounds can coelute with chemicals of potential concern, thereby obscuring the detection of target analytes and raising the analyte-specific quantitation limit. Phthalates and chlorinated compounds also produce additional peaks on the chromatogram that can be interpreted as false positive responses to pesticides. A second analysis using a different column provides an extra measure of confidence in identification. Alternatively, sample extracts from positive analyses can be further concentrated for confirmation by GC-MS if concentrations of analytes are sufficient.

Iron. Large quantities of iron in a sample affect the detection and quantitation of other metallic elements analyzed by ICP atomic emission spectroscopy at wavelengths near the iron signals. The strong iron response overlaps nearby signals, thereby obscuring the results of potentially toxic elements present at much lower concentrations. An interference check sample for ICP analyses monitors the effect of such elements. High concentrations of iron are analyzed with low concentrations of other metals in these samples to indicate whether iron interfered with metal detection at lower concentrations. If spectral interferences are observed, data may be qualified as overestimated. The risk assessor or RPM should consult the project chemist to determine if a particular method requires a performance check.

3.2.6 Sample Preparation and Sample Preservation

Some samples require preparation in the field to ensure that the results of analyses reflect the true characteristics of the sample. Sample filtration and compositing procedures are discussed in this section. Exhibit 34 summarizes the issues which the various sample preparation methods address. Exhibit 35 outlines the primary information gained with the various sampling techniques.

EXHIBIT 34. SAMPLE PREPARATION ISSUES

Issue	Action
Sample Integrity	Preservation --- acids, biocides (may be applicable to volatiles or metals).
Source of Analyte Media	Unfiltered samples -- measure total analytes Filtered samples -- discriminate sorbed and unsorbed analytes
Analyte Speciation	Choice of sample preparation protocols affects analyte speciation
Large Number of Samples to be Analyzed	Composite samples (However, this raises the effective detection limit in proportion to the number of samples composited.)

21-002-034

Filtration. If the risk assessor needs to discriminate between the amount of analyte present in true solution in a sample and that amount sorbed to solid particles, then the sample must be filtered and analyses should be performed for both filtered and unfiltered compounds. Some samples, such as tap water, are never filtered because there is no particulate content. Filtration should be performed in the field as soon as possible after the sample has been taken and before any preservative has been added to the sample. Filtration often does not proceed smoothly. It is common practice only to filter a small proportion of all samples taken, and to perform analyses for the total content of the analyte in the majority of samples. Filtered samples generally provide a good indication of the fraction of contaminant likely to be transported over large distances horizontally in a plume. However, in the immediate vicinity of a source or point of exposure, unfiltered samples may be valuable in providing an indication of suspended material that

EXHIBIT 35. INFORMATION AVAILABLE FROM DIFFERENT SAMPLING TECHNIQUES

Sample Type	Information
Filtered	Can differentiate sorbed and unsorbed analytes.
Unfiltered	Total amount of analyte in sample is measured.
Grab	Can be used to locate hot spots.
Composite	Can provide average concentrations over an area at reduced cost.

21-002-035

may act as a source or sink of dissolved contaminants and may therefore modify overall transport.

Compositing. Reducing the number of samples by compositing is also a form of sample preparation. Compositing may be performed to reduce analytical costs, or in situations where the risk assessor has determined that an average value will best characterize an exposure pathway. Compositing cannot be used to identify hot spots, but can be effective when averaging across the exposure area. Caution should be exercised when compositing since low level detects can be averaged out and become non-detects.

Preservation. Sample characteristics can be disturbed by post-sampling biological activity or by irreversible sorption of analytes of concern onto the walls of the sample container. A variety of acids and biocides used for preservation are discussed in standard works such as *Standard Methods for the Examination of Water and Wastewater* (Clesceri, *et. al.*, eds. 1989). Samples are also usually shipped with ice to reduce biological activity.

Preparation. Several factors in sample preparation affect analytical data. These factors include sample matrix, desired detection limit, extraction solvent, extraction efficiency, sample preparation technique, and whether the analysis is performed in the field or in a fixed laboratory. In addition, parameters such as turnaround time may preclude the use of some sample preparation alternatives.

