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Technology Evaluation Workshop Report for Tank Waste Chemical Characterization

Prepared for the U.S. Department of Energy
Office of Environmental Restoration and
Waste Management

Westinghouse
Hanford Company Richland, Washington

Hanford Operations and Engineering Contractor for the
U.S. Department of Energy under Contract DE-AC06-87RL10930

Approved for Public Release

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WORKSHOP REPORT

Technology Evaluation Workshop
Tank Waste Chemical Characterization

A Tank Waste Chemical Characterization Technology Evaluation Workshop was held August 24-26, 1993. The workshop was intended to identify and evaluate technologies appropriate for the in situ and hot cell characterization of the chemical composition of Hanford waste tank materials. The participants were asked to identify technologies that show applicability to the needs and good prospects for deployment in the hot cell or tanks. They were also asked to identify the tasks required to pursue the development of specific technologies to deployment readiness. This report describes the findings of the workshop.

Three focus areas were identified for detailed discussion: (1) elemental analysis, (2) molecular analysis, and (3) gas analysis. The technologies were restricted to those which do not require sample preparation. Attachment 1 contains the final workshop agenda and a complete list of attendees. An information package (Attachment 2) was provided to all participants in advance to provide information about the Hanford tank environment, needs, current characterization practices, potential deployment approaches, and the evaluation procedure. The participants also received a summary of potential technologies (Attachment 3). The workshop opened with a plenary session, describing the background and issues in more detail. Copies of these presentations are contained in Attachments 4, 5 and 6. This session was followed by breakout sessions in each of the three focus areas. The workshop closed with a plenary session where each focus group presented its findings. This report summarizes the findings of each of the focus groups. The evaluation criteria and information about specific technologies are tabulated in the tables attached at the end of each section in the report. The detailed notes from each focus group are contained in Attachments 7, 8 and 9.

1.0 PROBLEM STATEMENT

The Hanford Site contains 177 underground storage tanks containing a total of 61 million gallons of radioactive chemical waste materials. The tank contents are not well characterized at present; more complete characterization is required both to maintain safe operations and to plan for retrieval and processing. Currently characterization occurs by removing full depth core samples and performing analysis in a hot cell or laboratory. Problems identified with the current approach include:

- The current methods are very labor intensive and time consuming.
- The current methods, due to the homogenization of larger samples before subsampling, do not identify problems like concentrations of critical materials in narrow horizontal layers.

- The current methods primarily provide results that indicate the quantities of elements rather than the molecular species present in the waste.

- The current methods require sample removal from the tank; they are not adaptable to in situ analysis.

Several programs have been initiated to develop and deploy methods that can be deployed in the hot cell for core sample scanning/screening or directly in the waste tank. The intention of this workshop was to assess the methods that have already been identified in terms of appropriateness for hot cell and tank applications and to identify new methods that may have been overlooked.

2.0 WORKSHOP INTRODUCTORY SESSION

Following introductions during the opening session, background information about Hanford, a statement of the problem and the workshop scope were presented. The technology evaluation process was summarized and key evaluation criteria provided. The relevant presentation materials are contained in Attachment 4.

Leela Sasaki of Westinghouse Hanford Company (WHC) presented information about the current Tank Waste Remediation System Characterization Program (Attachment 5). Her presentation included the overall objectives of the program and a more detailed description of the tanks and the waste material. The current sampling methods were described and a number of flow charts were presented detailing the analysis scheme currently pursued for tank core sample analysis. A number of potential areas for improvement in characterization were identified. These areas include the following:

- The ability to perform real time checks on the homogeneity of samples.

- The ability to perform in situ analysis of physical properties of the waste.

- The ability to perform scanning of core samples to support safety analysis.

- The ability to provide rapid turnaround in the performance of high priority safety screening analysis.

Dale Price (WHC) provided information on waste tank access and sampler/sensor deployment platforms. This presentation (Attachment 6) covered tank access restrictions and operating parameters, as well as describing the current push mode core sampling procedure, the rotary core drill (to become operational soon) and the planned cone penetrometer deployment system.

Steve Mech (WHC) described a maturity evaluation sequence, summarized on the status chart contained in Attachment 2. This presentation emphasized the need for validation and verification of equipment and methods before they

are deployed in a hot cell or tank environment. The presentation described a sequence of testing a technology using well defined surrogate materials designed to simulate the properties that the technology was measuring (e.g., specific chemical or physical characteristics) followed by validation testing with real waste samples. A detailed series of activities and tests leading to validation were defined. It was noted that while not all activities need to be performed in the correct order, all the tests are required before stating that a method is validated.

3.0 SMALL GROUP EVALUATION SESSIONS

Following the background presentations, the list of potential technologies for evaluation were reviewed and new technologies suggested. The group had been provided with summary information on a number of technologies believed to be appropriate for tank waste characterization (included in Attachment 3). Small groups were selected at this time to address each of the three focus areas.

The focus groups were instructed to review technologies and select appropriate ones for their focus area, and to identify additional technologies. For each technology, the group was to perform the following:

- Ensure that all members understand method
- Determine the state of art
- Identify the areas where group needs more information

The groups asked for and obtained more information on specific topics (e.g., lists of analytes currently being sought in headspace gases, tank farm layout diagrams, analytic lab flow sheets). In some cases, additional technical experts were called in for a short time to provide information on current status of specific technical developments.

Following the initial assessment of which technologies addressed the needs, the groups were asked to evaluate deployability of the technologies. The suggested questions included the following:

- Do field systems exist?
- What is the probe configuration - electrical, optical components?
- Can the sensor element be separated from the main system?
- What are size and power requirements?
- Are there special material requirements?

The groups were then to prioritize the technologies that appeared to meet needs and to have prospects for deployment in the hot cell or tank environment. For the top priority methods, the groups were asked to address the following issues:

- Evaluate the current state of art
- What additional development is required?
- Are special materials required?
- Where in the testing sequence is the method? (similar/simulant/real material and environment)
- Are specific decision point activities identified?

The groups were provided with the following requirements as criteria for accepting a technology for hot cell operations. Equivalent criteria apply for the tank, with some additional safety constraints in specific tank environments.

The system must:

1. Operate in a radiation environment.
2. Provide waste characterization information based on the requirements of the hot cell data users.
3. Have the ability to assess real samples.
4. Meet life cycle availability and reliability requirements.
5. Remain within calibration standards and be able to be routinely re-calibrated.
6. Provide for disposal of by-products.
7. Meet operator requirements for training (documentation, support information) and safety (safe operations), etc.
8. Use minimal sample preparation (i.e., sample removal from tank and possible subsampling but no digests, extraction etc.)
9. Provide a means to prevent sample cross contamination.
10. Provide a means to allow decontamination of any components which contact waste material.
11. Be able to work within the constraints of the hot cell (physical, final and operational interfaces).
12. Provide information regarding tank and hot cell deployment mechanism.

In addition, the groups were given this list of questions to guide them through the steps of the evaluation process:

- Does the technology meet a need?
- Can the technology be deployed?
- What development and testing activities remain to be done?
- What species can be identified?
- Is the method species specific or does it cover a broad range?
- Will a single instrument address a broad range or are several required (e.g., tuneable vs fixed)?
- What are sensitivity, accuracy, reliability levels?
- Does the method require constant attendance of skilled operators?
- Can it be used for monitoring?
- Does the system require constant "tweaking?"
- Does the method require sample preparation?
- Can a probe be separated from the main instrument?
- Can a probe be made small enough for deployment?
- Can a probe survive in a high radiation environment?
- Does the method require sample contact? If so, can the probe survive high pH?
- Can the probe be cleaned and/or decontaminated?
- What is an operational life expectancy of the system?
- Does the system have specific sensitive parts?
- Can it be designed so that sensitive parts may be changed out?
- Can a probe operate safely in the expected environment (e.g., no spark hazard inside tanks)

The responses to these questions are summarized in the tables at the end of each section. The groups were given one and a half days to perform the technology evaluations and then their results were presented to the large group. The presentations of each focus group are summarized below. Note that these presentations reflect the knowledge and expertise of the participants in the focus group. In some cases, information that would alter the results may

have been unavailable to the participants. These summaries provide the recommendation of technical experts, but do not reflect any official position of Hanford or the U.S. Department of Energy (DOE).

4.0 GAS ANALYSIS SUMMARY

The Gas Analysis Group included the following participants:

Steve Sharp	Pacific Northwest Laboratory
John Moore	Massachusetts Institute of Technology
Scott Werschke	MIDAC Corporation
Hiroshi Hoida	Los Alamos National Laboratory
Mahadeva Sinha	Jet Propulsion Laboratory
Ishwar Aggarwal (part time)	Naval Research Laboratory
Steve Mech (part time)	Westinghouse Hanford Company

The Gas Analysis Group worked on the assumption that the driving motivation for performing gas analysis was the desire to know what critical activities are going on within the tank. Gases released from the waste may be indicative of specific reactions in the waste. A continuous monitoring system is required to provide this information. Prior to the installation of a continuous monitoring system, full characterization of the head space gases for each tank is required in order to select the proper monitoring equipment.

It was also noted that the problem of worker safety monitoring is an issue. In this case, the concern is with gases escaping from the tank to the above tank work area. Area monitoring and point sensor monitoring approaches were considered (see below) for this application.

The group conceived a two phase approach, working on the assumption that all headspace monitoring equipment would be located inside the tank farm boundaries. Phase 1 involves full characterization of each tank with the intention of identifying all gases present in the headspace. A thorough characterization in Phase 1 is anticipated to take several months for each tank to ensure that occasional evolution of low levels of unusual gases are not overlooked. It is not clear that this lengthy a characterization period is warranted for all tanks. It may be that most tanks will be characterized in a shorter period with only exceptional tanks being examined for several months. The instrumentation to support Phase 1 (listed below) needs little development.

Phase 2 covers the continuous monitoring period where the sensor package selected for each tank is based on the detailed gas composition determined in the characterization phase. The gases of interest may vary among tanks, depending on the specific operational or safety issues being addressed. Although a number of continuous monitoring devices are currently available, a great deal of development will likely be necessary to meet the unique requirements for waste tank monitoring.

For characterization and monitoring, two measurement procedures were considered: (1) Provide in-tank sensors to obtain a quicker response time, or

(2) Draw a gas sample out of the tank through a heated line and then to the instruments. The latter approach is currently used, is easier, and is fairly well developed. The latter approach may be configured so that fewer electronic components come into contact with tank vapor, thereby reducing risks.

The point was emphasized that gas sampling with Summa canisters is not an optimal approach. Summa canisters can bias samples containing low ppm concentrations of analytes; polar molecules will stick to the canisters; the sampling method does not give real time results.

4.1 COMPLETE GAS CHARACTERIZATION TECHNOLOGIES

The group recommended a combination of methods for complete characterization. Their primary suggestions were Fourier Transform Infrared (FTIR) spectroscopy and use of a Gas Chromatograph-Mass Spectrometer (GC-MS) system. A fixed path FTIR will measure anything except homonuclear compounds and a GC-MS will measure almost anything. Used together, the two data sets will provide a higher confidence measurement. Both of these methods are currently in use in tank farm gas characterization applications, and are commercially available. However, these methods are not yet well integrated.

Two additional methods were also recommended for consideration. Laser Induced Breakdown Spectroscopy (LIBS) was suggested for the analysis of samples containing aerosols or airborne particulate matter. The method will require validation for this application. The use of a GC linked to an Ion Mobility Spectrometer (IMS) was also suggested. In this instance, both the IMS and the GC are well developed technologies, but work is needed in the area of coupling the two of them.

It was noted that all methods required a heated sample line for removal of gas samples from the tank without condensation or differential recovery. A sampling line may be designed for insertion in the tank at several vertical positions to obtain information about gas stratification.

4.2 CONTINUOUS MONITORING TECHNOLOGIES

The group anticipated that continuous monitoring methods would be equipped with probes which could operate for a six-month period before requiring probe replacement. During that time, periodic checks and recalibrations of the probe may be required. The continuous monitoring probes would be deployed only after complete characterization had determined what critical gases should be monitored and what types of interferences might occur. Sensors for continuous monitoring could be placed in the tanks, on top of risers, or at ventilation points.

Sensors were broken down into several classes:

A. Electrical Transducers - including electrodes, surface acoustic wave (SAW) sensors and piezoelectric crystals. The sensing elements in these systems could be biological or chemical based. Chemical systems are more

mature but have the potential for more interferences. Biological systems are highly selective but are less stable and generally more developmental.

B. Fiber Optically Linked Systems - these systems could also incorporate either chemical or biological sensors.

C. Optical Systems - for example, a diode laser tuned to a specific wave length for sensing changes in absorption which indicate the chemical composition.

D. Photoacoustic sensors

E. Fiber Optically Linked Fluorescence Sensors

The above sensors all require extensive testing for radiation survival and other environmental issues.

It was suggested that some tanks (for example those posing safety concerns) may warrant having a dedicated GC-MS system for continuous monitoring.

4.3 AREA MONITORING TECHNOLOGY

The technologies considered here basically perform fence line monitoring:

A. FTIR - which is commercially available in open path and fixed path systems.

B. Ultraviolet (UV) Systems - which are newer and less well developed than FTIR, although one commercial supplier exists.

C. LIDAR - which needs more development for systems employing lasers.

It was noted that FTIR and UV sensing provide complementary results and may work well in combination.

4.4 QUESTIONS

This section summarizes the questions, answers and discussion which followed the Gas Analysis Group presentation. Note that the answers represent the information available to the participants at the time of the meeting, and more complete information may be required to answer some of the questions.

Would FTIR in tank have problems with fog, humidity?

- Fog is not currently causing problems at 101SY for the FTIR operating on removed samples. Condensation would cause a problem. Is it acceptable to put instruments inside the tank farm perimeter?

- It is preferred not to, but it is done if necessary. In the tank farm instruments may become contaminated. Instrument access becomes

more difficult; worker training is required for all operators going into the tank farm area, and special protective clothing must be worn. Servicing the instruments becomes an issue.

Would you have a scaling problem with FTIR? Because of the large number of compounds considered, would some be out of the instrument dynamic range?

- In most cases there is sufficient activity to see low concentration compounds. Even with band overlap some signal can be extracted. Using GC-MS in combination with the FTIR would improve detection.

Would electrical transducers be considered an explosive environment problem?

- Yes, it would have to be considered in the design. Allowable current levels need to be determined. It may be more of an engineering problem.

What resolution is required for the FTIR?

- Low resolution provides better signal to noise ratio. Higher resolution resolves overlapping bands. In many bases, the lower resolution is sufficient because there are not a large number of compounds being examined.

Why are Summa canisters being used? Are they an EPA approved method?

- They are EPA approved - but nobody in the Gas Analysis Group approves of them. It seems unnecessarily complex to be taking samples with the Summa canisters and sending them offsite for analysis when you could take a sample from a heated line at the tank farm and get an immediate reading. Summa canisters have been bought and are being used for some applications.

Will we compare all future methods to the Summa canister results?

- The use of Summa canister samples must be addressed in terms of data quality if those samples are being considered the basis of all future measurements. We may need a better reference method.

Is an EPA driver involved in the use of Summa canisters?

- There are multiple drivers. We have needs for gas sampling information (e.g., to understand in-tank processes) which have no reference to any EPA driver. If the Summa canisters are an accepted procedure and if the results are adequate, then they have to be used (even if the results are incorrect at some precision level). However, if the results are not adequate, the procedure must change.

- The need for real time information and worker safety concerns are also drivers, where Summa canisters are insufficient.

Can transducers achieve low enough detection levels to provide safety monitoring?

- The resolution could be great enough to provide monitoring function - it depends on what is being measured and the concentration. Transducers need to be more developed to reach OSHA standards.

Can SAW technology withstand radiation environments?

- SAW technology substrates have been tested at the Naval Research Lab and there is a significant concern regarding failure before an exposure level of 1 MegaRad is achieved.

4.5 GAS ANALYSIS TECHNOLOGY EVALUATION

See Table 1 parts 1 and 2.

5.0 ELEMENTAL ANALYSIS GROUP

The Elemental Analysis group consisted of the following participants:

Clarence Homi	Westinghouse Hanford Company
Herb Sutter	SAIC
John Hartman	Pacific Northwest Laboratory
Monty Smith	Pacific Northwest Laboratory
David Cremers	Los Alamos National Laboratory
Martin Edelson	Ames Laboratory
David Dodd (part time)	Westinghouse Hanford Company

5.1 MOTIVATION

The Elemental Analysis Group identified the following motivation for screening:

1. Identify similar cores in order to reduce the overall analysis requirement.

2. Provide preliminary data to direct the subsequent analysis (e.g., identify strata of different compounds in a core sample).

3. Provide quick turnaround data for process development and execution.

4. Provide a broad range of data quickly in the hot cell and in situ.

Table 1. Gas Analysis Technology Evaluation--Part 1 (2 sheets).

Questions	Ion mobility spec. / GC (full characterization)	LIBS (full characterization)	GC/MS (full characterization)	FT-IR fixed path (full tank characterization)
Does the technology meet a need?	yes	yes	yes	yes (homonuclear gases not seen)
Can the technology be deployed?	yes	yes	yes	yes
What development or testing needs to be done?	very little	moderate development	very little	very little unless in-situ required
What species can be identified?	organics	elemental, aerosols	everything	everything except homonuclear, molecular gases
Is the method species specific or broad range?	med range	broad	broad range	broad range
Will a single instrument address a broad range or are several required?	single	single	single instrument	single
What are sensitivity, accuracy, reliability levels?	high on all	unsure	ppm ~5% good	ppb-ppm ~5% good
Does the method require the constant attendance of skilled operators?	yes	yes	yes	yes some attendance
Can it be used for monitoring?	yes	yes	yes	yes
Does the method require constant tweaking?	no	no, but it does to be deployed	no	no

Table 1. Gas Analysis Technology Evaluation--Part 1 (2 sheets).

Questions	Ion mobility spec. / GC (full characterization)	LIBS (full characterization)	GC/MS (full characterization)	FT-IR fixed path (full tank characterization)
Does the method require sample preparation?	no	no	no	no
Can a probe be separated from the main instrument?	no	yes	no	yes with development
Can a probe be made small enough for deployment?	yes	yes	no	yes with development
Can a probe survive in a high radiation environment?	no	yes	n/a	yes with development
What is an operational life expectancy of the system?	5 years	1 year	5 years	
Does the system have specific sensitive parts that cannot be changed?	no	no	no	yes, depends on material composition in windows
Can a probe operate safely in the expected environment?	yes	no?	n/a	yes

Table 1. Gas Analysis Technology Evaluation--Part 2 (2 sheets).

Questions	Optical probes	Electrical transducers (includes bio/chem based)	LIDAR (worker safety)	FT-IR open path UV open path worker safety
Does the technology meet a need?	yes	yes	yes	yes
Can the technology be deployed?	yes	yes	yes	yes
What development or testing needs to be done?	not much	reliability and reproducibility need to be developed	validation, longer lasting laser	validation and verification concerns
What species can be identified?	aromatic organics	customized, species specific	10μ, .2μ absorbing molecules including aromatics, organics NO NO_2, NO_3, etc.	everything but homonuclear
Is the method species specific or broad range?	specific	specific	moderately broad range	broad range
Will a single instrument address a broad range or are several required?	several	several fixed are required	single instrument, or a few to cover the whole range	single
What are sensitivity, accuracy, reliability levels?	high if characterized	to be studied	meets need	meets need (?)
Does the method require the constant attendance of skilled operators?	no	no	yes	moderate
Can it be used for monitoring?	yes	yes	yes	yes

Table 1. Gas Analysis Technology Evaluation--Part 2 (2 sheets).

Questions	Optical probes	Electrical transducers (includes bio/chem based)	LIDAR (worker safety)	FT-IR open path UV open path worker safety
Does the method requires constant tweaking?	no	no	no	no
Does the method require sample preparation?	no	no	no	no
Can a probe be separated from the main instrument?	yes	yes with signal conditioning for noise reduction	n/a	n/a
Can a probe be made small enough for deployment?	yes	yes	n/a	n/a
Can a probe survive in a high radiation environment?	P.A. and D.L. - N/A	depends on transducer	n/a	n/a
What is an operational life expectancy of the system?	6 months	6 months	3 months YAG laser longer CO_2 laser	5 years
Does the system have specific sensitive parts that cannot be changed?	no	no	no	no
Can a probe operate safely in the expected environment?	yes	probably	n/a	n/a

5.2 DRIVERS

The primary drivers were considered for obtaining elemental information:

1. Safety
2. Operations
3. Retrieval
4. Pretreatment
5. Low level waste processing (e.g., grout) and high level waste processing (e.g., glass)
6. Compliance and regulatory requirements

The process flow was identified as:

Issue	Identify the issue or question
↓	
Chemical signature	Obtain a chemical signature
↓	
Elemental signature	Obtain the relevant elemental signature
↓	
Data	Extract the critical information addressing the issue
↓	
Resolution	Obtain resolution of the issue or question using the information

5.3 TECHNOLOGIES CONSIDERED

The following set of technologies were discussed during the evaluation process:

1. Laser Induced Breakdown Spectroscopy (LIBS)
2. Laser Ablation/Inductively Coupled Plasma/Atomic Emission Spectroscopy (LA-ICP-AES)
3. Laser Ablation/Inductively Coupled Plasma/Mass Spectroscopy (LA-ICP-MS)
4. Laser Ablation/Laser Induced Fluorescence (LA-LIF)
5. Laser Excited Atomic Fluorescence Spectroscopy (LEAFS)
6. Laser Ablation/Atomic Absorption (LA-AA)
7. Laser Ablation/Mass Spectroscopy (LA-MS)
8. X-ray Fluorescence (XRF)

9. Gamma Spectroscopy

10. Fluorescence

11. Long Range Alpha Detection (LRAD)

12. Foil activation based alpha detection

13. Gamma mapping

14. High resolution mass spectroscopy

5.4 DRIVER-BASED ANALYSIS

1. Safety

For the safety driver, five issues are known to the group. For each of these issues, the relevant elemental keys were identified.

Issue	Elemental keys
Ferrocyanide family compounds	Ni, Fe, Cs, (Al?)
High heat tanks	Sr, Cs
Criticality concerns	Pu, Am, Eu, Np
Flammable gas	none (see Gas Analysis section)
Organic compounds	none (see Molecular Analysis)

To obtain information on this list of elements, the group recommended that a combination of LA-ICP-MS and LA-ICP-AES be used. The mass spectroscopy sensing method is appropriate for elements with high atomic mass number and the atomic emission spectroscopy sensing method appropriate for elements with low atomic mass number. The point was made that there may be an advantage to developing data analysis approaches that combine the data from the two instruments.

In both of the above instrument systems, the laser ablation serves as a sampling method, which ablates solid or sludge material into a form that can be mobilized. It was noted that while laser ablation is being pursued for the hot cell analysis, there are safety concerns that may prevent it from being used in tanks. An alternate sampling method should also be pursued for tank work.

2. Operations

To enhance operational tank characterization, the group perceived the need to reduce the number of cores requiring a complete laboratory analysis and the need to substantiate the historical data analysis. To achieve these goals, fingerprints of core materials must be obtained which show the signatures of all elemental constituents. The same recommendations for analytic technologies were made as in the case of the safety driver.

3. Retrieval

Areas where characterization data is required to support retrieval activities include determining the physical properties of materials, determining the extent of retrieval (i.e., how much material has been retrieved) and determining whether the retrieval process itself is causing a buildup of materials that could cause a dangerous situation. An example of the third case is a situation where water dissolution is being used for retrieval and water insoluble fissile materials are becoming more concentrated as other materials are removed. It is not currently known if this is a realistic scenario but it was suggested that real time sensing of Pu, Am, Eu and Np during the retrieval process could alleviate concerns. The same technologies proposed for safety concerns were suggested here. Elemental analysis was not required to address the other retrieval issues.

4. Pretreatment

The pretreatment issues which were known to the group fell into two categories. Molecular destruction processes, such as organic destruction or nitrate/nitrite destruction, are not readily addressed with elemental analysis. Separations processing will be addressed by elemental analysis. Separation of transuranic materials requires the sensing of Pu, Am and Np. Separation of other materials may include sensing of Cs. Once again, the LA-ICP-MS and LS-ICP-AES combination was suggested.

5. Low Level Waste and High Level Waste

If low level waste is to be processed into a grout or cement form, the sensing requirements include organics (not accessible by elemental analysis) and Cs, I and actinides (all elemental).

If the low level or high level waste is to be processed into glass, a large number of elemental constituents may affect the process. These include Si, B, Na, Al, Zr, Li, Fe+3/Fe+2, noble metals, and volatiles (tritium, Cs, Te, Ru). Again, the LA-ICP-MS and LA-ICP-AES combination was suggested.

6. Compliance/Regulatory

The group did not have enough information about compliance and regulatory related issues to make suggestions in this area.

5.5 RANKINGS

As indicated above, the combination of LA-IPC-MS and LA-ICP-AES was considered the top candidate for all the elemental analysis areas identified by the group. However, a number of the other technologies were considered worth pursuing further. The technologies were placed in three classes:

A. Broad Element Techniques

These methods can measure a broad range of elements and thus have the greatest flexibility. In addition to LA-ICP-MS or AES, this class included X-ray fluorescence, possibly also linked to laser ablation for sampling.

B. Specific Element Methods

This class includes methods which only identify one or a few elements. The only method recommended in this class was gamma mapping which may have application in a number of safety or retrieval scenarios.

C. Non-Specific Methods

This class includes methods which identify elements belonging to a small class but which do not distinguish among the elements in that class. Long range alpha detection was included in this class as a method worth pursuing.

5.6 KEY ISSUES

Because the highest ranked methods included the use of laser ablation as a sampling method, the group felt it was imperative that the acceptability of deploying ablation in the tanks be evaluated as soon as possible. It was generally believed that safety issues would preclude the laser ablation from being deployed in some of the tanks; it was not known whether safety concerns would indicate that the method never be deployed in any tank. The laser ablation linked technologies were considered appropriate for use in the hot cell.

The most highly recommended analytic techniques are not in situ methods, but are methods that may be taken to the field and require the introduction of microgram sized samples. The group recommended that alternative sampling methods be developed for the in tank analysis (regardless of the outcome of the safety concern for laser ablation). A list of suggested methods included:

- micro-dissolution
- fluid/slurry extraction
- fluidized bed
- mechanical grinding
- freeze/grind
- sonic drill
- micro-boring

Later discussion of the issue suggested that the use of carbon dioxide pellets to pulverize solid samples may also provide an in situ micro sampling approach.

5.7 GENERAL ISSUES

A number of general issues were identified that applied equally to all the technologies identified and evaluated. These issues will need to be addressed in any technology development program. Some of them have the potential to prevent the development of a valuable technology.

1. Representative Sampling - The tank material is very heterogeneous and most hot cell or in situ methods sample very small volumes. Designing a sampling scheme so that the operator knows what the results mean in relation to the total volume of interest needs attention.

2. Hot Cell Access For Demonstration/Validation - New technology must be validated with the real tank waste material before it can be transferred into operational mode. This validation process will almost certainly require hot cell access and may be a rather lengthy process. The hot cells are scheduled tightly, and it is not certain that technology development or validation activities will be given hot cell access when needed. This is an area where agreements need to be reached between technology development and operational organizations. It is possible that the current complement of hot cells will not support both the operational and the developmental work that the Department of Energy is planning.

3. Good Information On Needs - Needs statements are currently poorly defined or rapidly changing. Since this was the case, the group took the approach of placing highest value on technologies that would address a broad range of elements. In many cases, tightly defined needs would allow a better suggestion to be made to meet a specific need.

4. Funding Stability - Technology development programs are often multi-year activities and they proceed most effectively if there is some stability in the funding sources and the expectation for deliverables.

5. Simulant/Standard/Real Material Availability - Development and evaluation activities depend on the use of simulants and standard materials. In the final stages real materials are required (generally in the hot cell - see 2 above). Some centralized source of the relevant materials may be needed to ensure that all technology development activities have timely access to the materials.

6. Single Tool/Suite Of Tools (and Data Fusion) - Ideally a single method will provide all the information needed for analysis. More realistically, a suite of technologies providing complementary information will probably be deployed. To achieve the greatest benefit from the multiple data sets, a method of combining the data and providing simultaneous interpretation of the results may be required. This moves into the category of data fusion, an area requiring attention for this application.

5.8 QUESTIONS

Is laser ablation the only viable sampling method?

- No, but it is currently the best developed method. It could be non-viable in the tank environment. We need to compare such methods as microdissolution to laser ablation to see if the recovery is similar.

Some ablation experiments have shown differential ablation of certain materials. Will this present a problem?

- Work at Ames Lab on soil samples has suggested that there is not a qualitative difference in the sample at the point of ablation and at the end of the transport distance. Work is continuing to address this issue.

Laser ablation is being used to turn samples into particles - is there variation in transport of differently sized particles?

- We are just starting to examine the relationship between particle size and transport. Particle size is dependent on the laser pulse parameters, also it may be possible to select settings to get a particle size that is transported well. There may also be differences depending on whether the material to be ablated is dry or wet.

Why was Prompt Gamma Neutron Activation Analysis not examined as a possible method?

- It was discussed briefly but no one at the workshop had enough expertise in the area to examine the method in detail. There were concerns that the high gamma background in both the tank and the hot cell would swamp any signal from the activation. There are probably some elements in the tank waste that could be quantified by this method; however, the levels of Al and Na in tank waste are high enough that it may be difficult to observe any signal from less prevalent elements. It is probably a method worth developing further to be able to assess its applicability.

5.9 ELEMENTAL ANALYSIS TECHNOLOGY EVALUATION

See Table 2 parts 1 and 2.

Table 2. Elemental Analysis Technology Evaluation--Part 1 (2 sheets).

	LIBS	LA/ICP/MS	LA/ICP/AES	LEAFS LA/LIF
Elements Measured	all	He F not detected	He not detected	single/several elements at a time, tunable
Sensitivity	Good for actinides Excellent for others	excellent for all except He, F	Excellent for all except He	Excellent where demonstrated
Dynamic Range		10^9	10^6	at least 10^4
Interferences	exist but can be compensated for use alternate lines	Molecular ion isobaric doubly ionized species	spectral interferences	very few
Sample Types	Liquid, wet solid, dry solid	liquid, wet solid, dry solid	liquid, wet solid, dry solid	liquid, wet solid, dry solid
Sample Size	.1mm diameter .1mm depth	.1mm diameter .1mm depth	.1mm diameter .1mm depth	.1mm diameter .1mm depth
Calibration	+,- 10% replicate samples match matrix	+,- 5% • sum of all detected ion masses •replicate samples, •match matrix	+,- 5% •replicate samples •match matrix	•replicate samples •match matrix
Test Conditions		•air beam path •multiple wavelengths •standoff - 2 in, •sample transport of up to 100 ft	•FO / air path •multiple wavelengths •standoff - 2 in, •transport up to 100ft	same as others 250-600nm
Deployment Options	Base equipment external, fiber optic link to waste	•Laser source cold •Fiber optic beam •Final optics sample collection in hot cell •ICP/MS in glove box	•ICP source hot, •monochrometer and detector cold	•base equipment external •fiber optic to sample, LA sampling
Maturity	field ready	lab experience no field system	lab experience fernald field test	research lab not mature

Table 2. Elemental Analysis Technology Evaluation--Part 1 (2 sheets).

	LIBS	LA/ICP/MS	LA/ICP/AES	LEAFS LA/LIF
Key Questions	•Calibration •matrix effects •throughput Rate •Fiberoptic Survival •TRUs •surface vs volume •tank safety •deployment time	•calibration •matrix effects •through put rate •F.O. survival •surface vs volume •tank safety •deployment time •plume transport •instrument •contamination	same as ICP/MS	•matrix effects •calibration •are single isotopic element measurements needed?

Table 2. Elemental Analysis Technology Evaluation--Part 2.

	X-Ray fluorescence	Gamma spectroscopy	High resolution mass spectroscopy with LA/ICP
Elements Measured	High Z number elements, Al and above	Cs Eu As Co Pu, only radioisotopes	all except He, F
Sensitivity	good for high z bad for low z	geometry and isotope specific	better than standard LA/ICP/MS
Dynamic Range			10^9
Interferences	Particle size effects	spectral interferences	reduced from LA/ICP/MS
Sample Types	all	all	all
Sample Size	diameter mm to inches depth microns to mm	Volumetric cone 2 inch diameter 3-4 inch depth	depends on sampling method eg LA
Calibration			same as LA/ICP/MS
Test Conditions		hot cell scanner liquid observation wells	not tested
Deployment Options	Probably not in tank Ablation plume, filter sample or scanning system	hot cell, liquid observation well cone penetrometer	same as LA/ICP/MS
Maturity	very mature fieldable instrument	very mature, hot cell, field systems at Hanford	Lab instrument
Key Questions	•calibration •matrix effects •low z sensitivity •surface vs volume •through put rate •deployment time •tank safety	•sizing for penetrometer •how valuable is this? •scan rate •matrix effects	•is there a need? •LA/ICP/MS questions apply

6.0 MOLECULAR ANALYSIS GROUP

The Molecular Analysis group consisted of the following participants:

Ishwar Aggarwal	Naval Research Laboratory
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Fred Milanovich	Lawrence Livermore National Laboratory
Roger Greenwell	Science Analysis Associates
David Veltkamp	Center for Process Analytic Chem, UW
Curtis Nakaishi	Morgantown Energy Technology Center
Tom Vickers	Florida State University
Steve Colson	Pacific Northwest Laboratory
David Dodd (part time)	Westinghouse Hanford Company
P. K. Melethil (part time)	Pacific Northwest Laboratory
Mahadeva Sinha (part time)	Jet Propulsion Laboratory
Bernadette Johnson (part time)	MIT Lincoln Laboratory

6.1 MOTIVATION AND DRIVERS

The Molecular Analysis Group felt that the goal of hot cell screening tools and in situ analysis tools was to provide advisory information. Since very small sample sizes were involved it would be difficult to consider these methods as providing broad characterization of all the tank contents. It was felt that characterization issues related to compliance should not currently be addressed with these types of screening technologies.

The primary deployment platform addressed by the group was the cone penetrometer. The primary driver considered by the Molecular Analysis Group was the safety issue. As a guide to the types of analysis currently performed, the group used the flowsheets provided in Leela Sasaki's presentation (Attachment 3). The safety issues addressed included those suggested to the Tank Waste Remediation System by Dr. Harry Babad and provided to the group in the preliminary information package. It is worth noting that those issues were stated in such a way that they could be addressed using the standard operating procedures of sample removal and laboratory analysis. It is possible that slightly different in situ approaches could provide information to address the same issues. Those issues included:

1. Water Content - Moisture of the waste itself needs to be greater than approximately 20% to ensure safety even in the presence of certain unstable compounds. In the region near 20% the accuracy needs to be measurable to approximately 1%. It was noted that all the current sampling techniques have the potential to change the moisture content of the sample; thus moisture measurement is best done in situ.

2. Total Organic Carbon Content - This becomes a concern when it is greater than 3% when measured on a dry weight basis. The group felt that it would actually be better to know what all the organic compounds are but that measurement is considered too difficult. Because of the potential loss of volatiles during a sample removal process, in situ analysis was considered preferable.

3. pH or Hydroxide Concentration - In order to minimize corrosion and protect the tank itself, the pH of the waste needs to be maintained at 9.5 or greater and the OH concentration needs to be greater than 0.001 N. This is also required to prevent toxic gas formation.

4. Energetics - Exothermic energy is currently measured in the laboratory by a differential scanning calorimeter. Fissile material content is of particular interest. This did not appear to be an issue that was directly amenable to solution by measurement of molecular species.

5. Cyanide Species - Currently total cyanide measurement is the approach being considered for laboratory analysis. In fact, the concentration of specific species, particularly the ferro/ferri-cyanide family, is of greater interest. In this case, the hot cell and in situ molecular speciation tools may offer a capability not available through standard lab methods.

6. Ammonia or Ammonium Ion Concentration - Concentrations greater than 0.1 M or greater than 25 ppm in the vapor cause a concern.

6.2 TECHNOLOGIES CONSIDERED

The group examined five technologies which they believed were sufficiently mature to have some near term application, and thus merited near term discussion. The technologies, which will be discussed in detail below, are:

1. Raman spectroscopy

2. Laser Ablation - Mass Spectroscopy (LA-MS)

3. Fourier Transform Infrared spectroscopy (FTIR)

4. Near Infrared (NIR) reflectance spectroscopy

5. Fiber optic sensors

The group also identified four technologies which are more developmental for this application but which may merit further attention. These methods are described briefly here but were not given any detailed evaluation. These four methods are:

1. Total Fluorescence Measurement - The concept proposed was the use of total fluorescence to provide real time in situ screening. An excitation source would be provided while inserting a penetrometer or other deployment device and total fluorescence sensed. In locations where significant fluorescence response occurred other devices could then be deployed for more sensitive measurements. The reasoning behind this approach was that although not all materials fluoresce, some materials of particular interest (e.g., organic nitrates) do. The total fluorescence screening would focus attention on areas of potential interest. A similar approach is being used for the detection of hydrocarbons in soils.

2. Raman Imaging - This approach is proposed for use in the hot cell to allow the rapid collection of Raman data from an entire core sample. A potential advantage to imaging rather than point sampling is that the simultaneous collection of data from many points allows the operator to note any significant differences in spectra across a spatial region. Questions arose about how much of the equipment could be placed outside the hot cell while performing Raman imaging. It remains to be seen whether this approach is feasible in a hot cell environment.

3. Micro Dissolution - This has been suggested separately as an alternative to the use of laser ablation for obtaining small samples. Micro sampling may be an alternative to taking complete core samples in some cases and may reduce the amount of waste generated. One approach is to use microliter quantities of hydrofluoric acid to dissolve solid materials. The question arises as to whether micro dissolution will be allowable for safety reasons.

4. Nuclear Magnetic Resonance (NMR) - NMR has been suggested on several occasions because of its capability to detect water. (It has the capacity to distinguish water from hydrogen ions in general as opposed to many other water measurement methods and can also distinguish bound from unbound water.) NMR can also be used to quantify many other materials. The current limitations to NMR stem from its size. Although a unit could be made small enough to insert into a tank, it is unlikely that a unit could be deployed with a cone penetrometer.

6.3 RAMAN SPECTROSCOPY

Of the technologies prioritized for near term pursuit, Raman spectroscopy was considered to have perhaps the greatest chance of successful application. It was noted that the group included a number of members with significant experience in the area of Raman spectroscopy and that this experience may have introduced some bias in the assessment.

Raman spectroscopy is a method which identifies a broad range of materials and has sensitivity to most of the macro-constituents of the tanks. In general, sensitivities are only around the 0.1% level. This may mean that there is a gap between the true capabilities of the technology and the desired level of sensitivity for safety applications. The possibility exists that fluorescence of background materials in the tank will interfere with Raman signals, although in general the fluorescence is much broader band than the Raman signals.

Two major issues were identified to be addressed as part of an ongoing program to develop, test and implement Raman spectroscopy. First, a coordinated, consolidated program is needed to develop a probe for hot cell and in situ use. Second, a thorough test program needs to be developed to ensure the environmental survival of all probe components that will be placed in a radiation environment. This includes not just fiber optics (the current focus of radiation tests), but also optical elements, coatings, epoxies and other materials. An effort is being made to coordinate the several sites that are working on Raman development and testing, but the probe development and testing program still contains gaps.

Future work to expand the capabilities of Raman spectroscopy may include the use of resonance Raman with a tunable laser source. This technology has the potential to provide greater sensitivity for selected compounds.

6.4 LASER ABLATION - MASS SPECTROSCOPY

Although in the past the primary focus of laser ablation linked with mass spectroscopy has been on elemental analysis, work is being directed at molecular speciation as well. The primary problem to be addressed is how to maintain the molecular nature of materials during ablation. The group speculated that one could conceivably get total cyanide species if cyanide could be maintained. However, it was pointed out that cyanide forms vary readily when nitrogen and carbon are present, so that this measurement may be erroneous.

6.5 NEAR INFRARED REFLECTANCE SPECTROSCOPY

Near infrared (IR) reflectance was considered to address two safety issues, the moisture concentration and the pH. The technology is viable for these two applications, and problems lie mainly in designing a system that can be deployed in a tank. Both moisture level and pH can be obtained using fiber optic linked systems that employ silica fibers (which are low loss and somewhat robust in radiation environments). There was a suggestion that fluoride fibers could be examined as well, although it is not clear that this is necessary.

6.6 FIBER OPTIC CHEMICAL SENSORS

Fiber optic chemical sensors are receiving a great deal of research attention, although few are currently being deployed. The first and simplest of these is the pH sensor. Since this sensor is fairly well established, it might be a reasonable one to deploy in the tank to determine how well the method works in a real environment. Questions were raised about the environmental sensitivity of the pH sensitive fluorescent dyes currently used in pH sensors. It was pointed out that the sensors used for medical applications are routinely sterilized with MRad radiation doses so survivability in a radiation environment seems promising.

The limitations of fiber optic sensors include the fact that most need direct contact with the analyte of interest, many are semi-specific, and the optical transducer design issue is complex. If sensors are needed for a specific analyte, it may be possible to design them. However, because of the specificity, when the target requirement changes all the previous work is lost. There was some speculation about the feasibility of making imaging bundles of chemical sensing fibers, with various different specificities associated with the various fibers.

6.7 FOURIER TRANSFORM INFRARED SPECTROSCOPY

This technology will focus primarily on the hot cell application due to problems with deployment in the tank. FTIR is one of the fastest growing areas of analysis and processing, with industrial applications driving technology development. One of the problems with this technology is that it employs the mid-infrared region where few tank materials show many features. It has many applications for detection of organic compounds.

There was some discussion of the possibility of developing optical fiber linked FTIR for use in the tank as well as in the hot cell. Although fiber development is showing improved transmission performance for fluoride fibers (up to 4 microns) and chalcogenide glass (up to 12 microns), the necessary transmission in the longer wavelength has not yet been achieved. The development of new fibers for process applications will bring down fiber prices but the market will never be as large as for silica fibers. Thus fiber optic linked FTIR is still an uncertain concept.

6.8 NEEDS

The molecular Analysis Group identified a number of needs for further concentration and development.

1. Raman Probe Design - A probe design for Raman analysis is required, defining the penetration scheme into the waste material. The probe needs to be thoroughly characterized. The mechanical integrity of the probe is a consideration when it is anticipated that the probe will be deployed with a cone penetrometer. For example, temperature may increase rapidly with rapid pushing.

2. Low Loss Infrared Fibers - If further developments with any infrared region except the near IR (less than 2 microns) is to be pursued, low loss IR fibers are required.

3. Data Analysis and Management - Data analysis and management is qualitatively different when dealing with real time data than when dealing with the results of laboratory analysis. To take best advantage of in situ probes, real time analysis should alert the operator to places where additional data or samples need to be taken. This is an area that could support a major development effort.

4. Probe Miniaturization - With a narrow bore cone penetrometer as a deployment platform, the issue of probe miniaturization needs to be addressed. A number of potentially useful characterization probes are available for use with larger penetrometers; it is not clear which of these can be miniaturized.

5. Umbilical Cord Threading - Penetrometer deployment of fiber optic or electrically linked sensors will require some sort of threading of the umbilical cable through the penetrometer segments. Large optical fibers are quite fragile and do not tolerate tight bends. Special cable design and handling will be required. Alternatives to umbilical cables, such as battery operated probes and in-tank lasers might be considered.

6.9 QUESTIONS AND COMMENTS

It was noted that not only the probes and optical fibers needed to be rugged, but also such instruments as van-mounted spectrometers.

Will contact probes be subject to probe fouling or carry-over of residue from one sample to the next?

- This is a potential problem. Potential approaches include placing transparent sleeving on a core sample to avoid direct contact or placing covers on probes. These are hot cell approaches; the problem is more complex in the tank.

Will sample analysis be affected by surface smearing of core material during sampling or extrusion?

- Probably. In the hot cell, it may be necessary to insert probes into the core to avoid the surface, or cut the core sample to create a clean surface for imaging. It may be possible to test how much smearing occurs using a simulant being extruded with a fluorescing dye on the surface.

6.10 MOLECULAR ANALYSIS TECHNOLOGY

See Table 3 parts 1 and 2.

6.11 NUMERIC EVALUATION OF MOLECULAR ANALYSIS TECHNOLOGY

See Table 4.

Table 3. Molecular Analysis Technology--Part 1 (2 sheets).