An extraction method must be able to release the chemicals of concern from the sample matrix. For example, organic solvents will extract non-polar organic compounds from water. Polar and ionic compounds

(such as unsymmetrically halogen-substituted compounds, phenols, and carboxylic acids) may require additional techniques for extraction from water. The choice of solvent is also critical to the extraction efficiency. Methanol would be expected to extract a larger quantity of volatile organic material from soils or sediments than from water. For inorganic analyses, the matrix may require additional acidification to dissolve metal salts that have precipitated from the solution.

Sample preparation procedures for organic analytes are applied based on volatility. Volatile organics are analyzed using head-space or purge and trap techniques. Extraction alternatives for the analysis of less volatile (extractable) organic chemicals include separatory funnels, Soxhlet extraction apparatus, continuous liquid-liquid extractors, and solid phase cartridges. Details of these extraction options can be obtained from the project chemist. Strengths and weaknesses of each of these preparation procedures are described in Exhibit 36.

For inorganic analyses, the sample matrix is usually digested in concentrated acid. The released metals are introduced into the instrument, then analyzed by flame AA or ICP atomic emission spectrophotometry. The selection of the acid for digestion influences the detection limit because different acids have different digestion abilities.

- If digestion is not used, the sample measurement corresponds to a determination of soluble metals rather than total metals. If soluble metals have a greater toxicological significance, this difference may be important to the risk assessment.
- If the sample is filtered in the field or the laboratory before digestion, any metals associated with particulates are removed before analysis. If particulates are an exposure pathway in the risk assessment, sample filteration would underestimate risk.

The analytical request must specify if the sample is to be filtered and whether or not it is to be digested (to measure soluble metals). Unless otherwise specified, samples are usually digested but not filtered.

3.2.7 Identification of Exposure Pathways

Exposure pathways and their components, such as source, mechanism of release, etc., should be designated prior to the design of the sampling procedures. For the risk assessment, at least one broad spectrum analytical sample is required and two or three are recommended for each medium and potential source in an exposure pathway. If the site sampling design fails to consider all exposure pathways and media, additional samples will be required.

Current and future exposure pathways may be limited to particular areas of a site. If sampling activity can be concentrated in these areas, the precision and accuracy of the data supporting risk assessments can be improved.

Risk assessment requires characterization of each exposure area for the site. Samples not falling within the areas of potential concern are not used in the identification of chemicals of potential concern nor in the calculation of reasonable maximum exposure concentration. Depending on exposure pathways, the risk assessor may utilize only a small number of samples that were collected at a site. Exhibit 37 shows why the identification of exposure pathways is critical to the sampling design in order to maximize the number of samples that are useable in the risk assessment.

3.2.8 Use of Judgmental or Purposive Sampling Design

Judgmental or purposive designs that specify sampling points based on existing site knowledge may be appropriate for the initial phase of site sampling or when the risk assessment is performed using few samples. In such instances, non-statistical approaches may be more effective in accomplishing the purpose of the risk assessment for human health, than statistical designs with unacceptably large sampling variability.

Judgmental samples can be incorporated into a statistical design if the samples designate the area of suspected contamination as an exposure area or stratum. The judgmental samples are then selected randomly or within a grid in the area of known contamination. Under the procedures described, the initial judgmental samples are not considered biased for the exposure area. Exhibit 38 summarizes some strengths and weaknesses of biased and unbiased sampling designs.

Resource constraints sometimes restrict the number of samples for the risk assessment and therefore potentially increase the variability associated with the results. When the number of samples that can be taken is restricted, judgmental sampling may identify the chemicals of potential concern, but cannot estimate the uncertainty of chemical quantities. The reasonable maximum exposure or upper confidence limit cannot be calculated from results of a judgmental design. Bias can be avoided with the procedures described in the previous paragraph.