Questions	Laser Ablation	Raman Spectroscopy
Does the technology meet a need?	yes	yes
Can the technology be deployed?	development and testing needed	no problems foreseen, more development needed
What development / testing needs to be done?	testing needs to address spark safety hazard	more real samples, in hot cell, development for deployment in tank, least squares algorithm in Fourier domain backgrounds
What species can be identified?	phosphate, carbonate, sulfate, has problems with nitrate / nitrite ratio	FeCN to 1000ppm, moisture, organic carbons, ammonium at 0.1 M
Is the method species specific or broad range?	fairly specific for those species listed above	works for species listed above
Will a single instrument address a broad range or are several required?	single instrument can be tuned to read for different spectra	single instrument covers a broad range, need different lasers or tunable lasers
What are sensitivity, accuracy, reliability levels?	dependent on matrix effects, detection limits all TBD, reaching ionic state w/o changing chemical species is another issue	ideally tested around +-1-.1%, in reality though around +-5% in complex samples
Does the method require the constant attendance of skilled operators?	In the short term yes, but in the long term others could be trained	no
Can it be used for monitoring?	too complex as a monitoring tool	yes could be used for monitoring
Does the method require constant tweaking?	not stand alone, same attention required as with other systems	no
Does the method require sample preparation?	no sample preparation	no
Can a probe be separated from the main instrument?	yes, with fiber optics	probe can be done remotely

Table 3. Molecular Analysis Technology--Part 1 (2 sheets).

Questions	Laser Ablation	Raman Spectroscopy
Can a probe be made small enough for deployment?	yes in a cone penetrometer	yes, with a cone penetrometer
Can a probe survive in a high radiation environment?	no foreseen problems	need testing in hot cell to see if probe will survive high radiation
What is an operational life expectancy of the system?	many months	many months
Does the system have specific sensitive parts that cannot be changed?	no - possible to change the capillaries 1/4 inch tubes	no, the design can be simplified and changed if needed
Can a probe operate safely in the expected environment?	no, there is a potential spark hazard problem that may limit this technology to the hot cell only	yes, none of the proposed probes present a safety hazard, and the safety problems associated with the cable configuration can be minimized in design

Table 3. Molecular Analysis Technology Evaluation--Part 2 (3 sheets).

Questions	Fourier transform infra-red spectroscopy	Near IR reflectance	Fiber optic chemical sensors
Does the technology meet a need?	yes	yes	yes possibly
Can the technology be deployed?	mostly / only in hot cell		yes
What development / testing needs to be done?	species ATR vs diffuse reflectance, need to evaluate which makes more sense		range needs to be extended for pH, fibers must also be tested in radiation environment
What species can be identified?	moisture, organics, cyanide, ammonia, carbonate and phosphate, also works for inorganics, but sensitivity questionable	pH, moisture the best possibly also for organics and maybe inorganics	pH, ammonia demonstrated directly, but liquid reagent must be deployed
Is the method species specific or broad range?	addresses those listed above	addresses above analytes	species specific
Will a single instrument address a broad range or are several required?		single instrument either tunable or fixed with filters or scanning	single instrument
What are sensitivity, accuracy, reliability levels?	unsure, more testing needs to be done, and additional uncertainty surrounding applicability due to lack of testing	water in surrogates to less than 0.5%, Ph better in caustic brines than in caustic normals	needs to be more heavily researched, sensitivity excellent if can work in pH range, but reliability a big question in environment

Table 3. Molecular Analysis Technology Evaluation--Part 2 (3 sheets).

Questions	Fourier transform infra-red spectroscopy	Near IR reflectance	Fiber optic chemical sensors
Does the method require the constant attendance of skilled operators?	unknown	no	no
Can it be used for monitoring?	yes could be used for monitoring with proper data treatment	most suited of all for pH monitoring	no
Does the method require constant tweaking?	unknown, seems no more than any other method, maybe some with sample alignment	no	no
Does the method require sample preparation?	no	no	no except in the case of deployed reagents or microdissolution
Can a probe be separated from the main instrument?	yes, some all ready used in process industry, however probe contact with sample may be required	yes	yes
Can a probe be made small enough for deployment?	probes significantly bigger than those for raman or laser ablation,	yes it can be made very small	yes
Can a probe survive in a high radiation environment?	fiber development in terms of radiation hardening needs to be improved	yes probably qualification of testing	fiber technology membrane and reagent will need to be radiation hardened
What is an operational life expectancy of the system?	unsure because of the number of components to consider: crystals, fibers, sample matrix etc.	many months, limited by lifetime of fibers	as long as reagent and membrane

Table 3. Molecular Analysis Technology Evaluation--Part 2 (3 sheets).

Questions	Fourier transform infra-red spectroscopy	Near IR reflectance	Fiber optic chemical sensors
Does the system have specific sensitive parts that cannot be changed?	no - can change crystal if necessary, but unsure of sensitivity of contact	simple design, parts can be changed out	no, parts can be easily disposed of
Can a probe operate safely in the expected environment?	yes will operate safely in a hot cell	inherently safe	inherently safe

Table 4. Numeric Evaluation of Molecular Analysis Technology.

	Laser ablation as a sampling method	FTIR / absorbance	Near IR reflectance	FOCS	Micro separation / dissolution	Raman spectroscopy
In-Situ Deployable	6	2	8	9	5	9
Non Destructive	3	10	10	9	5	10
Non Contact	8	10	10	0	0	10
Real Time	7	8	8	9	3	8
Remote Operations - 100, 300, 900 ft	10	3	10	10	8	10
No Sampling or out of tank preparation	10	10	10	10	5	10
Portable	5	7	9	9	7	8
Deployable	8	9	9	9	3	9
Qualitative - can speciate	8	5	5	2	5	8
Quantitative	3	5	6	8	7	7
Environmental Survivability (chemical, etc.)	8	6	8	2	8	8
Survives radiation	8	7	7	5	8	7
Size	2	6	9	7	6	6
Operator Skill	2	7	9	8	5	4
Inherently Safe	1	9	10	8	1	8
Cost	3	8	9	7	7	5

7.0 EVALUATION OF WORKSHOP AND METHODOLOGY

The final activity for all the workshop participants was to provide suggestions on ways to improve the evaluation methodology and workshop format so that the approach could better be applied to future problems.

The most driving need for a successful evaluation session is the requirement for clearly defined needs. Although this workshop was able to provide participants with information about current analysis procedures and high priority safety issues, a complete description of the needs and data quality objectives was not available. Part of the reason for this is that needs are changing and new needs being identified. It is not clear how well the needs and requirements can be defined in this problem domain.

It was noted that some technologies were more thoroughly discussed than others because of the distribution of domain experts. A few technologies were noted as potentially applicable but were not discussed in detail because of lack of technical knowledge. Since providing technical expertise in every technology increases the number of participants, it may be necessary to limit scope of such a workshop to ensure that the size does not grow out of control.

The suggestion was made that more site personnel be present to provide information on methods in current use, particularly in cases where a method being evaluated has already seen some field testing and deployment. In these cases it would not be necessary to have the site person present for the entire workshop rather a time period could be allotted to discussion of the specific technology.

There appeared to be general agreement among participants that there was no single magic technology that would address all problems. The pursuit of a number of development activities simultaneously is warranted. There was also general agreement that the operating environment is the driving and limiting factor for all the technologies considered.

Regarding the value of the workshop itself, the issue was raised as to whether the data produced could be updated at a later date. Past workshops have generated lists of technologies and priorities that essentially represent a snapshot in time. Later review of these lists without complete information about the evaluation criteria (or by persons with different expertise) may change the lists considerably. There is no way to address the issue that the results of this workshop represent the informed opinions of a finite group of participants. However, this report contains as much information as possible about the evaluation process and criteria (including the tables in Attachment 5). This should allow the questions to be revisited in the future with an understanding of how conclusions were reached and how changing priorities will affect those conclusions.

TECHNOLOGY EVALUATION WORKSHOP
TANK WASTE CHEMICAL CHARACTERIZATION

DATE: Tuesday August 24 - Thursday August 26

PLACE: Cavanaugh's
1101 N. Columbia Center Boulevard
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SCOPE: The workshop is intended to identify and evaluate technologies appropriate for the in situ and hot cell characterization of the chemical composition of Hanford waste tank materials. The participants will identify technologies that show applicability to the needs and good prospects for deployment, and will identify the tasks required to pursue the development of specific technologies. The technologies will be restricted to those which do not require sample preparation.

TECHNOLOGY EVALUATION WORKSHOP
TANK WASTE CHEMICAL CHARACTERIZATION

Final Agenda

Tuesday August 24

8:00	Introductions and Welcome	Susan Eberlein
8:20	Problem statement Scope of evaluation Workshop expectations Technology assessment process	Susan Eberlein
9:00	Current characterization process Characterization priorities Expected areas for improvement	Leela Sasaki
9:30	Constraints on tank entry Cone penetrometer deployment system	Dale Price
10:00	break	
10:20	Hot cell deployment system Requirements for field operation Light Duty Utility Arm	Susan Eberlein
11:00	Maturity evaluation Testing sequence Validation and Verification	Steve Mech
11:30	Potential technologies Selection of breakout groups Planning for afternoon session	Susan Eberlein
12:00	lunch	
1:00	Small group session Review technologies and select appropriate ones Identify additional technologies For each technology: · ensure all members understand method · determine state of art · identify areas where group needs more information Initiate process of matching technologies to needs	
5:00	end day 1	

Final Agenda

Wednesday August 25

8:00 Continue small group session
For each technology meeting needs, evaluate deployability
- do field systems exist?
- probe configuration - electrical, optical components
- possibility of separating sensor element from main system
- size, power requirements
- special material requirements

10:00 break

10:15 Prioritize technologies by need and deployability

10:45 For top priority methods:
- evaluate current state of art
- what additional development is required
- are special materials required
- where in the testing sequence is the method (similar/simulant/real material and environment)
- are specific decision point activities identified

12:00 Lunch

1:15 Continue evaluation and determination of needed development activities
Prepare summary presentation on top priority technology
Make note of reasons for rejecting specific methods as not worth further development

5:00 Finish

Thursday August 26

8:00 Large group convenes, small groups present results

8:15 Group 1

8:45 Group 2

9:15 Group 3

9:45 break

10:10 Discuss results of group findings

11:00 Discuss evaluation process

11:30 Finish

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TECHNOLOGY EVALUATION WORKSHOP
TANK WASTE CHEMICAL CHARACTERIZATION

Background

The Hanford site includes 177 underground waste storage tanks, each one containing anywhere from 50,000 up to one million gallons (200,000 to 4 million liters) of mixed chemical radioactive wastes. Most of the tanks are on the order of 75 feet (24 meters) in diameter and 37 to 51 feet (11 to 15 meters) high, buried under at least 6 feet (2 meters) of soil, with limited access through a small number of ports or "risers," many only 4 to 12 inches (10 to 30 cm) in diameter.

The primary constituents of the tank waste are sodium nitrate and sodium nitrite. These components result from the sodium hydroxide neutralization of nitric acid used for waste processing. Other components include sulfates, phosphates, and carbonates with a variety of cations. A limited number of organic compounds, mostly chelating agents, are present. One of the materials of concern is ferrocyanide (with ferricyanide and related breakdown products). This material poses a potential safety concern.

The pH of the tank waste is generally 12 or higher; this poses a constraint on the types of sensor materials that can be placed in the waste. For example, aluminum probes will degrade in the caustic material. The radiation level above the waste is expected to be 500-1000 R/hour. The primary radiation sources are strontium and cesium.

Current Approach to Waste Characterization

The current approach to the analysis of waste tank material is to remove a full depth core from the tank and transfer the core to the hot cell for standard laboratory analysis. Although each 19-inch long segment of the core sample may show significant internal heterogeneity, small scale subsampling to determine the level of heterogeneity is generally not possible. The usual practice is to homogenize core segments with a length of 4 inches or more into samples for analysis. These samples are then subsampled, digested, diluted, etc., in order to perform the necessary analytic procedures. The suite of laboratory instrumentation commonly used includes:

Inorganic analysis:

ICP-AES, ICP/MS, GFAA, GF Hydride System, IC, Colorimeter, pH and Conductivity meter
Electrochemistry devices
X-ray fluorescence analyzers

Organics:

GC, GC/MS, GC/MSD, LC/MS, HPLC, Flow-injection systems

Radionuclides:

Alpha and Gamma spectrometers
Beta counters
Liquid scintillation counters
X-ray detectors

Tables 1 and 2 are attached listing some needs and requirements. These are not complete, but do give a feeling for the current areas of concern.

Problem

- The current methods are very labor intensive and time consuming.
- The current methods, due to the homogenization of larger samples before subsampling, do not identify problems like concentrations of critical materials in narrow horizontal layers.
- The current methods primarily provide results that indicate the quantities of elements rather than the molecular species present in the waste.
- The current methods require sample removal from the tank; they are not adaptable to in situ analysis.

Several programs have been initiated to develop and deploy methods that can be deployed in the hot cell for core sample scanning/screening, or directly in the waste tank. An example of such a technology is Raman spectroscopy, which can be used in contact or non-contact mode with a fiber optic linked probe connecting the hot cell (or tank) work space to the instrument. The intention of this workshop is to assess the methods that have already been identified in terms of appropriateness for hot cell/tank applications, and to identify new methods that may have been overlooked.

Constraints

Because the sample scanning and in situ sensing methods diverge significantly from standard methods, levels of accuracy, precision, detection limits, and other data quality objectives have not been established. The following issues are important:

- Accuracy/precision of the measurements must be known in advance. This requires extensive testing and validation of the sensor or instrument in a controlled manner, with simulant and real materials. Even if the accuracy is not good, if the size of the error is known, this will provide useful information. Sensors that produce a measurement whose accuracy/precision is completely unknown will be rejected.

- Repeatable results are important. Testing of the system should show repeatable results within a known error range for the same measurement.

- Reliability and robustness are critical factors for field operation. Instruments in the field or hot cell environment are difficult to "tweak", since it is desirable to keep them environmentally closed while in the potentially contaminated areas.

Technical Acceptability Criteria

The following requirements were developed as criteria for accepting a technology for hot cell operations. Equivalent criteria apply for the tank, with some additional safety constraints in specific tank environments.

The system must:

1. Operate in a radiation environment

2. Provide waste characterization information based on the requirements of the hot cell data users

3. Have the ability to assess real samples

4. Meet life cycle availability and reliability requirements

5. Remain within calibration standards and be able to be routinely recalibrated

6. Provide for disposal of by products

7. Meet operator requirements for training (documentation, support information) safety (safe operations) etc.

8. Use minimal sample preparation (i.e. sample removal from tank and possible subsampling but no digests, extraction etc.)

9. Provide a means to prevent sample cross contamination

10. Provide a means to allow decontamination of any components which contact waste material

11. Be able to work within the constraints of the hot cell (physical and operational interfaces)

12. Provide information regarding tank and hot cell deployment mechanism

Workshop Plan

The workshop will evaluate currently available and developmental technologies which may be used for hot cell screening or in situ analysis of waste tank material. The workshop will NOT consider analytic methods which require sample preparation in a laboratory setting. The specific problems to be addressed are listed below.

Molecular analysis:

- Organics, chelating agents (EDTA, HEDTA, also citrate, acetate)
- Inorganics (ferrocyanide and related compounds, nitrates, nitrites, sulfates, carbonates, phosphates)
- Concentrations of bound and unbound water

Elemental analysis:

- Emphasis on metals (chromium, iron, sodium, bismuth, aluminum, manganese, nickel, lead, barium, cadmium)
- Emphasis on radionuclides (Am-241,242m Pu-238,239,240,241 Tc-99, Cs-137, C-14, Sr-90, Y-90, I-129, U-238,235 Ni-63)

Tank headspace gas analysis:

- Safety issues - hydrogen concentration
- Trace organic identification
- Overall characterization

The methods to be considered are primarily screening methods, providing qualitative or semi-quantitative results. It is not expected that the methods addressed in the workshop will produce EPA qualified measurements.

Deployment Methods

The likely deployment methods for the technologies are:

1. In a hot cell, with a probe attached to a manipulator device that is teleoperated by the user.

2. Directly into the tank waste headspace, for methods that do not require insertion into the waste.

3. Inside the waste tank with a probe attached to a robotic arm. The arm is constrained to fit through an opening of 10 inch diameter and the probe will have a weight limit on the order of 25 pounds.

4. Inside the waste tank, delivered by a cone penetrometer. The interior diameter of the penetrometer will be on the order of .75 to 1 inch.

New concepts for deployment will be considered for those technologies that do not integrate will with an existing concept.

Potential Technologies

A summary package has been compiled which briefly describes the various technologies already under consideration. Suggestions are welcome for methods and devices that should be considered. If suggestions and descriptive material are received in advance of the workshop, they will be distributed to all participants. Participants are also invited to come to the workshop prepared to present a 5-10 minute overview of a technology in which they have technical expertise. However, please note that the purpose of these presentations is to educate the other workshop participants to allow better evaluation to occur, and NOT to sell a particular pet project.

Evaluation Methodology

The evaluation methodology consists of three steps:

1. Determine whether the method will meet a need. Indicate which need(s). Since the needs prioritization seems to be a dynamic list, it will not be possible to prioritize the technologies according to needs met. However, there is significant interest in methods that are flexible or address several different characterization needs, rather than those which are very compound/element specific.

2. Determine whether the method will be deployable. More information about the deployment devices already planned will be presented at the workshop.

3. Determine the maturity level of the technology. A series of maturity levels will be provided, including the tests that need to be performed at each level in order to validate a technology for deployment. This step will allow the assessment process to determine what additional development efforts are needed to bring the technology to deployment readiness.

Workshop Format

The first morning of the workshop will be a general session for all participants. The plan, goals and guidelines will be reviewed. Background information about the Hanford environment, the tank problem and the planned remediation scenarios will be discussed. Information about additional sensors and instruments may be presented at this time.

The workshop will break into three subgroups for the afternoon session: molecular analysis methods, elemental analysis methods, and headspace gas analysis methods. Participants will determine which group they wish to participate in, and give advance consideration to the subset of technologies most appropriate for that problem area. Some overlap of technologies is anticipated. It is hoped that each subgroup will include 5-8 participants.

The subgroups will follow the three steps listed above for the evaluation process:

1. Determine which methods meet a need of the subgroup. Partial prioritization of the list is acceptable, based on participant knowledge of need priority, or number of problems addressed by a single method.

2. Determine deployability of each method that meets a need. Consider the type of development that would be needed to configure a technology for deployment.

   Based on the first steps, prioritize the technologies into at least two levels of priority: 1) those which meet needs and have some reasonable probability of successful deployment; and 2) those which don't really appear feasible. More detailed prioritization is acceptable. The goal is to find perhaps 2-4 methods that deserve further consideration.

3. For the selected methods, assess the technology maturity. Use the attached Table 3 to estimate what development, activities and tests must be performed for the instrument, sensor, probe, etc. prior to deploy. Indicate the current level of development for the technology and the testing that is already known to have been performed. This may include testing of materials from which the sensors or probes may be constructed, single components, or a complete system. From this assessment, produce a prioritized list of the activities that must still be done in order to bring the technology to deployment readiness.

Step 3 may include definition of decision points - activities where development or test results will indicate whether or not it is feasible to proceed with development. These decision points are particularly important, and should be notes. For most technologies there will be significant questions that need to be answered before we can be assured that the method will work in the proposed environment.

The subgroup discussions will continue through most of the second day of the workshop. There will be a brief meeting of the whole group the morning of the second day to assess progress and answer questions. By the end of the second day, a summary of the results of the 3-step evaluation process should be prepared. A technical note-taker will be provided to each group to help track discussions and document the ideas and decisions.

The morning of the third day will be devoted to presentations of the subgroup results, and discussion of the workshop process itself.

Workshop Output

The output of the workshop will be compiled into a two-part report. One part will address the technologies and the recommended development. The other will describe the process used for evaluation, and include suggestions for improving the process. This report will be provided to all workshop participants as well as to the Hanford site. If this workshop proves successful, a similar methodology may be applied to other problems including the characterization of waste physical properties and the improvement of laboratory analysis methods.

Analytes of Safety Concern

(Per Dr. Harry Babad)

- Analyte Specifications
  - %TOC >3% Dry Weight Basis
  - Ammonia or Ammonium Ion >0.1 Molar, or 25 ppm Vapor
  - Cyanide Species TBD. Method is under development. (Note 1. Relating a cyanide ion assay to a vapor risk is a complex issue since cyanide composition in the vapor is hydroxide and salt concentration dependent. Note 2. 50 ppm cyanide ion is approximately equal to 900 g-mole of sodium nickel ferrocyanide in a 500,000 gallon tank of waste whose density is 1.5 g/ml.)
  - Energetics (DSC): >75 calories/gram exotherm dry weight basis Fissile Material: >0.01 gram/liter in solution and/or >1 gram/liter solids (Criticality Specification Related)
  - Moisture: <20% by either TGA or gravimetric techniques
  - pH or hydroxide Conc.: pH <9.5 or OH <0.001 N (Related to corrosion and Actual Toxic Gas Formation)

CHARACTERIZATION PROGRAM STRATEGIES AND FUNCTIONS

Program Strategies	Measurements								
	Metal Ions	Anions (Wet Chemistry)	GEA	Other Rads	TOC	Organics			
Projected Baseline Analysis	ICP-AES -Acid -Fusion -Water CVAA (Hl_x) AA(AS, Se, Sb)	IC TIC (CO_3) SIE (NH_4) Spectrophotometric (Cr + 6)	Ge detector LEPS (Low energy photon spectrometry)	Separations -SX -IX -Dissolution/ precipitation -Distillation Counting -LS spectroscopy -gas proportional -alpha spec -LEPS/GEA	Solids Liquids UV/Heat Wet oxidation Furnace	Complexants Volatiles GC/MS purge & trap Non-Volatiles GC/MS LC/MS			
	CN/FeCN	Noble Metals	Weight % Water	Neutrons	Other	Alpha	Beta	Weak Beta	X-Ray
	Micro distillation *FeCN speciation*	*ICP/MS*	Gravimetry TCA	*In situ foils*	Laser fluorimetry ICP/MS	U Pu Am/Cm Np Total	Sr/Y Total	Tc-99 H-3 Se-79 Ni-59 Ni-63 C-14 Sm-151	I-129 Nb-93 Nb-94 Pd-107 Zr-93
	Comments:								

Table 3. Technology readiness review for determining development path. (Adapted from Fred Reich)

	Sample Material			Operating Environment		
	similar	simulant	real	similar	simulant	real
Concept Stage						
1. Problem Definition	x			[x]		
·Issues and ranges identified						
·Performance objectives, acceptance criteria identified						
2. Basic Technology Research	x			[x]		
·Basic principle tests formulated						
·Basic principles observed and reported						
Feasibility Study						
3. Research to Prove Feasability	x			x		
·Feasible concept/application identified						
·Feasibility tests identified						
·Feasibility tests completed						
Prototype Stage						
4. Integrate, Demo, Test Method	x			x		
·Integrated mock-up/breadboard design completed						
·Tests identified to demo performance, objectives						
·Design performance objectives met						
5. Prototype Demo and Test	x	x		x	x	
·Functions and requirements identified						
·Prototype system designed, reviewed						
·Safety, deployment issues identified and met						
Cold Test - Hot Sample						
6. Validation and Verification	x	x	x	x	x	
·Validation, verification, qualification criteria identified						
·Performance, acceptance, qualification criteria met						
7. Full System Integration	x	x	x	x	x	
·Deployable systems functions, requirements identified						
·Deployable systems F & R documented and reviewed						
·System design completed and reviewed						
Hot Test						
8. Technology Deployment	x	x	x	x	x	x
·Deployment plan developed, reviewed						
·Deployment issues identified, met						
·Operational procedure documents completed, reviewed						
·Full system reviewed, demonstration completed						
Hot Operations						
9. Technology Transfer	x	x	x	x	x	x
·Technology applications, recipients identified						
·Technology transfer documentation completed						

TECHNOLOGY EVALUATION WORKSHOP
TANK WASTE CHEMICAL CHARACTERIZATION

POTENTIAL TECHNOLOGIES FOR EVALUATION

LASER ABLATION TECHNIQUES

Laser Induced Breakdown Spectroscopy

Laser Induced Breakdown Spectroscopy (LIBS) is most often used for the analysis of solids and liquids, particularly to determine metals. Laser plasmas or optically induced breakdowns are generated by focusing the output of a pulsed laser onto a small spot. The breakdown threshold is the minimum power density necessary for a plasma to form. Breakdown thresholds are generally on the order of several megawatts/cm^2, however different materials have different breakdown thresholds.

A basic system utilizes a laser with a focusing lens. The plasma causes a breakdown of the analyte, and the emissions are collected by a monochromator. The monochromator runs the emissions through a detector and generates a spectrum.

The temperature on the sample generated by the laser plasma can be as high as 25000 K. The small focused spot (on the order of 100 μm or less) provides excellent spatial resolution. The sample vaporization via laser ablation eliminates the need for any sample preparation.

Complex sample matrices and irregular surface geometries present problems with cross-contamination of the plasma (i.e., material from the previous spot sample is still in the plasma when doing the second sample analysis). Also the presence of certain materials can inhibit or exaggerate the emission of other materials.

Laser Ablation ICP Atomic Emissions Spectroscopy

For this technique, the sample is ablated to the breakdown threshold, in the same manner as in LIBS, but the ablated sample is fed using a flow of argon into an inductively coupled plasma (ICP) which then generates a spectrum based on the plasma. As an example of findings in other applications, the approach works fairly well for nickel manganese and chromium in low alloy steels. Sulfur and phosphorus in alloy steels don't have very accurate detection limits.

Laser Ablation ICP Mass Spectroscopy

ICP mass spectroscopy uses the ICP as an ion source for mass spectroscopy. The technique works very well for metals analysis. Current methods place

the sample in a pyrex cell with an inlet for the laser beam and an outlet into the ICP torch. The detection limits of ICP mass spec systems are quite low as are the error percentages ±5%.

INFRARED TECHNIQUES

Infrared (IR) techniques most often utilize light from a laser or a broad band light source in the infrared. The light may be transmitted to and received back from the sample using a fiber optic cable. The returned light then produces an infrared spectrum showing the absorbance or reflectance properties of the material. Transmission sensing of infrared light requires configuration of a probe that allows material to be placed between the light source and the detector. While transmission sensing is widely used for gas analysis, its application to solid or liquid waste will require special probe configuration.

Three major techniques that use light in the infrared spectrum are Fourier Transform infrared spectroscopy (commonly 3 to 25 micron range), near IR spectroscopy (0.8 to 2.5 microns) and thermal emission spectroscopy (often favoring 8 to 10 microns).

Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is an analytical technique sometimes used in conjunction with chromatography. FTIR employs an interferometer which splits the light source and reflects it by means of mirrors. An interferogram is generated, representing the signal in the time domain. From the interferogram, a spectrum in the frequency domain is generated by means of a Fourier Transform.

FTIR instrumentation is often combined with some form of chromatography because of similar sampling needs. IR spectroscopy is often not good for analyzing complex matrices because of the elemental interferences with the signal. FTIR spectrometry is much better in terms of sensitivity than dispersive IR. The technique works best for sampling and analysis of gaseous samples, as it is suited best for organics, and no sample preparation is required.

Near Infrared Spectroscopic Techniques

Near Infrared Spectroscopy (NIR) results from light absorption by molecules. NIR utilizes the middle 4000-6000 cm-1 of the infrared range, and sometimes extends to the visible for certain applications. NIR works best for analyzing organics (hydrocarbon compounds) and for moisture analysis.

Thermal Mapping

Infrared imaging techniques have been used to map out tank waste surface temperatures to determine whether hot spots were present. (Thermal hot spots might be considered indicative of high concentrations of radiolytic

activity or chemical reactions.) The system that has been deployed in the tanks uses an infrared imaging sensor with no light source. The underlying principle of the detector is that the infrared photon moves an electron across the detector's energy gap. The photoconductive detector then has its properties changed as the electrons move from a valence band into a conduction band. This change in conductive properties is then measured and from that the image is produced. The more the conductive properties change, the hotter the surface is (in terms of temperature). Infrared imagers are commercially available.

RAMAN SPECTROSCOPY

Technologies involving the Raman spectroscopy technique provide a range of analysis that encompasses both the chemical and physical properties of a sample. In Raman spectroscopy, a sample is irradiated with an intense source of monochromatic radiation, of a frequency higher than vibrational frequencies and lower than electronic frequencies of the sample. (Lasers at about 514 nm and 830 nm are popular choices.) The radiation scattering is then analyzed by the spectrometer. The Raman effect involves monitoring the change in rotational or vibrational energy of a molecule due to an inelastic collision with the incident photon.

The basic setup of many current Raman systems involves fiber optics to deliver and collect the radiation. An argon-ion or diode laser provides the radiation source that bombards the sample. The optical cables then collect both Rayleigh and Raman scattering. A filter then rejects the Rayleigh scattering, and allows the Raman scattering to pass into a detector. In many cases a Charge Coupled Device (CCD) detector is used to sense the spectrum. Raman scattering is used for several analytical techniques, including Resonance Raman Spectroscopy (RRS) and Surface Enhanced Raman Spectroscopy (SERS).

Problems in the past with the fiber optic Raman probes included limited cable length due to the increase in background fluorescence emissions that came with longer fibers. New advances in fiber configuration geometries have greatly reduced this problem. Good results have been demonstrated with fibers up to 100 feet in length, and it is anticipated that much greater distances will be achievable.

Although to date Raman has not been deployed in situ for waste tank characterization, some tests have been run to evaluate the technology in environments similar to those found in the tanks. Preliminary tests using optical Raman analysis in high pH environments have shown that high pH (specifically near pH 14) causes no significant deviations from the standard spectra. The detection limits when looking at solid materials, are very low which is beneficial, as the cyanide compound concentration in the tanks has been found to be fairly low.

The current focus of Raman research in terms of waste tank characterization has been on developing the technology to provide in situ monitoring of

cyanide compounds which present a safety concern. A fiber optically linked Raman system is currently undergoing testing in the hot cell at Hanford.

Surface Enhanced Raman Spectroscopy

SERS systems can be used to screen a wide variety of molecules. The theory of Raman scattering is the same as that used in standard Raman spectroscopy. However, the surface of a SERS probe is coated with material that interacts specifically with the target analytes of interest. This allows detection of specific compounds at concentrations orders of magnitude lower than would otherwise be possible. The result is a high signal to noise ratio, and detection capability in the parts per billion range for specific compounds. The disadvantage of SERS is the requirement for direct probe surface interaction with the target materials, limiting its applicability to gas or liquid samples. Portable SERS units have been reduced down to suitcase size.

Resonance Raman Spectroscopy

RRS uses Raman scattering to identify specific chemical species. Most systems utilize a tunable laser tuned to a species specific frequency. This provides a high signal to noise ratio because the analysis is so specific. The major problem with Resonance Raman is that it is very analyte specific and the laser must be retuned for multispecies analysis.

X-RAY FLUORESCENCE

X-Ray Fluorescence (XRF) is an analytical technique that is used to determine both the presence and concentration of metals in a given sample. Different XRF equipment is used to detect either specific groups of metallic elements or a wide range of metals. One very common application is for the determination of lead in paint samples, with an XRF that specifically detects lead.

The basic setup of an XRF apparatus involves the irradiation of a sample by an x-ray source. The x-ray source excites the sample and causes the sample to emit photons which are then detected as fluorescent spectra. The fluorescent spectra are then analyzed to determine the composition and concentration of each element.

Problems with XRF have involved the need for extensive calibration in order for the equipment to perform highly accurate analysis. XRF only provides limited depth resolution of the analyte. The general consensus is that XRF is a better tool when good spectral resolution is not required, but analytical sensitivity is. Another drawback is that if the material is highly absorbent, the technique will not work well, so it is important to have a general idea of the absorption coefficient of the sample matrix.

The technique works best on solids and requires little or no sample preparation. The maximum amount of sample preparation requires that the sample be put in a vacuum environment during the analysis.

Major applications to waste tank characterization would involve metals concentration characterization at the sample point. Portable XRF models are available that would allow for sampling to be done very easily tank-side, using a sampling tube. A wide range of commercial XRF systems are available and most likely one could be adapted for use at Hanford either to detect a wide range of metals or one specific metal of interest.

LASER INDUCED FLUORESCENCE

Laser Induced Fluorescence (LIF) techniques utilize an ultraviolet (UV) light source which is responsible for creating the fluorescence spectrum. Usually, the source is a laser set to transmit light in the UV spectrum. The system for LIF works much as the other spectroscopy systems do (light source, detector filter, spectrum produced). The UV source lasers generally are very wavelength specific, as the wavelength that causes the analyte to fluoresce is very narrow. The fluorescent emissions of the sample are measured by the detector and generate the spectrum.

Thus far, laser induced fluorescence has been proposed for use at Hanford as a system to detect polyaromatic hydrocarbons, uranium salts and plant stress (as indicator of toxic materials in soil).

GAS CHROMATOGRAPHY AND MASS SPECTROSCOPY UNITS

Portable Gas Chromatography and Mass Spectroscopy (GCMS) units present a unique opportunity for in situ measurement of gases in waste tanks. Recent developments have in reducing size and increasing sensitivity have made GCMS more feasible for eventual field deployment.

Three major systems have been developed, one at the Jet Propulsion Laboratory (JPL) one at University of Utah and one at Los Alamos National Laboratories (LANL). The need for high power has usually implied a massive unit, but equipment improvement has reduced the weight requirement.

The JPL system utilizes an electrooptical ion detector (EOID) which makes it possible to use non-scanning mass spectroscopy which is more sensitive to spectra and was previously not feasible because the appropriate detector had not been developed. The EOID works by using a photoplate in the focal plare of the spectrograph and an electron multiplier simultaneously. The sensitivity can be modulated by the signal integration time (20ms to 30s) thereby allowing for many mass spectral readings. The detector sensitivity also allows for small sample volumes as dictated by the size of the columns (in this case 50μm internal diameter by 3m in length). The smaller column size is acceptable because of the increased sensitivity of the detector.

Some road blocks to the deployment of a system such as the one at JPL involve how well the hardware will endure a waste tank environment. It is reasonable to assume that the instrument itself will remain outside the tank, requiring development of a sampling mechanism. Deployment of the instrument close to the tank is in itself a field deployment challenge; most equipment that will be in close proximity to tanks need to be placed in environmentally closed containers to avoid contamination with contaminated soil.

PROMPT GAMMA NEUTRON ACTIVATION ANALYSIS

Prompt Gamma Neutron Activation Analysis (PGNAA) provides a means of elemental analysis in various matrices. The analysis uses a neutron which interacts with the nucleus and generates an energy signature for element detection.

A PGNAA system has been developed by Westinghouse Science and Technology Center, that provides a high signal to noise ratio and high spatial resolution. The hardware involved requires a neutron source, a moderating material (generally high in carbon or hydrogen), a gamma ray detection system, and radiation shielding. The moderating material acts to slow the neutrons down to thermal energies through collisions. The slower rate of neutron flow allows the energy signals to be read more easily.

PGNAA can be used to detect elements throughout the periodic table, and although detection limits vary, equipment can be sensitized or desensitized to different elements, to provide more accurate detection. In the Westinghouse system, neutron penetration of up to 40 inches in packed soil has been achieved.

FIBER OPTIC CHEMICAL SENSORS

The two basic types of fiber optic chemical sensors differ in the way they utilize the optical fiber end that is in contact with the sample. Chromionophores measure the optical signal resulting from the change in optical absorption, or fluorescence (chrominofluores). Field sensitive dye optical sensors utilize the interaction of the dye dipole with the local electric field (as described by the Stark Effect) and measure the modulation of optical properties of the dye.

The above described sensors all rely on reversible reaction. Another class of fiber optic chemical sensors uses irreversible reactions. In this case a reagent is continuously released from the membrane and a reaction is measured in the sample by the sensor. The lifetime of these type of sensors in situ depends on the amount and flow rate of the reagent. The flow rate is reduced by coating the tip of the optrode with a polymer. However, the coating generally doesn't fair well in a radioactive environment.

Although fiber optic chemical sensors have been used in carbon-dioxide, pH, gasoline (hydrocarbon), and specific ion detection, limitations exist for

application to a waste tank environment. In ion detection, the need for some sort of reference in the same in situ environment requires that another set of hardware be deployed to monitor the reference.

ION MOBILITY SPECTROSCOPY

Ion Mobility Spectroscopy (IMS) is a promising technique for organics analysis. A portable IMS has shown promise for detection of the whole organic spectrum with very low detection rates. A gas chromatograph can be very easily added on to the IMS equipment without substantial size increase.

No sample preparation is involved for IMS gas sampling. Air samples are introduced directly into the machine containing the electric drift field tube with an ionizer and a reactor coupled with a shutter to an ion drift region. The relative motion of the different sized particles through the drift tube is used by the fast electrometer amplifier to generate a spectrum. Commercial portable IMS units are available for field use.

Technology Evaluation Workshop

Tank Waste Chemical Characterization

WESTINGHOUSE HANFORD COMPANY

Technology Evaluation Workshop
Tank Waste Chemical Characterization
TANK BACKGROUND

- Hanford has 177 Underground Storage Tanks
- Tank capacity is 500,000 to 1,000,000 gallons
- Tanks are 75 feet in diameter, approximately 35 feet high
- Tank access is through pipes or "risers", mostly 4 to 12 inches in diameter
- Tanks are buried under 6-8 feet of soil

Technology Evaluation Workshop
Tank Waste Chemical Characterization

Problem 1:
- Characterization process involving removed core analysis is slow
- Characterization process is costly
- Characterization process involves risk of personnel exposure

Need:
- Hot cell screening tools to increase efficiency
- In-situ characterization tools to reduce sample removal

Scope:
- Chemical characterization - molecular, elemental, gas analysis
- Address only technologies requiring minimal sample preparation
- Examine both in-situ and in hot cell deployment

Outcome:
- List of technologies addressing problems with deployment potential
- Outline of tasks required to continue technology development

Technology Evaluation Workshop
Tank Waste Chemical Characterization

Problem 2:
- Current technology assessment process is not thorough or objective
- Potentially valuable technologies may be overlooked
- Developers do not understand entire path to deployment

Need:
- Documented process to identify and assess technologies addressing a specific problem
- Documented process to identify required development steps

Scope:
- Apply initial evaluation process as objectively as possible
- Identify problems with process, needs for team members
- Suggest improvements

Outcome:
- Documented procedures for assessing technology
- Documented process improvements for next implementation

Technology Evaluation Workshop
Tank Waste Chemical Characterization
ASSESSMENT PROCESS

- Does the technology meet a need?
- Can the technology be deployed?
- What development and testing activities remain to be done?

Technology Evaluation Workshop
Tank Waste Chemical Characterization
NEEDS-BASED ASSESSMENT ISSUES

- What species can be identified?
- Is the method species specific or does it cover a broad range?
- Will a single instrument address a broad range or are several required? (e.g. tunable vs fixed)
- What are sensitivity, accuracy, reliability levels?
- Does the method require constant attendance of skilled operators? Can it be used for monitoring?
- Does the system require constant "tweaking"?

Technology Evaluation Workshop
Tank Waste Chemical Characterization
NEEDS

- Elemental analysis of solid and liquid waste
- Molecular speciation of solid and liquid waste
- Analysis of headspace gases and fugitive emissions

Technology Evaluation Workshop
Tank Waste Chemical Characterization
DEPLOYMENT ISSUES

- Does the method require sample preparation?
- Can a probe be separated from the main instrument?
- Can a probe be made small enough for deployment?
- Can a probe survive in a high radiation environment?
- Does the method require sample contact? If so can the probe survive high pH?
- Can the probe be cleaned, decontaminated?

Technology Evaluation Workshop
Tank Waste Chemical Characterization
DEPLOYMENT ISSUES

- Does the method require constant attendance of skilled operators?
- Does the system require constant "tweaking"?
- What is an operational life expectancy of the system?
- Does the system have specific sensitive parts? Can it be designed so that these parts may be changed out?
- Can a probe operate safely in the expected environment (e.g. no spark hazard inside tanks)

Technology Evaluation Workshop

Tank Waste Chemical Characterization

HOT CELL DEPLOYMENT

Technology Evaluation Workshop
Tank Waste Chemical Characterization
FIELD OPERATION REQUIREMENTS

- Operate in a radiation environment
- Provide waste characterization information based on the requirements of the data users
- Have the ability to assess real samples
- Meet life cycle availability and reliability requirements
- Remain within calibration standards and be able to be routinely re-calibrated
- Provide for disposal of by products
- Meet operator requirements for training (documentation, support information) safety (safe operations) etc.

Technology Evaluation Workshop
Tank Waste Chemical Characterization
FIELD OPERATION REQUIREMENTS

- Use minimal sample preparation (i.e. sample removal from tank and possible subsampling but no digests, extraction etc.)
- Provide a means to prevent sample cross contamination
- Provide a means to allow decontamination of any components which contact waste material
- Be able to work within the constraints of the hot cell or tank (physical and operational interfaces)
- Provide information regarding tank and hot cell deployment mechanism

Technology Evaluation Workshop
Tank Waste Chemical Characterization

Potential Technologies for Evaluation

- X-Ray Fluorescence
- Laser Induced Fluorescence
- Gas Chromatography and Mass Spectroscopy Units
- Prompt Gamma Neutron Activation Analysis
- Fiber Optic Chemical Sensors
- Ion Mobility Spectroscopy

Technology Evaluation Workshop
Tank Waste Chemical Characterization

Potential Technologies for Evaluation

- Laser Ablation Techniques
  - Laser Induced Breakdown Spectroscopy
  - Laser Ablation ICP Atomic Emissions Spectroscopy
  - Laser Ablation ICP Mass Spectroscopy
- Infrared Techniques
  - Fourier Transform Infrared Spectroscopy
  - Near Infrared Spectroscopic Techniques
  - Thermal mapping
- Raman Spectroscopy
  - Surface Enhanced Raman Spectroscopy
  - Resonance Raman Spectroscopy

Status Chart

Development Level / Status	Sample Material			Operating Environment			Deployment	
	Similar	Surrogate	Real	Similar	Surrogate	Real	Safety	Regs.
Concept Stage 1. Problem Definition – Issues and ranges identified – Performance objectives, acceptance criteria identified 2. Basic Technology Research – Basic principle tests formulated – Basic principles observed and reported								
Feasibility Study 3. Research to Prove Feasibility – Feasible concept/application identified – Feasibility tests identified – Feasibility tests completed								
Prototype Stage 4. Intergrate, Demo, Test Method – Integrated mock-up/breadboard design completed – Tests identified to demo performance, objectives – Design performance objectives met 5. Prototype Demo and Test – Functions and requirements identified – Prototype system designed, reviewed – Safety, deployment issues identified and met								
Cold Test – Hot Sample 6. Validation and Verification – Validation, verification, qualification criteria identified – Performance, acceptance, qualification criteria met 7. Full System Integration – Deployable systems functions, requirements identified – Deployable systems F & R documented and reviewed – System design completed and reviewed								
Hot Test 8. Technology Development – Deployment plan developed, reviewed – Deployment issues identified, met – Operational procedure documents completed, reviewed – Full sytem reviewed, demonstration completed								
Hot Operations 9. Technology Transfer – Technology applications, recipients identified – Technology transfer documentation completed								

Technology Evaluation Workshop
Tank Waste Chemical Characterization

- Does the technology meet a need?
- Can the technology be deployed?
- What development and testing activities remain to be done?

NEEDS-BASED ASSESSMENT ISSUES

- What species can be identified?
- Is the method species specific or does it cover a broad range?
- Will a single instrument address a broad range or are several required? (e.g. tunable vs fixed)
- What are sensitivity, accuracy, reliability levels?
- Does the method require constant attendance of skilled operators? Can it be used for monitoring?
- Does the system require constant "tweaking"?