EXHIBIT 36. COMPARISON OF SAMPLE PREPARATION OPTIONS

Fraction & Matrix	Preparation	Strengths	Weaknesses
Volatile Soil/Water	Head-space	Rapid, simple, potentially automated and minimal interferences if standards are prepared using sample media to minimize the effects of ionic strength variability between samples and standards.	Qualitative identification; comparison of concentration possible but quantitative standardization is difficult, especially true for complex matrix (e.g., particulates and clay in soil); no mechanism for concentration; application and sensitivity are very analyte-specific.
	Purge and Trap	Generally recommended for this analysis (comparabilities); can be automated; broadly applicable and allows concentration factor; good recoveries across analyte list.	Sacrifice of either highly volatile analytes or inadequate purge of low volatility analytes; dependent on purge and trap parameters.
		High precision and recoveries for waters.	Soils have variable response dependent on soil characteristics. Efficiency of soil purge is not monitored.
Extractable Organics in Water	Separatory Funnel	Relatively rapid processing and low set-up costs; relatively high PAH recovery.	Generally low recovery of target analytes; high potential for matrix problems; poor method precision.
	Continuous Extraction	Minimal matrix problems; generally higher analytical precision and high phenol recoveries; overall high extraction efficiency (accuracy).	Lower recovery of PAH and phthalates (especially higher molecular weight); time-consuming procedure and high initial set-up costs; more potential for contamination.
	Solid Phase Extraction	Very rapid, simple technique; samples can be extracted in the field for laboratory analysis; potentially low MDL in a clean matrix.	Procedure has limited available performance data. Presence of interference and matrix problems can affect extraction efficiency and data quality. Each batch of extraction medium must be tested for efficiency by recovery of standards, preferably in the same matrix. Breakthrough (loss) occurs at high sample concentrations.
Extractable Organics in Soil	Sonication	Rapid sample preparation; relatively low solvent requirement; good efficiency of analyte recovery/matrix exposure to solvent.	Labor intensive; constant attention to procedure; relatively high initial cost. Methylene chloride/acetone solvent mixture results in many condensation products and often in method blank contamination.
	Soxhlet Extraction	Relatively routine requirement for direct analytical support; relatively good exposure of sample to solvent if sample texture appropriate; relatively low initial cost.	Relatively high operating cost-replacement apparatus; solvent; for some matrices may not provide efficient sample/solvent contact (e.g., channeling, very slow sample output).
Inorganics	Acid Digestion	Dissolves particulates; provides results for total metals.	Some compounds are acid insoluble; digestion may promote interference effects.
	0.45 um Membrane Filtration	Isolates dissolved metals species.	Filtration problems in field; does not provide a total metals assay; is an extra step in sample collection.
	Direct Aspiration	No preparation required; provides results for dissolved metals.	Particulates affect sample introduction.

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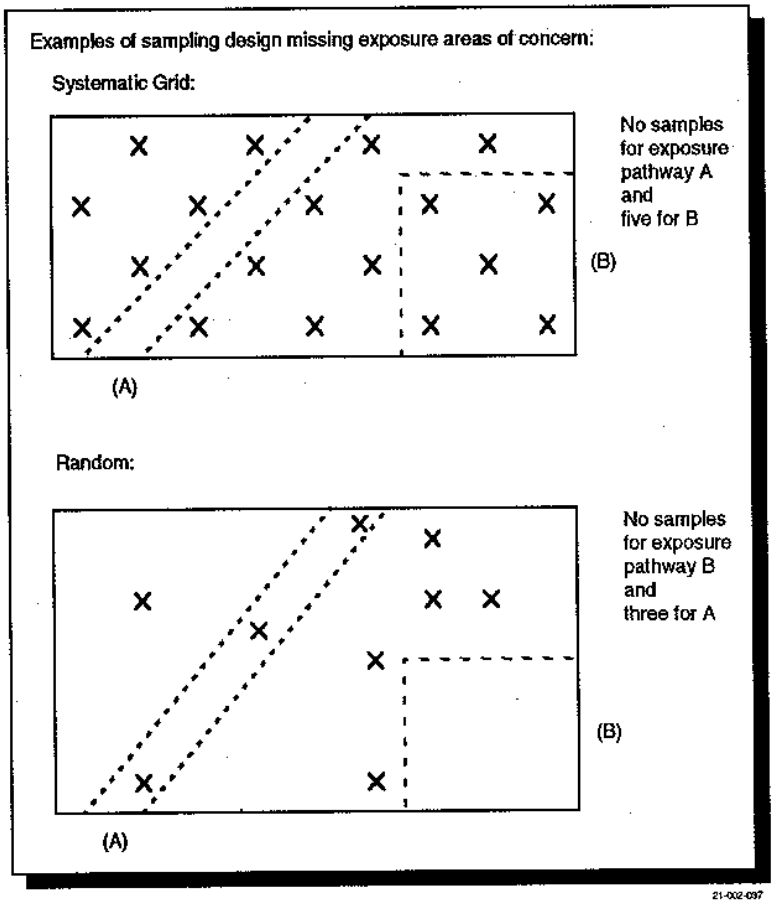
EXHIBIT 37. IDENTIFICATION OF EXPOSURE PATHWAYS PRIOR TO SAMPLING DESIGN IS CRITICAL TO RISK ASSESSMENT



3.2.9 Field Analyses Versus Fixed Laboratory Analyses

Field analyses are typically used to gather preliminary information to reduce errors associated with spatial heterogeneity, or to prepare preliminary maps to guide further sampling. Field analyses are often conducted during the RI to provide data to determine worker protection levels, the extent of contamination, well screen casing depths, and the presence of underground contamination, and to locate hot spots. For many sites, field analyses can often provide useful data for risk assessment. The analyses provide semi-quantitative results, often free of significant matrix interference, that can be used quantitatively if confirmed by a quantitative analysis from fixed laboratories.

Field instruments are usually divided into three classes: field portable instruments that can be carried by a single person, field transportable instruments that can be moved and used in the field or in a mobile laboratory, and mobile laboratory instruments that are installed in a trailer for transport to a site. Instrumentation used may be GC, X-ray fluorescence (XRF), or organic vapor analyzer (OVA). Examples and applications of these instruments might include on-site GC analysis of soil gas to indicate the presence of underground contamination, XRF for soil lead analyses, and the OVA to detect volatile organics, reported in benzene equivalents rather than in standard units of concentration.

Analytical methods that have traditionally been restricted to off-site laboratories can now be employed in the field. In addition, the quality of field instrumentation has improved steadily, allowing for better measurements at the site. Rugged versions of fixed laboratory instrumentation, such as XRF and GCs, can often be performed in trailers if adequate ventilation and power supplies are available. With field analyses, greater numbers of samples can be analyzed with immediate, or very short, holding times with no shipping and storage requirements. At least 10% of field analyses should be confirmed by fixed laboratory analyses to ensure comparability.

> ☛ *Field methods can produce legally defensible data if appropriate method QC is available and if documentation is adequate.*

EXHIBIT 38. STRENGTHS AND WEAKNESSES OF BIASED AND UNBIASED SAMPLING DESIGNS

Sampling Design	Strengths	Weaknesses
Biased (judgmental, purposive)	• Uses knowledge of location • Fewer resources • Timeliness • Focuses sampling effort	• Inability to calculate uncertainty • Inability to determine upper confidence limit • Decreases representativeness • Increases probability of false negatives
Unbiased (random, systematic grid, geostatistical)	• Ability to calculate uncertainty • Ability to determine upper confidence limit • Representativeness • Reduces probability of false negative	• Resource intensive • May require statistician • Timeliness • More samples required

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Significant QA oversight of field analyses is recommended to enable the data to be widely used. Field analysis performance data are often not available—in part because of the variety of equipment and operating environments, variety of sample matrices, and relative "newness" of certain technologies. Therefore, an in-field method validation program is recommended. Spikes and performance evaluation materials should be incorporated, if available in addition to other standard QC measures such as blanks, calibration standards, and duplicates.

The precision and accuracy of individual measurements may be lower in the field than at fixed laboratories, but the quicker turnaround and the possibility of analyzing a larger number of samples may compensate for this factor. A final consideration is the qualifications of operators in the field. The RPM, in consultation with chemists and quality assurance personnel, should set proficiency levels required for each instrument class and decide whether proposed instrument operators comply with these specifications.

Fixed laboratory analyses are particularly useful for conducting broad spectrum analyses for target compounds, to avoid the possibility of false negatives. They generally provide more information for a wider range of analytes than field analyses, and are generally more reliable than field screening or field analytical techniques.

> ☛ *To minimize the potential for false negatives, obtain data from a broad spectrum analysis from each medium and exposure pathway.*

Fixed laboratory analysis commonly uses mass spectrometry for organic analyses, which provides greatly enhanced abilities for compound identification. For inorganics, AA spectroscopy or ICP atomic emission spectroscopy should be used for reliable identification of target analytes. Once the broad spectrum analysis and contaminant identification has occurred, other methods may be employed that offer lower detection limits, better quantitate specific analytes of concern, and that may be less expensive.