DEPLOYMENT ISSUES

- Does the method require sample preparation?
- Can a probe be separated from the main instrument?
- Can a probe be made small enough for deployment?
- Can a probe survive in a high radiation environment?
- Does the method require sample contact? If so can the probe survive high pH?
- Can the probe be cleaned, decontaminated?
- Does the method require constant attendance of skilled operators?
- Does the system require constant "tweaking"?
- What is an operational life expectancy of the system?
- Does the system have specific sensitive parts? Can it be designed so that these parts may be changed out?
- Can a probe operate safely in the expected environment (e.g. no spark hazard inside tanks)

TANK WASTE REMEDIATION SYSTEM
TANK CHARACTERIZATION PROGRAM

L. M. Sasaki
Characterization Program
Westinghouse Hanford Company

Technology Evaluation Workshop
Tank Waste Chemical Characterization
Kennewick, Washington
August 24, 1993

Outline

- Characterization program objectives
- Tank and waste descriptions
- Sampling methods
- Current core sample analysis schemes
- Potential areas for improvement

Waste Characterization Program - Objectives

- Obtain tank waste samples and determine chemical, physical, and radiochemical properties
- Provide limited amounts of waste material for development testing
- Provide characterization data to meet program needs
  - Safety
  - Retrieval
  - Pretreatment
  - Disposal
- Provide integration for all TWRS characterization work
  - Characterization program
  - DST RCRA (Part B)
  - Grout candidate and feed tank
  - Evaporator

Description of Tanks and Wastes

Double-Shell Tanks	Single-Shell Tanks
28 tanks - 1 million gal capacity - 75 ft diameter	149 tanks - 55,000 to 1,000,000 gal capacity - 20 and 75 ft dia.
Constructed 1968 to 1986	Constructed 1943 to 1964
Two carbon steel liners - 1.5 ft annulus between liners Reinforced concrete shell	One carbon steel liner Reinforced concrete shell
Active storage and waste management	No waste added since 1980 Liquids pumped to DSTs
24 million gallons of waste	37 million gallons of sludge, salt cake, and liquids

General Chemical and Physical Properties of Tank Wastes

- Wastes consist of alkaline liquids, sludges, and salts resulting from the chemical processing used to recover Pu, U and Np from irradiated reactor fuel
  - sludges: hydrous metal oxides (Fe, Mn,...) precipitated from neutralization of acid wastes before transfer to tanks
  - salt cake: salts from the evaporation of water from the wastes (sodium hydroxide, nitrate, nitrite, aluminate,...)
- Almost 300 different chemicals used at the Hanford site may have been added to the tanks

Examples of Physical Properties

Physical Property	AZ-101 AZ-102 (NCAW)	AW-103 AW-105 (NCRW)	SY-102 (PFP)	AN-102 (CC)	SY-103 (CC & DSS)	B-110 ($BiPO_4$)
shear strength ($dynes/cm^2$)	26,000	48,000	39,000	2,900	32,000	—
sludge density (g/ml)	1.3-1.8	1.4-1.8	1.2-1.8	1.3-1.8	1.8-1.9	1.3-1.4
supernate density (g/ml)	1.2	1.06	1.03	0.36	—	—
mean particle diameter (μm) (based on number density)	1.2	1.0	0.9	0.9	—	1.2
penetration resistance (psi)	2.5	6	11	—	—	<2
Miller number	8	23	—	—	—	—

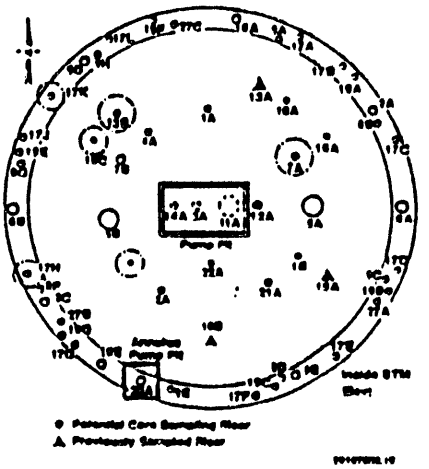
Tank Sampling Methods

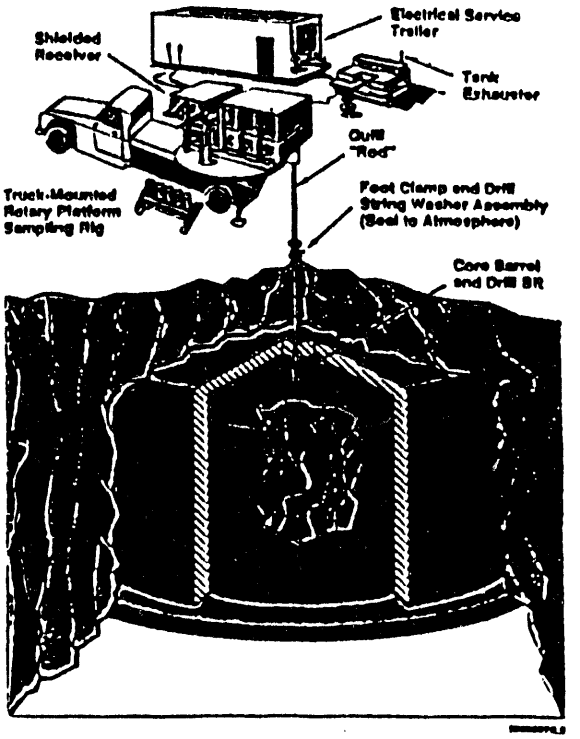
- "Bottle-on-a-String" sampling
- Auger sampling
- Core sampling Truck
  - Uses a modified drilling design
  - Obtains 1-inch diameter 19-inch long core segments
  - Takes multiple segments to obtain full core sample of tank waste
  - Samples liquids, slurries, and sludges
  - Capability for hard waste sampling in development

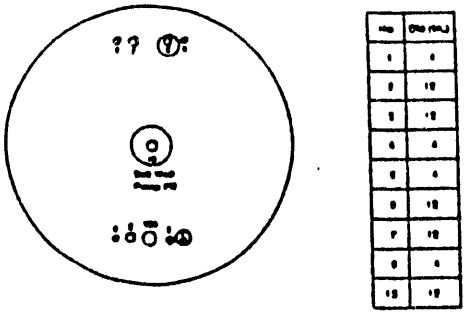
Potential Areas for Improvement

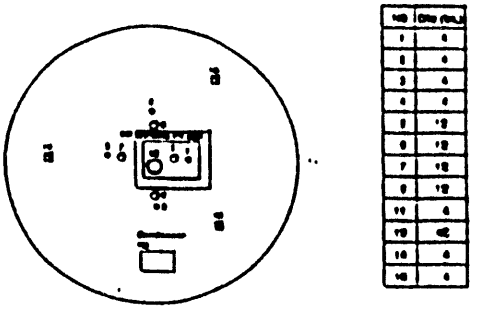
- Real time homogenization checks
- In situ physical property measurement
- Core scanning for safety analyses
- Rapid turnaround for high priority safety screening analyses

Example of Tank Access for Sampling
Tank 105-AW



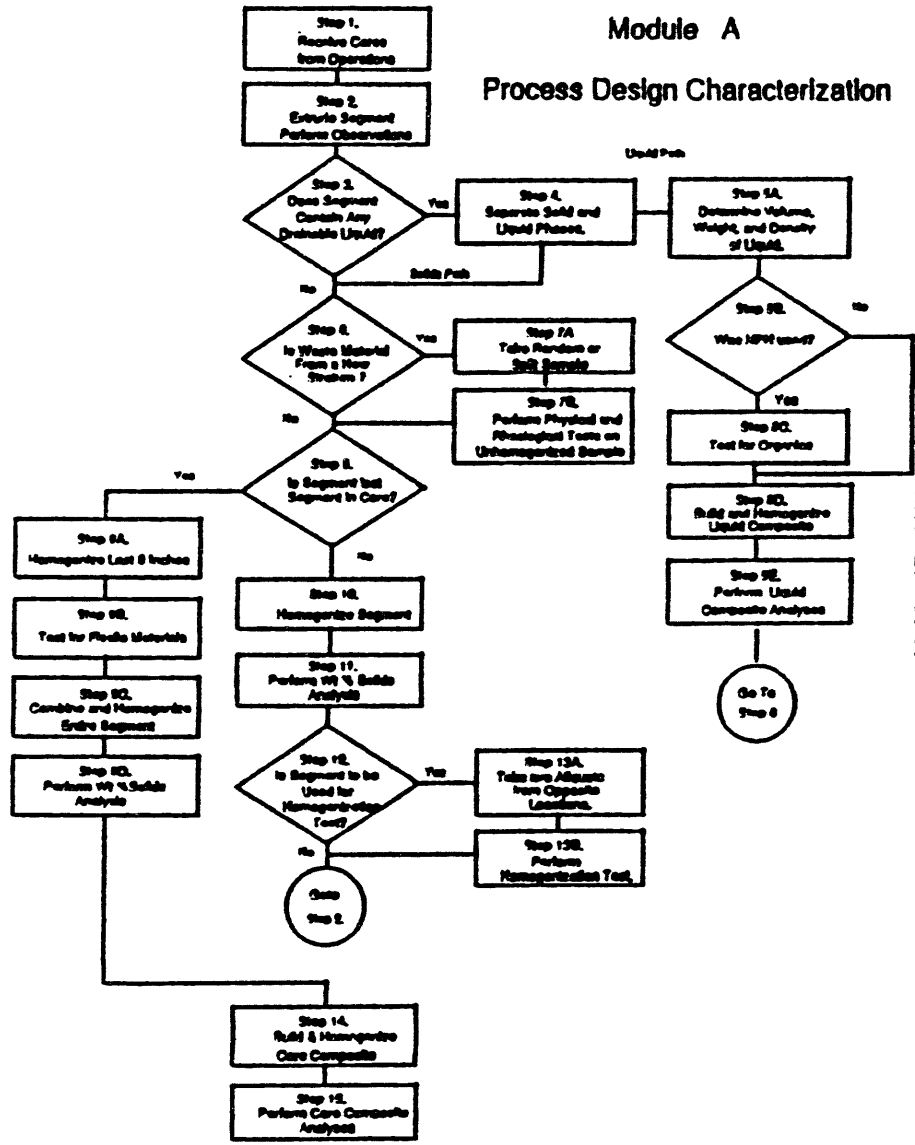






Examples of Chemical Properties

Chemical (concentrations in g/L, except as noted)	SY-103 (CC & DSS)	B-110 ($BiPO_4$)
Al	8.9E+01	1.6E+00
Ca	1.2E+00	1.2E+00
Cr	7.6E+00	1.1E+00
Fe	2.6E+00	2.6E+01
K	5.1E+00	5.1E-01
Mn	6.3E-01	1.4E-01
Na	3.8E+02	1.3E+02
Si	1.3E+00	1.3E+01
Zr	3.6E-02	1.3E-01
CO_3	3.5E+01	---
F	---	2.6E+00
NO_2	1.2E+02	1.4E+01
PO_4	5.7E+00	3.4E+01
NO_3	2.4E+02	2.5E+02
SO_4	5.6E+00	1.5E+01
OH	3.0E+01	---
Pu 239+240 (μCi/L)	9.5E+01	1.5E+02
Am 241 (μCi/L)	7.7E+02	1.0E+02
Cs 137 (μCi/L)	6.8E+05	1.9E+04
Sr 90 (μCi/L)	---	1.2E+05



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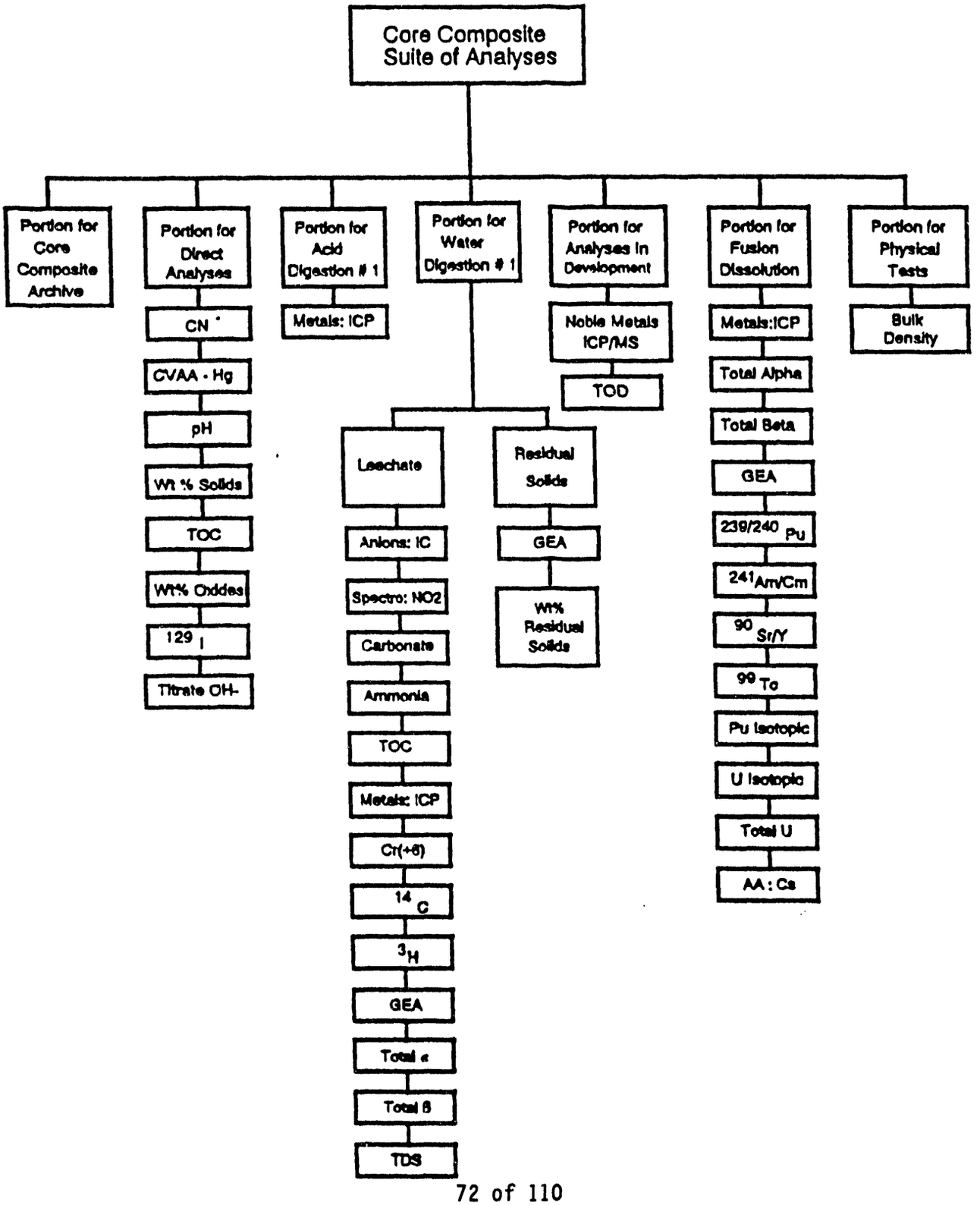
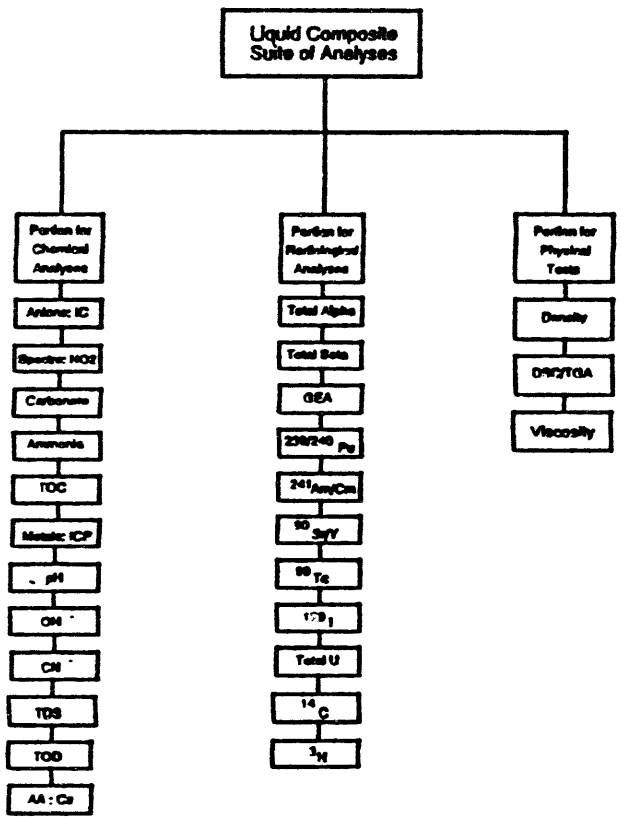
Module A

Process Design Characterization



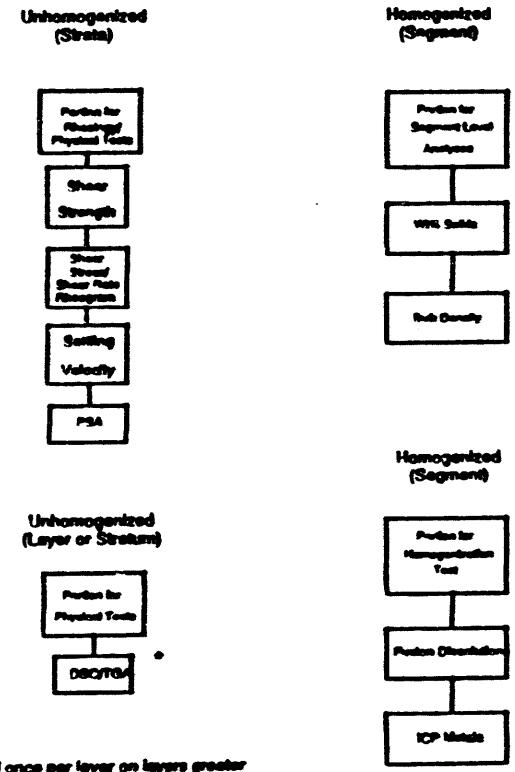
Module A

Process Design Characterization

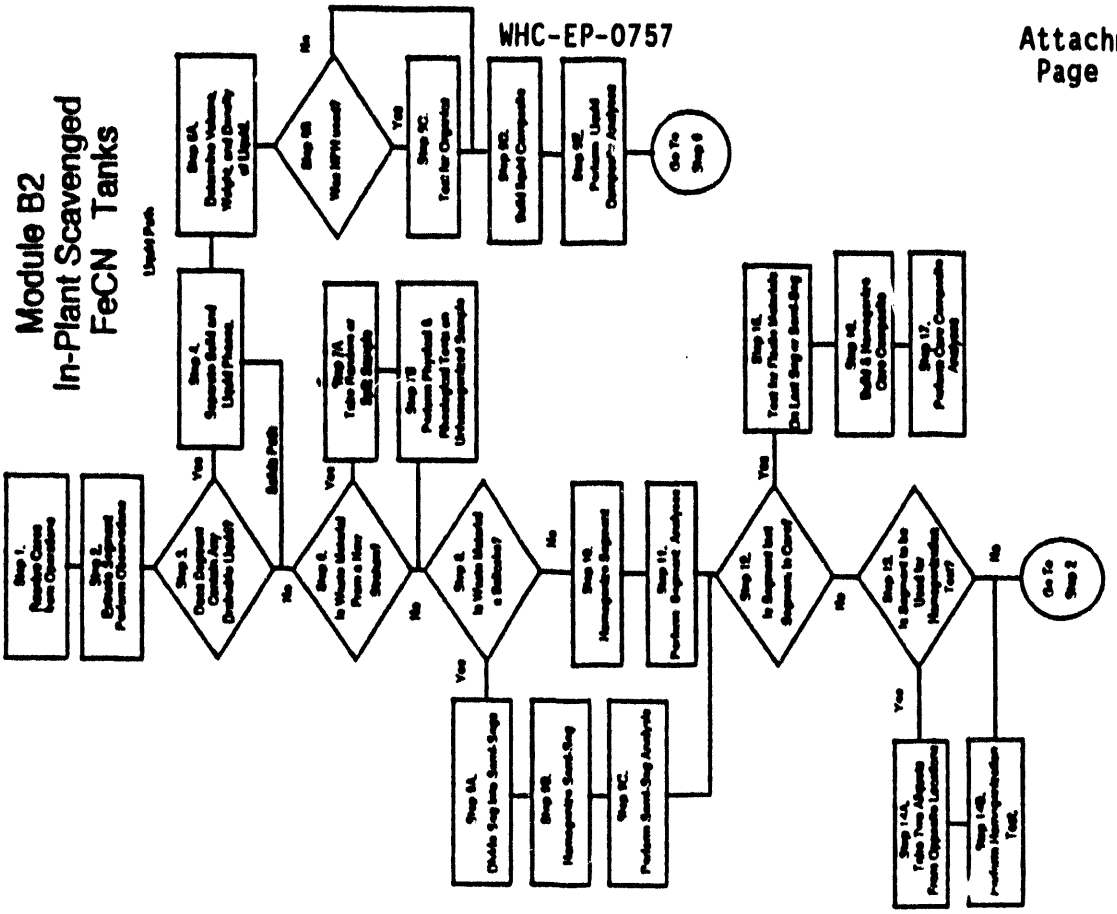


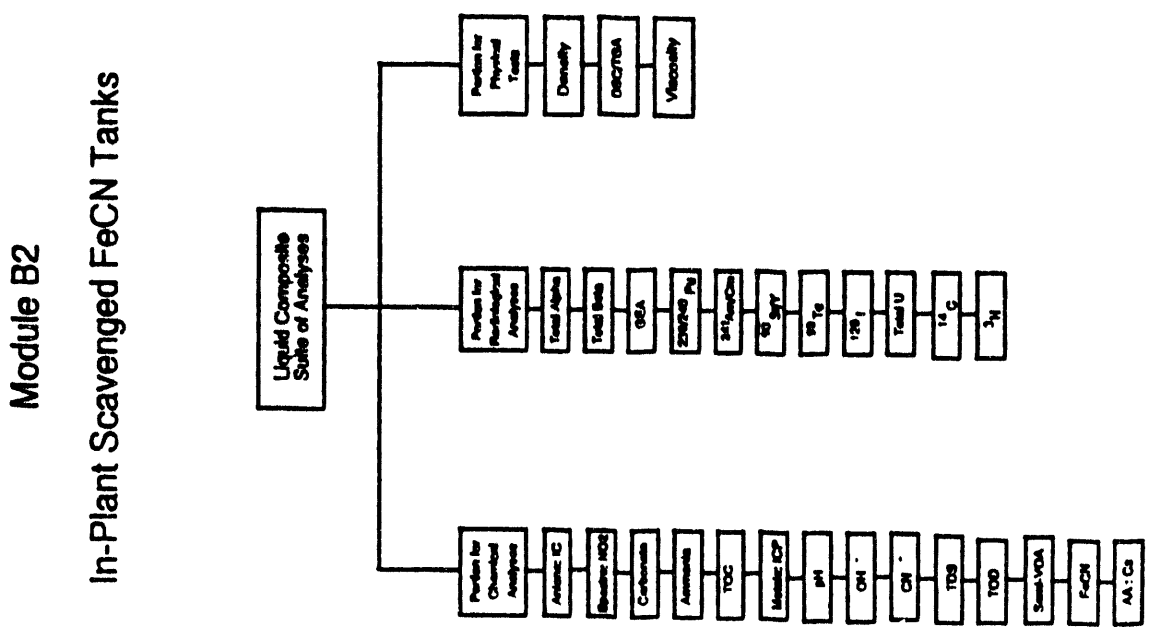
Module A

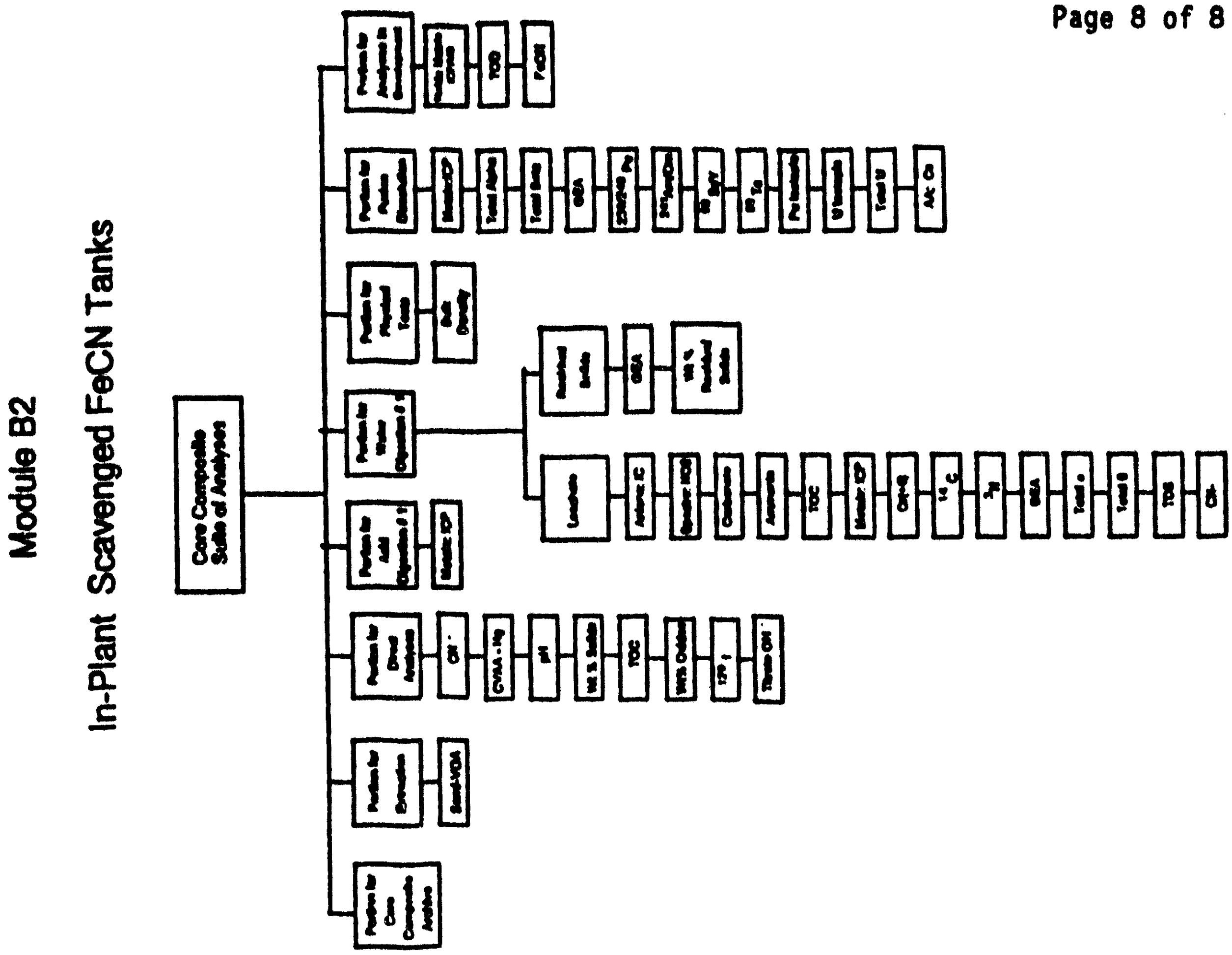
Process Design Characterization

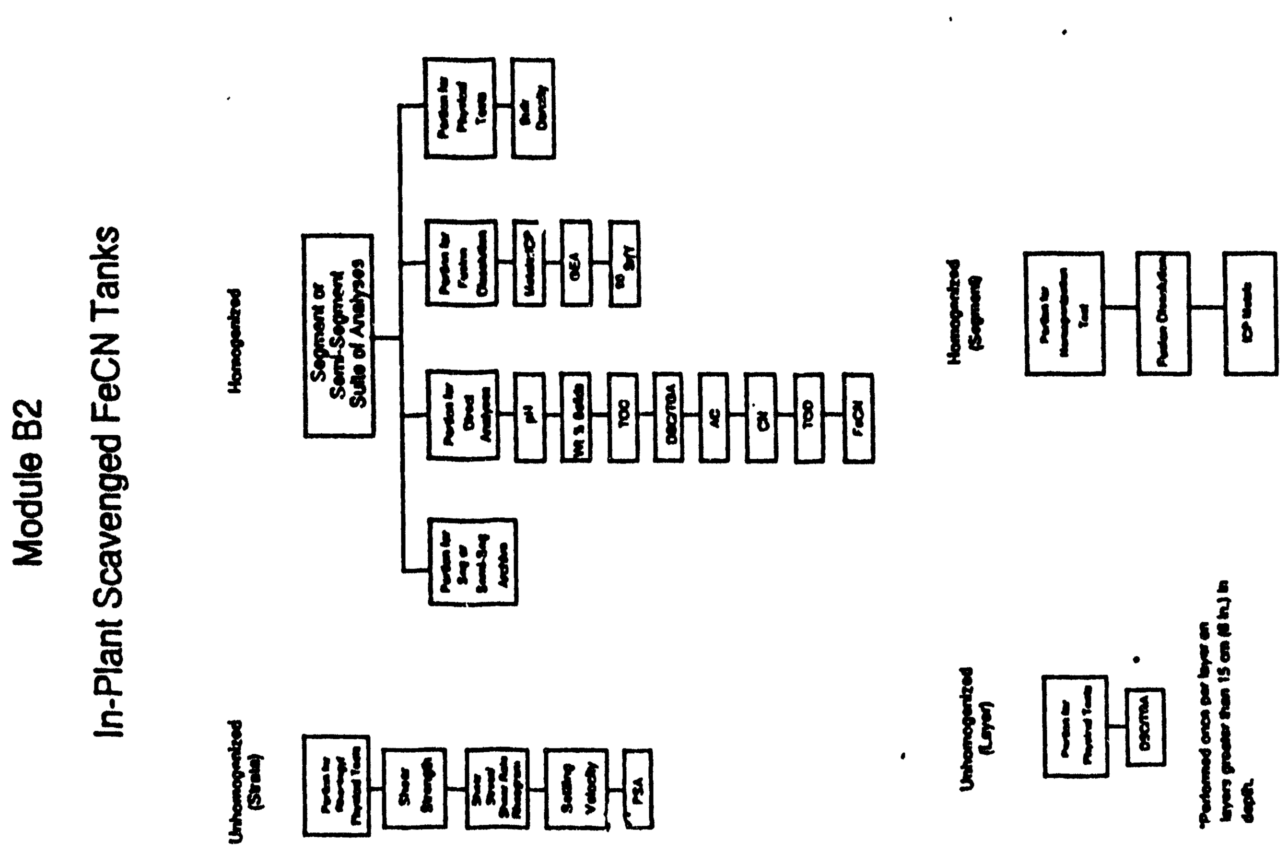


* Performed once per layer on layers greater than 15 cm (6 in.) in depth, and once per stratum unless the stratum is greater than two segments in depth. In this case, an analysis is performed on every other segment until a new stratum is encountered


Module B2
In-Plant Scavenged
FeCN Tanks


Module B2
In-Plant Scavenged FeCN Tanks
Liquid Composite Suite of Analyses
Perform for Physical Tests
Density
DSC/TGA
Viscosity
Perform for Radiological Analyses
Total Alpha
Total Beta
GEA
Total U
Perform for Chemical Analyses
Anions: IC
Cyanide
Ammonia
TOC
Metals: ICP
pH
OH-
CN-
TDS
TOD
Sum VOA
FeCN
Al:Cs


Module B2
In-Plant Scavenged FeCN Tanks
Core Composite
Suite of Analyses


Module B2
In-Plant Scavenged FeCN Tanks
Homogenized
Segment or
Semi-Segment
Suite of Analyses
Unhomogenized
(Strata)
Homogenized
(Segment)
Unhomogenized
(Layer)
*Performed once per layer on
layers greater than 15 cm (6 in.) in
depth.

WASTE TANK ENTRY
AND
DEPLOYMENT PLATFORM DEVELOPMENT

D. N. Price

Westinghouse Hanford Company

CHARACTERIZATION PROGRAM

Tank Access Constraints

- Area Restrictions to Qualified Personnel
- Physical Access Restrictions
- Typical Activities Associated With Deployment

Area Restrictions to Qualified Personnel

- 40hr(Operator) / 24hr Hazardous Waste Training
- Radiation Worker Initial Training
- Physical Examination / Mask Fit

Physical Access Restrictions

- Load Limits (S.S.T.)
  - 100 tons total for 75' Dia. tanks
  - 30 tons over 30 ft^2
  - 17 tons over 1 ft^3
- Burms
  - Restricts riser access
- Tank Equipment
  - Thermocouple Trees
  - Liquid Level Indicators
  - Exhausters
  - S.S.T's. risers are generally located ~4' from edge.
  - Only readily access is through 4" and 12" risers.

Single-Shell Tank Surveillance Monitoring

Physical Access Restrictions(Cont.)

- Containment Control
  - Cannot break containment with present wind speeds greater than 15 M.P.H. without weather barriers.
  - Cannot break containment when raining without weather barriers.
  - Cannot create any mixed waste.
- Waste Disposal
  - All parts must be cleaned to low level waste specifications.
- H.P.T. Requirement
- Sniffer

Physical Access Restrictions(Cont.)

- Tank Equipment (Cont.)
  - Riser configuration is tank farm dependent and availability is tank dependent.
  - General assumptions regarding riser qty. and availability.
    - S.S.T. risers; ~8 total, 2 or fewer usable.
    - D.S.T. risers; ~25 total, at least 3 usable.
- Tank Specific Operating Parameters
  - Tank ventilation generally limited to range: $-3.0"H_2O$ to $+4.0"H_2O$
  - Highly corrosive environment
  - Any added gasses cannot create organic or chemical reaction (i.e. oxygen)

Physical Access Restrictions(Cont.)

- Tank Specific Operating Parameters(Cont.)
  - Limited on water addition(150gal./day & 1500gal. total)
  - Radioactive environment (assume 2000R/hr)
  - Lowest temperature tank is @ $-58°F$
  - Vapor space assumed to contain organics and ammonia
  - Ferrocyanide tank waste temperature must not exceed 150°C

Physical Access Restrictions(Cont.)

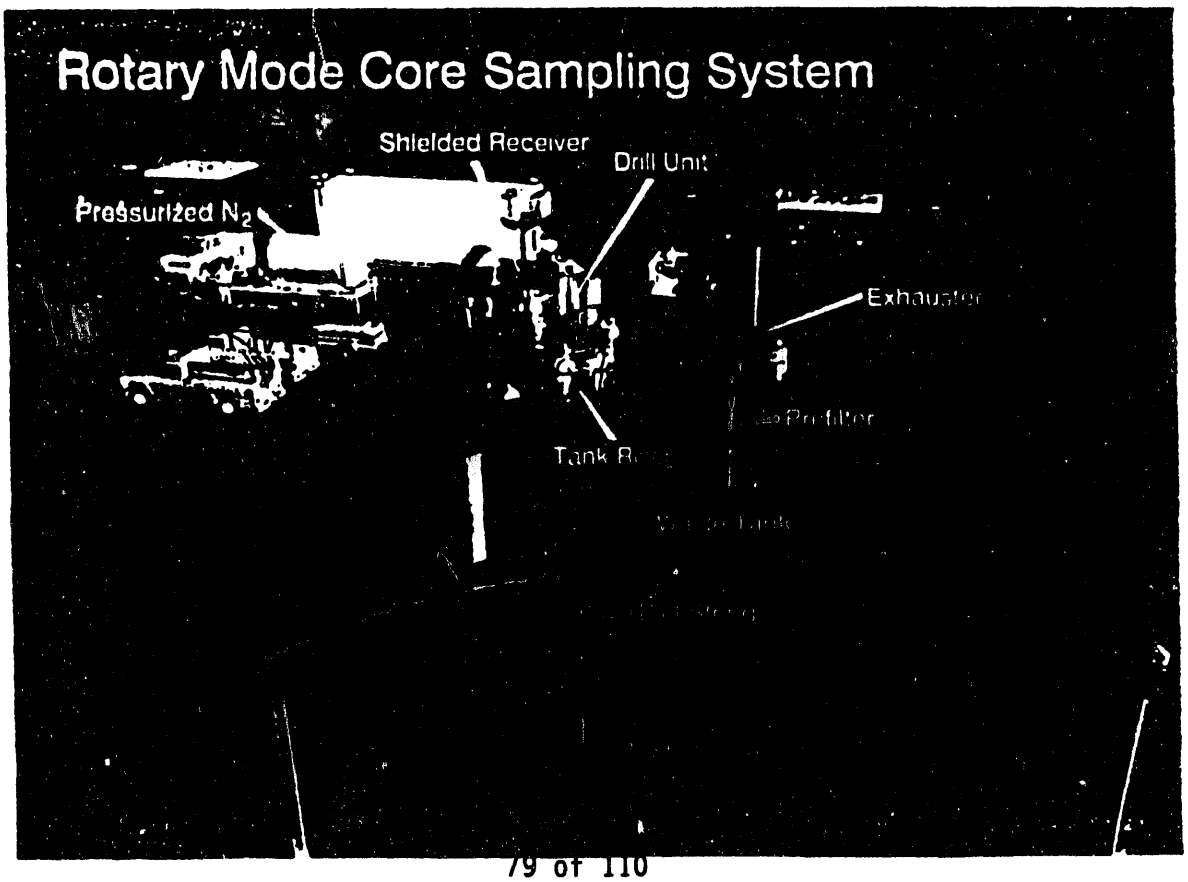
- Tank Specific Operating Parameters(Cont.)
  - Cannot initiate exothermic reaction
  - Equipment entering tank must be intrinsically safe (i.e. limited electronics ect.)
  - Cannot compromise waste tanks structural integrity
  - Waste material consistency can vary from: Salt Crystals ==> Sludges ==> Liquids
  - Cannot introduce new waste into tanks
  - Possible debris material in tanks (i.e. metals, plastics, canvas)

Typical Activities Associated With Deployment

- Safety Assessment
  - → Safety Documentation
- Environmental Assessment
  - → National Environmental Policy Act (NEPA) Documentation
- Acceptance Test Procedure
  -or-
  Formal Design Review
- Operational Test Procedure
- Readiness Review

Typical Activities Associated With Deployment (Cont.)

- Hazardous Waste Disposal Plan
- Work Plan
- Watch List Tanks
  - → Requires D.O.E. letter of approval for work.
- Radiation Work Permit



Waste Sampling Techniques

- Dip Samples - Supernate
- Auger - Salt Cake
- Push Mode Core Sampler - Liquids, Sludges, Soft Salt Cake
- Rotary Mode Core Sampler (9/93) - Liquids, Sludges, Hard Salt Cake

Program Objectives

- *Overall* - Develop, demonstrate, and deploy integrated sampling and analytical systems to meet characterization information needs
- *Hot Cell* - Develop and deliver instrumentation to perform routine scanning analysis of Hanford Waste Tank Core Samples
- *Field Systems* - Develop and deliver integrated analytical instrumentation and associated tank deployment equipment to perform infield characterization and monitoring to meet critical Tank Waste Remediation data needs

Promising Research and Development Activities

- Objectives
- Background
- Program Description
- Priority Technologies
- Conclusions

Applications

- Hot Cell
- Underground Waste Tanks (In situ characterization
- Other Field Applications
  - Ongoing tank waste characterization (in outyears)
  - Retrieval
  - Pretreatment
  - Grout
  - HWVP
  - External technology transfer (private sector)

TRUCK-MOUNTED CONE PENETROMETER
SYSTEM

Benefits

- Hot Cell
  - Increases laboratory throughput
  - Reduces analytical burden per sample
  - Reduces exposure (ALARA) and saves dollars
- Underground Waste Tanks
  - Provide information that will be used to resolve safety issues (TRU's, moisture, FeCN)
  - Reduces core sampling requirements
  - Expedites acquisition of selected information
  - Reduces costs and exposure (ALARA)
  - Reduces sampling/secondary waste generation
  - Increases potential technology transfer (Savannah River, Fernald, Oak Ridge, West Valley)
- In-line/Real-time Monitoring
- Outyear Characterization Verification Requirements

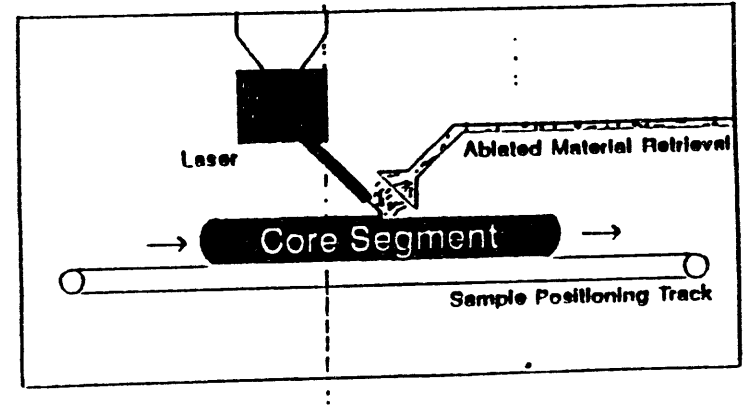
Promising Technologies

- Hot Cell
  - Laser ablation
- Hot Cell and Field Applications
  - Raman/Infrared Spectroscopy
  - Gamma and fast neutron scanning

Promising Technologies (continued)

- Field-only Applications
  - Activation Foils (for TRU's and moisture)
  - In situ physical property measurements (penetrometers)
- Deployment Platforms
  - Existing core sampling system
  - Truck-mounted cone penetrometer

Laser Ablation Hot Cell Scanning



Headspace Gas Analysis Group Notes

This section covers the notes taked during the small group discussion of the Headspace Gas Analysis Group. The notes represent a record of the questions and discussions of the group. The detailed evaluation of each technology has been put into tabular form in table 1, section 4.5 of the main report. Editoral comments and clarification have been added in square brackets [].

Panel Members

Steve Sharp - PNL
John Moore - MIT, Mass.
Scott Werschke - Midac - Longbeach, Calf.
Hiroshi Hoida Los Alamos
Mahadeva Sinh - Jet Propulsion Lab
Ishwa Aggarwal - Naval Research Laboratory

The above panel decided to take the approach of characterizing the gases first and then installing probes or monitors to watch what the gases are doing.

Pros & Cons of In-situ gas measurement - Stratification, - depends on whether or not tanks are actively ventilated - stratification might not be a problem. Another issue is time response - how long does it take to get it out. How long does it take to make it homogeneous.
Fourier Transform Infrared (FTIR) and Mass spectroscopy (MS) typically take a couple of minutes.

FTIR - problems with qualitative analysis - data bases are low resolution data bases.

Safety, environmental safety and understanding what's going on with the gases are the major objectives.

Gas Chromatographs (GC) and Whitaker sensors were recommended by the Tank Instrumentation Panel - only for flammable gases though. (HH)

Existing methods are FTIR, MS, GC-MS
Fiber Optics might be able to be used. Why not use a periscope?

The only reason you'd want to go in the tank is for stratification - fiber optical sensor could be used to take a precursor monitor of an event - it would have to be something that can sit in the environment of the tank for a certain amount of time - something with chromium gold would work. Surface Acoustic Wave is an idea.

List for brainstorming ideas:

Acoustic Wave

Fiber Optic
Open Path UV
FTIR Open Path
FTIR Closed Path
Raman Spectroscopy coupled with Lidar
LIBS
Point monitors at each riser

MS is too people-intensive (HH) from instrumentation panel

Organics need GC and MS combo
MS is good for non organics
GC is nothing more than a separator of the spectrums
FAIR doesn't require a vacuum pump

Determined that technology development for inside tank gas monitoring is probably not needed - existing systems being used MS, GC, FTIR are fine - but need fine tuning engineering. Less labor intensive methods would be helpful.

ABOVE TANK MONITORING

Light Detection and Ranging (Lidar)
Individual monitors at each riser

SAW = Surface Acoustic Wave

The following are comments made by the panel when discussing individual techniques.

FTIR-Open Path - lots of ways to implement in tank but would take some development - a lot of development. Would rank low relative to fixed path (FTIR fixed path). Easy to implement - but nobody wants it or needs it - doesn't give you the selectivity. Ease of implementation - operator use. Easy implementation, but special selectivity is difficult - but can be done. Easy to integrate over long path range.

FTIR - Fixed Path -

GC - can't do in tank directly; Sample must be taken out of tank - can't be continuous; area monitoring not so good - method is very mature; have to interface with computers and understand the data - calibrate once in a while.

Can print out PPM - but automatically needs calibration. Reliability is good. Maintainability - every once in a while you have to change a sensor . Could leave it for at least a month without worrying about it.

MS: In tank is impossible; Take sample out of tank - it will work, but it's labor intensive. Pretty well developed - but hard to use because you have to know fragmentation patterns - reliability , maintenance high vacuum system

requires regular maintenance.

GC/MS: Combination is Fairly Mature and reliable.

Fiber Optic chemical sensing - usually have particular species in mind for monitoring. Laser must be maintained. If fiber optic end gets dirty, it can't be calibrated out. Only one piece of data out of the intensity of light [generated by interaction with specific chemical species]. Single point monitor. Frequent calibration, replacement.

Surface Acoustic Wave - SAW - Must be intrinsically safe if in tank. Easily calibrated.

Raman spectroscopy - need a fairly intensive laser pulse in tank for the gas phase. (non-linear process) but could have multiple path. Could do in tank, but probably high risk , therefore preferably not in tank. Out of tank yes. Systems are commercially available, pretty good maturity. Lasers are hard to maintain - trained tech is needed to maintain them.

Lidar: interpretation is difficult - more selective than fiber optic or SAW techniques.

LIBS - Laser Induced Breakdown Spectroscopy: technique for metals - probably works on sodium; produces a plasma which may be a safety problem. Would break down aerosols - could see hydrogen, alpha, practically anything. Safety is a major concern for in tank. Currently used to monitor exhausts. Can buy some lasers that are very reliable, pretty straight forward for ease of use.

Photo-acoustic: pretty well developed - it's just absorption. Pretty simple to use. Uses pulse light source vs. laser. Good for non-radioactive sources. Produces shock wave.

FTIR - open path: Somewhat less mature than fixed path FTIR. Easy to use, can handle band overlap, know where your noise level is, expensive maintainability - but easy to maintain b, using Sterling Engine. A lot of consumable and a lot of electronics.

FTIR - fixed path - low maintainability .