> ☛ *The CLP or other fixed laboratory sources are most appropriate for broad spectrum analysis or for confirmatory analysis.*

Characteristics such as turnaround time, detection and identification ability of the instruments, precision and accuracy requirements of the measurements, and operator qualifications should be considered when selecting field or fixed laboratory instrumentation. Exhibit 39 compares the characteristics of field and fixed laboratory analyses. The risk assessor and RPM should consult the project chemist to consider the available options and make a choice of analysis based on method parameters, turnaround time, and cost, as well as other data requirements pertinent to risk assessment needs (e.g., legal defensibility). Exhibit 40 compares the strengths and weaknesses of field and fixed laboratory analyses.

3.2.10 Laboratory Performance Problems

The RPM should be aware of problems that occur during laboratory analyses, even though the resolution of such problems are usually handled by the project chemist. This section discusses common performance problems and explains how to differentiate laboratory performance problems from method performance problems.

> ☛ *Solicit the advice of the chemist to ensure proper laboratory selection and to minimize laboratory and/or methods performance problems that occur in sample analysis.*

EXHIBIT 39. CHARACTERISTICS OF FIELD AND FIXED LABORATORY ANALYSES

Characteristic	Field Analysis	Fixed Laboratory Analysis
Prevention of false negatives	Immediate analysis means volatiles not lost due to shipment and storage.	More extensive sample preparation available to increase recovery of analytes.
Prevention of false positives	No sample to sample contamination during shipment and storage.	Contamination by laboratory solvents minimized by storage away from analytical system.
Analytical Turnaround Time	Data available immediately or in up to 24 to 48 hours (additional time necessary for data review).	Data available in 7 to 35 days unless quick turnaround time requested (at increased cost).
Sample Preparation	Limited ability to prepare samples prior to analysis.	Samples can be extracted or digested, thereby increasing the range of analyses available.

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Laboratory performance problems may occur for routine or non-routine analytical services and can happen with the most technically experienced and responsive laboratories. Laboratory problems include instrument problems and down-time, personnel inexperience or insufficient training, and overload of samples. Issues that may appear to be laboratory problems, although they are actually planning problems, include inadequate access to standards, unclear requirements in the analytical specifications, difficulty in implementing non-routine methods, and some sample-related problems. Another problem for the RPM may be a lack of laboratories with appropriate experience or available capacity to meet analytical needs. These problems can usually be averted by "up-front" planning and by a detailed description of required analytical specifications.

- Instrument problems can be revealed with a unique identifier for each instrument in the laboratory that is reported with the analyses. Calibration and performance standards, such as calibration check standards, internal standards, or system monitoring compounds, should be specified in the analytical method to monitor performance of each instrument. In addition, the use of instrument blanks should be specified (to avoid the possibility of carry-over during the analysis).
- Some degradation in data quality may appear when new personnel are operating or when the sample load for a laboratory is high. The contributing personnel for each analysis should be identified clearly in laboratory records and reports, and qualifications of personnel required in contracts should be documented.
- Sample and method problems can often be distinguished from laboratory problems if they are not associated with a specific instrument or analyst. A review of method QC data should distinguish between laboratory and sample problems.