UV-OP: fairly mature but only one manufacturer - Swedish Company. ease of use - doesn't distinguish interferences very well. No moving parts for reliability ease. Absorption.

Electro Chemical Cells: pH electrode is fairly mature - depends on what you are measuring, very easily used and maintained. Usually have to run a buffer on them; many times they don't last very long, a couple of months maybe.

ChemFETs (Field Effect Transistors): Fairly new technology. Easily used - sometimes have to be relaminated - but fairly cheep to replace- you'd just through them away.

Diode Detectors - simple to design - susceptible to radiation. Not very mature. If there is a contaminant, (interference) there is no way of knowing. Very specific to measuring only one particulate.

Bio Sensors: Single point detector

HH Comment: gauges are good to use; but you need an analytical instrument to back it up.

IMS- Ion Mobility Spectrometer - have to flush for contamination - doesn't require a pump - may have to bake it if it gets contaminated - detector doesn't have to be vacuumed to get the ions - simple technique - very portable - similar to a sniffer.

Note: Open path is a remote sensing with a telescope.

NOTE: Fiber is highly desirable.

NOTE: FTIR could use the same equipment (but different probes) for characterizing head space gas and also characterizing the solid wastes.

GC's alone can not detect hydrogen - GC/MS would detect hydrogen.

PRIORITIZED LISTS

Overall Characterization of Tank:**

GC/MS

FTIR Fixed Path - Would have to be coupled with a hydrogen monitor

LIBS

IMS

GAUGES**

Electrical Transducers
1. SAW
2. Bio-Based
3. Chem- based

Fiber Optic
1. Bio-Based
2. Chemical Based

Optical
1. Diode Laser

2. Fiber Acoustic
3. Fiber optic Fluorescence

** see table 1, section 4.5 of main report

Eliminate Raman because it's not very sensitive

Lidar - Lidar has the advantage of longer distances -only advantage would be spatial resolution - it won't tell you position along the path(?) - probably not worth looking at it as there is really no advantage - may be worker safety advantages ?

Didn't look at GC or MS because we basically covered them under the GC/MS category.

Area Monitoring - Worker Safety

Prioritized List **

- FTIR -Open Path
- UV - Open Path
- Lidar

FTIR and UV basically have the same rating except that UV has only one manufacturer now. Higher sensitivity that FAIR (OP)

**See table 1, section 4.5 of main report

CONCLUSION NOTES:

The reason to go in-tank monitoring was because of response time and a desire to eliminate the stratification concerns. [The importance of stratification was not known by this group. May not be of great concern.]

Heated sample lines are a requirement for removed samples.

Gauges would be both in tank and out of tank, at the exhaust ports. These would be part of a continuous monitoring type of system which comes after characterization.

Elemental Analysis Group Notes

This section covers the notes taken during the small group discussion of the Elemental Analysis Group. The notes represent a record of the discussions and questions of the group. The detailed evaluation of each technology is included. Editorial comments, queries and clarification have been added in [] square brackets.

GROUP PARTICIPANTS:

Clarence Homi (WHC)
Herb Sutter (SAIC)
John Hartman (PNL)
Monty Smith (WHC)
David Cremers (LANL)
Milt Campbell (MACTECH)
Martin Edelson (AMES)
Dave Dodd (WHC) (part time)

GENERAL DISCUSSION:

Heterogeneity -- All tanks should be considered heterogeneous. The retrieval process will mix the wastes anyway and characterization will have to be done again. This pre-retrieval characterization step is required for safety and regulatory reasons.

-- The Wyden bill [addressing "watch list" tanks] requires us to characterize the tanks, but to what extent? The Tri-Party agreement [DOE, EPA, Washington State Department of Ecology] required two complete core samples with specific lab analysis for each tank. [Revision of the agreement is underway, and will probably have variable requirements for sampling depending on the nature of the tank waste.]

-- You need several cores at different locations in the tank to validate the core samples. The cores are very expensive for the information that is gathered. Why are we taking these samples? What data are we trying get? We are interested in Safety concerns and (somewhat) regulatory requirements for characterization. Currently no horizontal mapping is being performed. Recommendations have been made to consider horizontal surface thermal mapping methods for high heat tanks and ferrocyanide (FeCN) tanks. We still need to provide accurate data. The retrieval needs can probably be met by determining major chemical constituents at percentage level accuracy and physical characteristics, in addition to addressing safety concerns. Techniques that are adequately successful and accurate that can provide the analysis needed.

Cesium will be easily viewable except where it was treated with FeCN. [FeCN treatment caused preciptation of Cs; it is anticipated that Cs may be concentrated at lower layers in the FeCN treated tanks.]

Discussion of the lateral heterogeneity of tank materials: If cores taken from different lateral positions in the tank are similar (same Z profile), then you only have to analyze one core. In this case there would be interest in proposing that one core sample should be able to represent the entire tank. [The feasibility of this scenario has not been determined.]

The DREAM program is intended to include studies and statistical modeling to determine what constitutes adequate sampling.

Good technology and bad sampling do not lead to good results.

Do elemental methods need to be done in situ?
-- In situ analysis would validate core analysis; therefore reducing cost, risk, and decreasing waste.

Laser Ablation can currently be deployed only in the hot cell. It is not expected that it will ever be allowed to be used in situ for safety reasons. [Much discussion has occurred regarding the possibility of laser ablation being deployed in a subset of tanks. It was concluded that development of alternate sampling methods was warranted. Note that the laser ablation-linked methods are not true in situ analysis, but remove minute quantities of material for analysis with a field instrument.]

Hot Cell availability issue. The Hot Cells are available on site, but they are not set up for chemical analysis. It is currently difficult to find hot cell space, but that is being addressed now. There are other options that are being considered to address the Hot Cell availability.

Should the availability of real material be one of our issues?
-- Yes, but how about making the real tests occur at the Hanford Site. There is a data acquisition consistency issue. There needs to be consistency among the simulants and real materials tested with any method.

Question: Which of the safety issues can be addressed with elemental information? This remains to be determined.

SUMMARY of GENERAL ISSUES:

Representative Sampling
Hot Cell Access for Technology Demonstration & Validation
Good Needs Data
Programmatic drivers for In-Situ Analysis
Needs, objectives, funding stability
Simulant/Standards Availability

Single "perfect" tool vs. suite of tools and integrated data analysis
Availability of real materials for technical evaluation

CRITERIA FOR EVALUATING TECHNOLOGIES:

Applicable in Hot Cell or In-Situ
Capability vs. Need
- -- Elements
- -- Sensitivity
  - Excellent 10^{-6}
  - Good 10^{-4}
  - Bad 10^{-2}
- -- Accuracy
- -- Calibration
- -- Stability
- -- Sampling Rate
- -- Sampling area & volume
- -- Volume vs. Surface sampling
- -- Precision

Deployment Options
- -- Decontamination/minimizing creation of contaminated material
- -- Equipment External
- -- Equipment Some in/ Some out

Operability/maintainability
- -- Staff Training
- -- Longevity of product

Matrix Effects
Interferences
Upper Limits
Development Time/ Maturity - This is an issue because we are required to have tank samples for ALL tanks by 1999 & for safety issues we need tank samples by 1996/97.
Cost -- Technical feasibility is more important than cost. Most of the cost will be in the deployment to the field after testing in the hot cell.

TECHNOLOGIES TO CONSIDER:

Laser Induced Breakdown Spectroscopy (optical emission)
Laser Ablation (LA)/Mass Spectroscopy (MS)
LA/Inductively Coupled Plasma (ICP)/Atomic Emission Spectroscopy (AES)
LA/ICP/MS
Laser Excited Atomic Fluorescence Spectroscopy (LEAFS)
LA/Laser Induced Fluorescence (LIF)

X-Ray Fluorescence (XRF) (potential problem with background radiation/ contested issue); Ask John McCowan & Ron Sanders;
Neutron Probe? (equivalent technologies)
Gamma Spectroscopy (existing/proven technology)
Fluorescence technologies -- is it elemental?? Can locate uranium
Long Range Alpha detection
Atomic Absorption methods (Laser Ablation AA, Furnace AA) This would be a difficult method to control heat wise; requires sample preparation & doesn't provide the sensitivity that other technologies do.
Foils -- Technology to measure Sr90 in tank. Beta measurements needed. Need measurement of neutron flow rate. Foils can be used to measure Pu, H, & water. Copper Foil (24 hours measurement time, passive probe)
Gamma Maps (surface mounted)
High Resolution Mass Spectroscopy
Technologies to measure transuranics (TRU) -- Ion specific probes

NOTE: Inductively Couple Plasma (ICP) is not necessarily the only technology to be used in conjunction with Laser Ablation (LA). Another option of fluid injection may work instead of LA. Mechanical method for ICP/MS.

ALTERNATIVE SAMPLING TECHNOLOGIES
- Micro-Dissolution
- Fluid/Slurry Sampling/Extraction
- Fluidized Bed
- Mechanical Grinding
- Freeze Sample -- Grind
- Sonic Drill
- Micro Boring

The smaller your sample is, the higher probability that the sample is not representative of the tank. This is an issue with micro-boring. [Note - Since the tanks are known not to be homogeneous, are there any cut off points in sample size that are statistically significant in terms of obtaining some idea of what the overall tank contents are? What is the relative merit of obtaining multiple small samples as opposed to a single larger sample?]

Issue - an alternative approach would be not to remove the sample from the tank, but do all analysis in the tank.
Concern - Safety & regulatory requirements may keep this from happening.
[Note - The nature of analysis and the means for performing it in the tank were not recorded. Technical issues may also be present.]

Issue - The alternative sampling technologies are not addressing the in situ sampling issue. It is not clear that the list of alternative sampling methods

could be deployed directly in the tanks. One panel member feels in situ characterization or direct sampling of materials in tank should be the focus and rejects technologies which would not work in tank.
Response - It is agreed that in tank sampling/analysis is ideal, but the reality is that the group may have to consider only Hot Cell technologies.

LASER INDUCED BREAKDOWN SPECTROSCOPY

Sensitivity: LIBS can detect all elements with varying sensitivity. What level of sensitivity constitutes good, excellent, poor? The majority of elements (or all elements) can be identified at part per thousand levels. Is there a problem with linearity? Yes, you choose which element you want to look at. LIBS is poorer at measuring actinides. Noble metals have not been tested. Remote measurements have been done at 80 feet (in sunlight) and they gave results similar to what was expected.

Benefits of LIBS include the fact that it is entirely an optical technique and it does not have to contact the sample. The sampling spot on surface has a diameter in the micrometers. Approximately .03 cubic centimeters is volume of the sample. Standard rate is 30 samples per second. Testing conditions include a laser with wavelength of 1.06 micron, 150 mJ power, 30 Hz pulse rate, and 2 inch stand off distance. The signal detection is sensed in the range of 250-700 nanometers. Fiber optics may be used for the input beam and signal collection.

DEPLOYMENT - Base Equipment (Source & Detection) External; Fiber Optic probe to waste; APPLICABLE in HOT CELL
ELEMENTS - ALL
SENSITIVITY - EXCELLENT Detection: Be, As, Cd, Se, Alkalide, Alkalide Earth, Hg, P, Tl
GOOD Detection: Actinides
POOR: None found to this point
PRECISION - secondary to sensitivity because of matrix effects
ACCURACY - secondary to sensitivity because of matrix effects
INTERFERENCES - There are interferences, but they can be adjusted for through selection of alternative lines. Have not run into any insoluble elements.
ISOTOPIC Selectivity - Do not know yet.
UPPER Detection Limits - Dynamic range - few % - matrix specific; selection of weaker lines
SAMPLE TYPE - Can be used in all three Liquid, Wet & Dry samples.
AREA - .1MM
DEPTH - .1MM
CALIBRATION - +/- 10% ; Replicate Samples, Match matrix.
MATURITY - Field ready. Transferred to scientific laboratory operated by individuals with British High School Education (equivalent to 2 years of American College); Lab Experience; Field System (1 element) Beryllium; R&D is near finish, theoretically ready for moving to Hot Cell.

DEPLOYMENT OPTION - Base Equipment (source & Detection) External; Fiber-optic probe to waste.

KEY QUESTIONS - Calibration and matrix effects
(need relaxed if sample has internal standard/reference)
Throughput rate (estimated 10 minutes per seg.)
Fiber Optic Survival
Sensitivity for TRUs
Surface volume analysis
Tank Safety Approval
Deployment time

LA-ICP/MS

The major difference between LIBS and the other Laser Ablation (LA) linked methods is that with LA methods you must transport material to the sensor.

Capability:

ELEMENTS - He and F not detected, but all other elements are.
Isotopic selectivity - yes, isobaric interference

SENSITIVITY - Excellent for all, except He & F

DYNAMIC RANGE - 10+9

INTERFERENCES - Molecular-Ion Int.; Isobaric; Doubly Ionized Species

SAMPLE TYPES - Liquid, wet, & dry.

SAMPLING - AREA ~.1mm
DEPTH ~.1mm

CALIBRATION - Sum of all detected ion masses; for best accuracy (5%);
Replicate samples, match matrix.

TEST CONDITIONS - Air Beam path, 1.06, 532, 355, 255; 20-500Hz; Opt. Standoff ~2"; Ablation -- ICP/MS up to 100'.

DEPLOYMENT OPTIONS - Laser Source (cold); Fiber-optic beam transport; Final optics/plume collection (HOT); ICP/MS (Glove Box)

MATURITY - Lab Experience; including ICP/MS in Glove Box; Round robin results for HWVP noble metals; senior staff for operation today; NO field systems to date; AME/P-E are preparing for cold site; V.G./Fissions, P-E, Sieko, Finegan have commercial version for 'polite' samples (lab). (all Nd:YAGs at 1.06um)

KEY QUESTIONS - Calibration & Matrix effects
(need relaxed if sample has an internal standard/reference)
Fiber-Optics Survival
Tank Safety Approval
Throughput Rate
Surface vs. volume analysis
Deployment time
Plume transport efficiency
Instrument Contamination

LA - ICP/AES

Capability:

ELEMENTS -	No He, but all others. Isotopic selectivity - yes, for actinides
SENSITIVITY -	Excellent for all except He, He is 10-5
DYNAMIC RANGE -	10-6
INTERFERENCES -	Spectral interferences - use alternate lines - high resolution monochrometer to eliminate interferences
SAMPLE TYPES -	Liquid, wet, & dry.
SAMPLING -	AREA ~.1mm DEPTH ~.1mm
CALIBRATION -	For best accuracy (5%); Replicate samples, match matrix.
TEST CONDITIONS -	Fiber optic/air path; 1.06, 532 excimer (248); 20-500Hz; Opt. Standoff ~2"; Ablation -- ICP/MS up to 100'.
DEPLOYMENT OPTIONS -	ICP source (HOT); Monochrometer/Detector (COLD)
MATURITY -	Lab Experience; Fernald Field Test; commercial sources are available.
KEY QUESTIONS -	Calibration & Matrix effects (need relaxed if sample has an internal standard/reference) Fiber-Optics Survival Tank Safety Approval Throughput Rate Surface vs. volume analysis Deployment time Plume transport efficiency ICP Instrument Contamination

LEAFS and LA/LIF

Requires a plume for sample to go to ICP. Might require Laser Ablation or alternative technologies discussed yesterday. Tremendously Selective Capability:

ELEMENTS -	Single (several element) technology Laser must be tuned to element specific line Isotopic specific for actinides Very useful for very specific Isotope detection, experience with U, Pu, many other elements. Reference for the isotope detection tests: Omenatto, et all ~1985 Eastborough)
SENSITIVITY -	Excellent where Demonstrated (10-6)
DYNAMIC RANGE -	?No Experience Known, at least 10-4
INTERFERENCE -	Very few.
SAMPLE TYPE -	works well with liquid, wet & dry sample types, BUT needs plume to read the sample.
SAMPLING -	Area .1mm diameter Depth .1mm

CALIBRATION - Repl. Samples, Match Matrix
TEST CONDITIONS - same as other LA-ICP techniques, except need lasers to promote fluorescence, used cover.
250nm-600nm wavelength
Tunable Dye Lasers - no good, use Diode Lasers or hollow cathode lamp, instead. Dye lasers my not be suitable for routine operations.
Best way to perform spectroscopy is sweep over sample.
DEPLOYMENT OPTIONS - Base Equipment (Source & Det.) External; Consistent with fiber optics to sample. Assume LA sampling.
MATURITY - Research lab technique at this time; NOT A MATURE Technology. Needs more work than some of the options that have been suggested so far. LA/ICP LEAFS could be used for routine lab analysis at this time. Not used in Hot Cells or to field system yet.
LA/ICP/AFS - This is commercially available (except the LA part, which is actually available), from BAIRD, CO. Will need highly trained research staff to operate. Long time before Deployment.

KEY QUESTIONS - Why is this an option?
Versatility
Calibration of matrix. Can you get away from matrix effects?
Is there a need for single element isotopic specific measurements of tank waste samples? This is not available with other techniques. 4&5 - Same as LIBS

LA/AA

Provides more accuracy than ICP methods, but do we need that level of accuracy at this stage in the game?? It is beneficial for alkalides, but once again, is that necessary? More limited number of elements (less elemental capability than ICP based techniques), lacks versatility. Excellent single element technique if you need that. Best silicant analysis you can use, if you need that information. This technology has be demonstrated, but the group does not feel it is necessary to consider this technology.

FLUORESCENCE TECHNIQUES that do not use LA

Work without LA techniques; no material removal. Technique is semi-quantitative, because it can only see certain elements at certain states. Very restrictive on the number of elements/compounds it can identify. Highly Matrix dependent. Not isotopic. Not a recommended technology, considering the alternatives.

Induce fluorescent emission without altering sample form. No material removed.
Highly matrix dependent
Semi-Quantitative
Limited number of elements/compounds
not isotopic

X-RAY FLUORESCENCE

This technology will provide valuable information. There is an ASTM standard that gives information on this technique.
Capability:

ELEMENTS - Boron at high concentrations, Al & larger Z number in percentage levels. Better for High Z. Not isotope specific. Limited to X-Ray source, better sensitivity as Z increases.

SENSITIVITY - Good for high Z, poor for low Z. The angle could increase the sensitivity of the techniques

INTERFERENCES - particle size effects. Surface area technique

SAMPLE TYPE - works well in all sample types

SAMPLING - Probably need to collect sample on a filter. In Tank, surface technique, as received - Area relatively large; mm to in; Depth um to mm. On filter paper similar area & depth, but probably more accurate sampling. This will probably not become applicable in tank.

DEPLOYMENT OPTION - Sample as received: potential local rad level restriction. Possible sample matrix problems. Could not be done in tank because it is probably too hot. Can be done in Hot Cell, practical if done in a plume. Rapid, non-destructive analysis. Can be designed as scanning system.
Filter Sample: (sample analysis of filter paper) Totally non-destructive. Practical technique, provides more substantial data than other techniques, and allows for an archived sample. Use Ablation Plume sample. Can archive sample. Toll in Low radiation environment.

MATURITY - Very mature. Many routine labs use this technology. Fieldable instruments in existence commercially. Mining industry, lead Analysis, ... Current systems are looking for very specific analysis. Does that make it easier to transfer technology? The commercial techniques for soil do have several elements that they can detect.

KEY QUESTIONS - Valid tool. Matrix Effects, calibration effects, some interference. For screening this has AWESOME capabilities. Rad level tolerance/limits. Configuration options to reduce rad sensors. Some interferences. Tank to LeRoy Lewis at

Idaho Falls about this technology. Archivability of laser plume is a BONUS. Low Z sensitivity is an issue. Not currently proven for in situ use, and probably not likely. Surface vs. volume analysis. Deployment time. Throughput rate. Tank safety approval if use LA with it to generate the plume for filter analysis. Durable, less down time.

FOR SCREENING of tank waste this is one of the TOP TECHNOLOGIES!!!!

GAMMA Spectroscopy/GEA

Measures Cesium 137 & Arsenic, Eu154, Co60 could see Plutonium if it is in high enough concentrations. Vertical profiles, horizontal maps. Hot Cell gamma scanner with CdTe for NDE core analysis. In-tank LOW's, Cone Penetrometer, & S mount array. Experience with demonstration of CdTe detector system in LOW's. Mapped vertical strata for a couple of inches; strata resolution 2". Approximately, 2 inches for tank. CdTe does not work well above 80 degrees F. Documented in letter reports to FeCN program. Semi-quantitative data. Calibrated, & needed high power source for proper calibration. Resolution of isotopes of interest were clearly discernable. Very Good/excellent qualitative analysis. This has been focussed on FeCN tanks. The detector itself is 1 mm, the total of 2 inches in size was mostly in shielding required for collimation. Part of the FeCN tank safety program. Probe safety factors - detector voltage is probably low. Gamma probe penetration is probably less than 6 inches, which would make sluicing an inappropriate deployment method.
SENSITIVITY - Geometry & Isotope specific.

PROBE Geometry dependence
Calibration / spatial resolution; probably cannot calibrate because semi-quantitative method.
Sensitivity - can only do radio-isotopes, not elements
SAMPLE Type - all
INTERFERENCE - spectral interference could be a problem. Mostly a problem in newer tanks, old tanks have reached the maturity decay cycle which may decrease interferences.
SAMPLE - Volumetric - truncated cone
2 inch starting point. 3-4 inches in depth which is dependent on the source strength & energy dependent / spectral dependent. Geometry Sensitive.
TEST CONDITIONS - Hot Cell Scanner, Liquid Observation Well's (LOW's). Mature technology.
DEPLOYMENT OPTIONS - hot Cell, LOW's, in-situ with appropriate hole size. Potentially okay for small bore cone penetrometer (1 inch).
MATURITY - Excellent. French are working toward improving the resolution. H.C. systems used at Hanford. Field systems used at hanford.

KEY QUESTIONS - How possible is it for them to meet the 1 inch constraint and what will the impact of that size change be. Safety for in-situ deployment. Is the limited knowledge we get from this technology worth the work/investment we make. Applicable to limited species. Ability to reduce probe size while maintaining required performance. Data acquisition is dependent on the activity in the tank. Cs was 5 minutes per measurement. Scan rate - spatial resolution; source strength, counting statistics. One of the most mature technologies - and the most that has been in situ. Hot Cell deployment for cores is expected to be 1994. LOW Tank deployment experience (dry well) was 1992. Detection limit & Matrix effects may be an issue when dealing with DQO. Sensitivity for required data (DQO's). Matrix effects
Looked for Europium to be sure that the Plutonium quantity is truly represented.

Gamma Maps (Surface detector Array)

Lateral map of gamma from above tank waste surface.
Locate lateral hot spots.
Total gamma mapping. Detects total gamma in tank. Locates Hot spots in the tank. Have to do collimation. The method must stay in tank for more than 24 hours. Non-intrusive technique, sitting on the burm, NOT in the tank. Have used this to locate the burial pits. Measures radiation dose, not looking for discrete isotopes. Potential difficulty with attenuation. Experience from nuclear burial sites characterization. Collimation vs. Standoff distance effects on Resolution in waste. Will the data answer the questions that we have/need to answer.

What is the NEEDS Driver for this technology?? Has to be far along in development or it is not worth doing. If it is easy & useful, it would be worth it. Array could be portable to allow sequential analysis of series of tanks.
Analysis of array data required / 3-d capability to determine strata of tank. DOES NOT REQUIRE TANK ENTRY. Surface contamination may be a problem. Can it be used in SSB detection, safety detection of leaking tanks. Off-tank position to detect leakers. Could be useful for monitoring sub-surface barriers effectiveness. THIS IS a Surveillance & Monitoring technology more than a characterization technologies. Possible interference from surface contamination.
Gamma mapping with circumferential arrays in annulus. Tomography analysis -- More of Surveillance & Inspection technology than characterization tech.

Questions arose about the absorption length in waste and solid and steel/concrete. No information was available.

Long Range Alpha Detection (L-RAD)

Allows for characterization of items with intricate detail (example: typewriter) Measures upper alpha emissions; close to the surface. Gives you a true measurement of the alpha particles, and low-energy beta. Signal proportional to alpha flux's and low energy beta's.
In a combination with other technologies this could be considered a pre-screening use. Has no elemental or isotopic specificity capability, just notes that there are alpha particles there. But there is no mystery on whether there are alpha's in the tanks. does not require sample preparation. Immune to gamma's, which eliminates background noise. Just gives you alpha on the surface. Low maturity. Alpha could be related to TRU's distribution, therefore, the technology would give you this information. What is the difference between standard Alpha or Gamma Detector?

Sensitive & very fast. CMST-IP is funding in FY94 for air monitoring. May be interesting to BW-ID. Technologists need to consider possible TWRS applications & deployment techniques.

This might hold promise, might be useful, but let the LANL group work on it.

Activation Foils

(Brodzinski is expert) [Foils are passive detectors of neutrons, used to detect transuranics; used with an active neutron source to measure water. As with any neutron activation method, the active measurement is of hydrogen rather than water per se. Foils require exposure for periods of several hours followed by removal and calibration of the results in a lab.] Another kind of detector. If you have a large enough hole that an active detector can be used, you should use it vs. foils. Foil could be used in interior of drill string or cone penetrometer which requires 1 inch diameter. Anything you can do with foil you can do with an active detector, except with size problems and high background areas. Two step process. 1) foil itself, 2) neutron detector in the foil.

Don't use foils unless you have to, but the current situation encourages/requires the use of foils.

Adaptable to small sizes. Intrinsically safe. Exposure time required ~ 1 day. Requires Development of calibration & validation. Requires lab analysis of foil after exposure. Has been demonstrated in LOW in 1980's. Technique is proven/mature; doesn't require Technology Development, except in calibration and validation work. +/- 20% in detection of absolute moisture data. Relative changes in +/- 5% - good for relative moisture data.
Potential uncertainty in true concentration measurement is the matrix effect. Alpha measurement, Fluoride monitor needed or historical information. Matrix Effects (F effect on TRU #) Max distance is 3-20 cm. Volumetric sampling ~40cm diameter. Curium 242 showed itself as a major contributor to TRU's when it was not intentionally being detected. n detection/no element specific.

LOW's - some are fiberglass & have 10% boron content which could cause interference. CMST-IP is funding this in FY94. Consider a mature technology and do not support until ready to deploy.

Probably best moisture monitor that we have; even considering its flaws. Mature technology, so time frame is reasonable. Measure moisture by including a neutron generator. Measure of the low Z material which can be calibrated to determine moisture content. Neutron Probe is the active detector.
TIAP - Tanks Instrumentation Assessment Program

High Resolution Mass Spectrometer

Def: Resolving Power 10 time to 100 times better than standard ICP\MS (10-4 AMU's). Solves some isobaric Interferences. Superior detection limits due to reduced background current levels. Souped-up ICP/MS with higher resolution & sensitivity. Can be used to determine iron levels. Commercial - can be purchased from VG as a system.
Capability: (commercial availability, but would need to be modified for our purposes.
ELEMENTS - ALL, except He, F
Isotopic selectivity is excellent
SENSITIVITY - Better than standard ICP/MS; field deployable may require high maintenance. Mass Scan Rates: 20-30 minutes ?? Depends on resolution & range.
DETECTION LIMITS - Dynamic Range, 10+9
INTERFERENCES - Significantly reduced from ICP/MS; more intrinsic isobaric interferences [some very close isobaric cases] are still there (e.g. cannot detect differences between Pu238 & U238).
SAMPLE TYPE - All
SAMPLING - Requires LA or some other sampling technique.
CALIBRATION - same as ICP/MS
TEST CONDITIONS - ?? DO not know? No knowledge of LA/High Resolution MS application
DEPLOYMENT OPTION - Same as ICP/MS, except a larger, slightly more sensitive instrument.
Maturity - the lab instrument (system) is commercially available.
Intelligent/well-trained operator. No field experience

KEY QUESTION
Why would you want to do this?
Is there a need for the high resolution data?
Is increased mass scan time suitable? Sampling homogeneous limits, throughput requirements.
SAME QUESTIONS as ICP/MS

2nd technique
High Resolution MS Lab Development System
University of Florida (John Eiler)
Comm. Brucker High Res MS (Ion Cyclotron resource instrument)
Glow discharge ion source (ion trap instrument)
Resolution (1/600000 AMU's) Currently at the experimental status. Critical requests for sources. Offers a way to transmit many isobaric substances. Decreases isobaric interferences. Estimated cost?

Probably a very specialized tool for specific tests.

Screening method per Milton - means of deciding should we, or should we not do something. purpose of a screening method is to determine % of main chemicals. What chemicals would you choose if you had to select ones to screen.

Molecular Analysis Group Notes

This section covers the notes taken during the small group discussion of the Molecular Characterization Group. The notes represent a record of the discussions and questions of the group. The detailed evaluation of each technology has been put into tabular form in table 3 of the main report. Editorial comments and clarification have been added in square brackets [].

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OPENING DISCUSSION:

Defining what species we are looking for:
CN (cyanide), moisture or water content, NO2 (nitrate) and NO2 (nitrite), TOC (total organic carbon), Organic Compounds, TBP, Chelating agents (particularly EDTA), kerosene, NH3 (ammonia), Metal OH (hydroxides), NaOH

Requirements For The Techniques:

- Must work in situ
- Non Destructive
- Non Contact
- Real Time
- Remote Operations 100 ft, 300 ft, 900 ft
- No Sampling or out of Tank Preparation
- Portable
- Deployable
- Qualitative (speciation capability)
- Quantitative analytical results
- Environmental Survivability (chemical and radiation)
- Radiation Survivability
- Size
- Operator Skills Required
- Inherently Safe
    - -Cost
    - -Effective sampling Area

GOALS OF CHARACTERIZATION:

Short Term:
An initial goal of characterization is to provide a screening device to indicate whether a tank fits into one of the safety concern categories: high heat, FeCN, hydrogen. All major constituents should be screened for in the tank at % levels with analytical accuracy of 1 to 10%.

Long Term:
In the long term, the purpose of characterization should be to assist in determining pretreatment options and processing options such as clean salt.

Additional Techniques to consider:
Nuclear Magnetic Resonance (NMR) Techniques, Raman Imaging, Infrared (IR) imaging, IR Reflectance spectroscopy, mass spectroscopy independent of laser ablation, liquid chromatography, micro-sampling methods for techniques in general

Each method was rated for each of the above categories on a scale of 1 to 10 the results of these rankings are summarized in Table 3, section 6.10 of the main report.

Analysis of each technique in terms of the above requirements:

In general it was felt that most of the technologies could be engineered to fit into a cone penetrometer for deployment. It was also felt that the radiation survivability of all of the technologies relied on the effectiveness of radiation hardening of the fiber optics. For most techniques, it was thought that in early stages of deployment skilled operators would be necessary to perform the analysis. With time, others could be trained to monitor the instrumentation in the case of monitoring tools, and use the instrumentation in terms of the analytical tools. It was also felt that all technologies would require about the same amount adjustment before they were fully operational. It was felt that a great deal of development still needs to be done on all of the technologies before they go in the hot cell or the tank (with the exception of Raman Spectroscopy which is already being tested in the hot cell). All of the techniques discussed seriously involved little / no sample contact.

TECHNOLOGY EVALUATION:

An initial attempt was made at performing numerical rankings of technologies, shown in Table 4, Section 6.10 of the main report. It was decided that instead of performing numerical rankings, the focus should be on determining what techniques were best for different types of analysis. It was felt that the numerical weightings had helped to identify strengths and shortcomings of different techniques, and now it was possible to discuss what steps needed to be taken before the techniques could be deployed, both in tank and in the hot cell. It was also felt that the group could identify in general what needed

to be done, and leave it up to the experts in each area to identify the specific details.

The group also thought it was important to divide up the techniques into those that were more for monitoring and those that were more for analysis. It was additionally discussed and resolved that the techniques should not all be graded against each other, but rather be graded against the different techniques that worked for the same analytes.

Laser Ablation as a sampling method:

Laser ablation was considered to be a very good sampling method for coupling with various analytic techniques for elemental analysis. More research needs to be done to determine its effectiveness for molecular analysis. However the overriding question in its effectiveness as a sampling technique for the tank environment concerns the possible spark hazard associated with ablation. Another question of concern in the molecular analysis involves the probable loss of specific molecular species as the material is ionized.

Laser Ablation can be coupled with Mass Spectroscopy for species identification for phosphate, carbonate, and sulfate. The technique can also be used for nitrate and nitrite although problems in nitrate to nitrite ratio have been experienced. One problem with using laser ablation for molecular analysis is getting to an ionic state without changing the chemical composition. Laser ablation cannot be used as a monitoring tool as it requires the attendance of skilled operators. It is felt that the "spark" hazard will most likely limit laser ablation to use in the hot cell. One laser ablation instrument can cover a broad range, and the only really sensitive parts of the hardware are the 0.25" capillary tubes which can be changed in and out fairly easily. Although laser ablation has good potential for molecular analysis, it was felt that a lot more development was needed for this application.

Fourier Transform Infra Red Spectroscopy (FTIR) / IR absorbance spectroscopy:

The major concern in FTIR analysis was the attenuation of light in the fiber optics or light pipes required for in situ deployment. [FTIR generally transmits light at IR wavelengths in the range of 3 to 15 microns. Silica optical fibers used for shorter wavelength IR and Raman spectroscopy do not transmit at these wavelengths.] It was decided that not enough work had been done in this area and more development was needed.

FTIR analysis can be preformed two different ways: sampling with diffuse reflectance, or using attenuated total reflection (ATR) sampling. Diffuse reflectance generally uses parabolic mirrors, and does not require sample contact, while ATR requires touching, through a coupling between the fiber optic and probe cover. Dow has used ATR for remote sensing. The first decision that needs to be made involves which type of sampling method makes

more sense. A potential setup of hardware would include a miniature ATOF, with Fiber optic shielding, with a lead shielded box in the headspace at 10 micrometer wavelength of fiber. Longer wavelength work has been done in the application of this technology on smoke stacks, for california emissions standards. FTIR could be used for monitoring even though it utilizes a broad band width, if there was proper data fitting, (ie least squares). The probe will most likely be larger than those used for laser ablation and raman spectroscopy. Probe contact with the sample of some kind will probably be required if ATR sampling is used. Sample alignment is seen to be the only potential area where tweaking with the instrumentation would be necessary. It is uncertain what type of contact would be required with a sapphire or diamond window were used, as in the past zinc celinide crystals have been used effectively.

Due to the fact that this technique is in its infancy, the life span of the instrumentation is too hard to predict, but will probably be limited by the fibers, as the crystals can easily be changed out and replaced. In order for the technique to fully realize its potential, more development work needs to be done in chacoginide glass and fluoride fibers, especially if they are to withstand the high radiation environment. Fiber development is thought to be the key limiting factor of FTIR. The techniques is thought to be best suited for use in the hot cell, and not in the tank.

Near IR Reflectance spectroscopy:

Near IR Reflectance spectroscopy utilizes a broad band source, with wave numbers ranging from 4000-6000 inverse cm [1.6 to 2.5 microns wavelength]. The major concerns with this technique involved data quality. Most people were unsure how the instrumentation would react in the hostile environment, and skew both qualitative and quantitative data.
The basic setup of a near IR reflectance spectrometer would involve a tungsten halogen lamp, typically with a bundle of fibers to transmit broad band source. In Gallium Arsenide fibers, the signal to noise ratio is generally quite good for fibers up to 100 ft in length. With fluoride fibers, a 1/8 inch diameter bundle for diffuse reflectance sampling can either use one bundle for sending light and another for receiving, or it can collect within the same bundle and be separated by a monochrometer. Fluoride fibers are generally not used because they are expensive.

The speciation capabilities are dependent on how well you can make reference measurements. That is you cannot perform blind searches, you have to have an idea what you are looking for. The method is thought to be best suited for moisture and pH, as it was previously used in industry to determine octane numbers. In surrogate samples, it could detect water at limits of less than .5%. For pH it is much more accurate in caustic brines than caustic normals. Of all the techniques, this is thought to have the most promise for pH monitoring. It potentially could also look for CN and organics, and possibly inorganics as well. One instrument that is tunable with filters would be sufficient; fixed instruments are also a possibility. The technology could be

adapted for use in both the hot cell and the tank, however it is very operations intense, not requiring PhD level operators, but does require constant attention. This technique could be used safely both in the hot cell and in the tank.

IR emissions imaging:

Debate on applicability and usefulness of IR imaging and what its applications are. Applicable to temperature and moisture, not necessarily molecular speciation. Difficulty in quantification and qualification of data.

Raman Spectroscopy:

Raman spectroscopy is the the best developed technique in terms of in situ analysis at Hanford. The major concerns voiced by the group were the need for highly skilled operators and the expense of the program.

Raman spectroscopy may be the best technique for molecular analysis of ferrocyanide, with a detection limit of 1000 ppm. Raman spectroscopy may also be useful for moisture, organic carbon, and ammonium with a detection limit of .1M. The accuracy of the technique is somewhere in the realm of +-5% in complex samples. More testing is needed on real materials and some sort of least squares fitting is thought to be needed in the Fourier domain background. It is felt that it is important to have a concentrated development effort on the probe design, fitting and testing.

Surface Enhanced Raman Spectroscopy:

This technique was determined to be inapplicable, because both sample preparation and direct contact between the instrument and the sample is required.

Resonance Raman Spectroscopy:

This technique was also determined to be inapplicable because it is used mainly for low concentration aromatics and it was felt that it did not have a wide enough analytical scope to meet the needs of molecular characterization.

Raman Imaging:

Not really enough was known about Raman imaging in terms of data quality as it was not really known how much potential there was in the raw data for serious analysis.

X-Ray Fluorescence:

This was also determined to be inapplicable for molecular analysis because it is an elemental analysis technique.

Fiber Optic Chemical Sensors:

Fiber optic chemical sensors that use optical transducers at the end of the fiber to sense with an evanescent wave were looked at as they were thought to have the most potential for waste tank applications. It was thought that fiber optic chemical sensors would be most useful in terms of pH monitoring, if they could be developed to work in the realm of waste tank pH (9.5 or higher). The major drawbacks foreseen were the lack of the ability for speciation, and the difficulty in getting the sensor radiation hardened and chemically resistant to survive the waste tank environment. The need for sample contact is another major drawback in using fiber optic chemical sensors for analysis, as sample contact brings added sensor contamination, and an increased potential for cross sample contamination.

Currently fiber optic chemical sensors do not have the ability to take pH measurements in the necessary range for waste tanks. Fiber optic sensors also might work for ammonia, with a membrane deployable reagent. Fiber optic chemical sensors are ideal monitoring tools that need not be constantly attended, and don't require tweaking. Besides range, the other big question is the fiber and membrane reliability in a harsh radiation environment. Its lifespan would be dependent on the membrane and also on the amount of reagent.

Micro separation, micro sampling and micro dissolution:

Micro sampling and micro separation were thought to have good potential in waste analysis, however many people felt that it had not been fully developed enough in order to evaluate properly. Bernadette Johnson from MIT Lincoln Labs explained and presented her ideas about the techniques. Some major drawbacks include the need for sampling and the fact that the samples can lose specific speciation before they are analyzed. The technique is also not seen as having very much potential for in situ real time monitoring, and it was thought that it was probably better suited for hot cell work.

GENERAL ISSUES AND REQUIREMENTS:

The requirements of accuracy for the different analytes were then discussed, and the list of what the group felt was reasonable is presented below. It was not known whether DOE or EPA standards in terms of accuracy would have to be followed, so the group determined the standards in terms of the needs. Except in the case of the hot cell, where the EPA has already determined requirements for analysis. [Editor is unaware of EPA hot cell standards, and assumes this

refers to standards for laboratory analytic methods performed following subsampling of a core sample in the hot cell.]

Then the focus of the eventual goal of characterization came under discussion, whether it was indeed monitoring, or just straight characterization. Susan iterated that in the short term the goal is characterization, but in the long term, in situ monitoring is the goal for perceived safety reasons.

Safety related needs and perceived accuracy requirements:

1) H20 Moisture 20%>= +-1% [safety concern]
Best done in situ
Neutron moisture probe, measure thermal neutron flux working on putting it in tank

2) Organic Carbon 3% +-1%
H generation, breakdown of toxic gases....really like to have total complexants of what organics are, but too difficult, hot cell some core sampling methods, in situ important because there is a lot of loss to the core

3) pH < 9.5
Corrosion concern
Not an easy measurement to make in the laboratory
OH- <.001N for safety
Hot cell or in situ measurement

4) high heat: > 75 Cal/g exothermic energy (measure by DSC in lab)
[Safety issue, may also generate high hydrogen]

5) total cyanide > 50 ppm still maybe out of reach... but is total cyanide really an issue or are the species of cyanide more important. [Total cyanide measurement is the standard approach, although ferrocyanide family compounds are the specific molecules of concern for safety reasons.]

6) ammonium ion > 0.1 Molar

7) hydrogen generation [safety issue]

Discussion of in tank Deployment techniques:

The participants discussed the direction that the development of the cone penetrometer and the light duty utility arm should take, based on what they felt was needed for analytical techniques to work in tank. It was also mentioned that both the light duty utility arm and the cone penetrometer should be designed very generally so that they could easily be adapted for use with different techniques.

Ideas and Techniques that Merit More Discussion at a Later Date:

It was felt that some potential techniques could not be properly assessed because among those in the group there was not enough known about them. They decided to simply list them and defer evaluation of their analytical potential to others at a later date.

1. Total Fluorescence Measurement: Has been used in a penetrometer at Waterways Station by Stafford Cooper, have made similar developments for the testing of hydrocarbons in water. Could be useful in finding organics which are broken down into hydrogen in the high pH waste tank environment.

2. Raman Imaging: It was felt that not enough was known about the windows in the hot cell to properly asses this technique. [In this case it was suggested in a configuration where the detectors remain outside the hot cell. Other configurations are also possible.]

3. Micro dissolution: While it was felt that this sampling technique could be used to address total cyanide, it is not know whether or not it is allowable due to the direct contact with the waste tank material. Despite this safety concern, it was felt that its use in situ would greatly increase the rate at which knowledge could be gained.

4. Nuclear Magnetic Resonance: No one in the group felt prepared to discuss or evaluate this technique.

5. Bernadette Johnson (MIT Lincoln Labs) briefly discussed microchip lasers coupled to off the shelf diode lasers. This approach allows one to pump with diode laser at standard wavelength, and use microchips to generate other wavelengths. It allows in situ use of lasers at wavelengths which generally cannot be transmitted will with optical fibers, such as ultraviolet. Pulsing elements can be added to get nanosecond pulses. A one watt diode laser with fiber connection propagates 800 nm light over long distances. A chip at the tip, changes the light to UV radiation. Can use array of lasers as well, with multiple crystals delivering different wavelengths. Requires no electric power at tip. The technology is licensed to Microcore in Acton MA. MIT-LL is looking at advancing laser pumping technology, turning method into environmental monitoring system. Applications were not immediately apparent for the tanks, but the potential of the technology was noted. No current plans exist for UV sensing in tank, but developers may want to bear in mind possibility of future applications, for example, not create windows that are non-transmissive in UV.

Techniques were re-evaluated in terms of all of the above discussion and qualifying parameters (listed below). The discussion summarized in table 3, section 6.10 of the main report.

Needs Based Assessment Issues:

1. What species can be identified?
2. Is the method species specific or does it cover a broad range?

3. Will a single instrument address a broad range or are several required? (e.g. tunable vs fixed)
4. What are sensitivity, accuracy, reliability levels?
5. Does the method require constant attendance of skilled operators?
6. Can it be used for monitoring?
7. Does the system require constant "tweaking"?

Deployment Issues:

8. Does the method require sample preparation?
9. Can a probe be separated from the main instrument?
10. Can a probe be made small enough for deployment?
11. Can a probe survive in a high radiation environment?
12. Does the method require sample contact? If so can the probe survive high pH?
13. Can the probe be cleaned, decontaminated?
14. Does the method require constant attendance of skilled operators?
15. Does the system require constant "tweaking"?
16. What is an operational life expectancy of the system?
17. Does the system have specific sensitive parts? Can it be designed so that these parts may be changed out?
18. Can a probe operate safely in the expected environment (e.g. no spark hazard inside tanks)

Problems or comments that were felt to globally apply to all techniques are summarized below.

All of the techniques discussed below were thought to have their analytical accuracy affected adversely by the radiation environment. A short term need for highly skilled technicians was also thought to be necessary for almost all of the techniques. Most of the techniques that are seriously considered require no sample preparation, but all of the hardware is felt to require about the same amount of "tweaking" to begin with in order to get a functional technique.

In terms of general development, many of the techniques have similar steps, so that once one has been fully developed, implementation of the other techniques will not be a problem either. The radiation hardening of fibers is a development step is necessary for all of the techniques to succeed. The miniaturization step for deployment into a cone penetrometer or with the light duty utility arm is also something that needs further development before any hardware can be deployed in-situ. It was felt that the development of all of the analytical instrumentation would require a coordinated effort of many different groups in different areas of expertise. It was also felt that better software packages for data interpretation would help to provide greater accuracy in analysis.

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