EXHIBIT 40. STRENGTHS AND WEAKNESSES OF FIELD AND FIXED LABORATORY ANALYSES

Analysis*	Strengths	Weaknesses
Field -Portable XRF (Metals)	Extremely high volume sampling and analysis; compatible with sophisticated sampling and data handling software. Detection limit may be above laboratory instrument values but applicable to specific site levels of interest.	Confirmation technique recommended. Comparability may require external standardization of calibration because quantitation is based on soil surface area versus a soil volume. Results often lower than from AA analyses.
Field GC	Rapid analysis supporting high volume sampling for variety of volatile and extractable organic target compounds (includes pesticides/PCBs). Minimization of sample handling variability and data quality indicators comparable to fixed laboratory methods.	Requires prior site knowledge to ensure applicability to specific conditions (e.g., soil-gas may not be appropriate for investigation in sandy area). Confidence in identification is matrix- and site-specific and highly variable depending on sample complexity. Confirmation technique recommended.
Mobile Laboratory XRF, AA (Metals)	Combines the high volume sample capacity of field analyses with the detection limits, data quality and confidence associated with laboratory analyses.	Requires significant resources, time, and personnel to transport, maintain and operate; generally most appropriate at high volume sites, especially remote.
Mobile Laboratory Luminescence	Rapid survey of analytes that routinely require sample preparation (e.g., PAHs and PCBs). Detection limits can be adjusted within limits to site-specific concentrations of concern.	Technique has had minimal use in EPA site investigation. Comparability may be an issue and require extensive confirmatory analyses.
Mobile Laboratory GC, GC-MS	Combines high volume capacity of field analyses with increased confidence in identification (GC-MS) or improved data quality (GC). GC methods may be identical to laboratory procedures but quality is intermediate due to site conditions (e.g., temperature, humidity and power requirements).	Same weaknesses as for mobile laboratory inorganics. An additional weakness is the increased training requirements and decreased availability of experienced GC-MS operators for totally independent system operation. Possibiity of site contamination and cross-contamination.
Fixed Laboratory XRF, AA, ICP (Metals - Available Routine Methods)	Highest comparability and representativeness. Data quality, including detection limits, generally predictable. Efficient match of analyses required to instrument (e.g., multiple analyses run simultaneously by ICP).	Slow delivery of data; increased documentation requirement due to the number of participants--relatively high sample cost.
Fixed Laboratory GC & GC-MS (Organics - Available Routine Methods)	Highest comparability and representativeness. Necessary confirmation of qualitative identification. Data quality and detection limits generally predictable. In depth analysis and sample archives for follow-up testing.	Same weaknesses as for fixed laboratory metals; analyte-specific performance.

* ICP = Inductively Coupled Plasma Spectroscopy. Graphite AA = Graphite Furnace (electrothermal) Atomic Absorption Spectroscopy. Flame AA = Flame Atomic Absorption Spectroscopy. ICP-MS = Inductively Coupled Plasma-Mass Spectroscopy. XRF = X-Ray Fluorescence. GC = Gas Chromatography. GC-MS = Gas Chromatography-Mass Spectrometry. AA = Atomic Absorption Spectroscopy.

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EXHIBIT 40. STRENGTHS AND WEAKNESSES OF FIELD AND FIXED LABORATORY ANALYSES (Cont'd)

Analysis*	Strengths	Weaknesses
ICP	Simple, automated, extremely rapid; can assay metals simultaneously; can detect ppb levels.	Subject to salt or iron interferences; lacks detection capability at low levels; not suitable for less than 20 ppb Arsenic, Lead, Selenium, Thallium, Cadmium, Antimony; requires background and interelement correction.
Graphite AA	Simple, automated; can assay most metals; can assay low level metals; can detect ppb levels.	Lower precision and accuracy result unless methods of standard additions used. Method is time-consuming; requires background correction; requires matrix modifiers; subject to spectral interferences. Graphite tube requires replacement frequently.
Flame AA	Simple, rapid, very suitable for high concentration sodium and potassium assays; commonly used and rugged.	Not as sensitive as graphite AA; salts can interfere; limited by lamp capabilities; detects ppm levels.
ICP-MS	Rapid; can detect low levels; accurate.	Method is subject to isobaric molecular and ion interferences. Nebulization, transport process, and memory physical interferences occur. Method is relatively new and is expensive. Specialized training is required.
ICP-Hydride	Rapid; can detect low levels of Antimony, Arsenic, Selenium; Hydride formation eliminates spectral interferences.	Dependent on analyte oxidation state; especially sensitive to copper interference. Method is relatively new. Specialized training is required.

* ICP = Inductively Coupled Plasma Spectroscopy. Graphite AA = Graphite Furnace (electrothermal) Atomic Absorption Spectroscopy. Flame AA = Flame Atomic Absorption Spectroscopy. ICP-MS = Inductively Coupled Plasma-Mass Spectroscopy. XRF = X-Ray Fluorescence. GC = Gas Chromatography. GC-MS = Gas Chromatography-Mass Spectrometry. AA = Atomic Absorption Spectroscopy.

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