U.S. Department of Energy
Office of River Protection
P.O. Box 450, MSIN H6-60
Richland, Washington 99352

07-WTP-237

SEP 10 2007

Mr. C. M. Albert, Project Manager
Bechtel National, Inc.
2435 Stevens Center Place
Richland, Washington 99354

Dear Mr. Albert:

CONTRACT NO. DE-AC27-01RV14136 – TRANSMITTAL OF THE U.S. DEPARTMENT OF ENERGY, OFFICE OF RIVER PROTECTION (ORP) DESIGN OVERSIGHT ASSESSMENT REPORT NUMBER D-07-DESIGN-041: LASER ABLATION-INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY (LA-ICP-AES) DESIGN

ORP conducted an assessment of the Waste Treatment and Immobilization Plant (WTP) LA-ICP-AES design. The objectives of this assessment were to evaluate the design and performance of the LA-ICP-AES in relation to: (1) the adequacy of the LA-ICP-AES design; (2) the WTP contract and Bechtel National, Inc. (BNI) design requirements; and (3) whether the appropriate safety and performance requirements were incorporated into the design. The Design Assessment Team evaluated BNI's LA-ICP-AES design with an understanding that the design has not been finalized. The attached report documents the results of this assessment.

No Findings or Observations were noted by this Assessment Team at this stage of LA-ICP-AES development. Additional action, by BNI, as a result of this assessment is not required. The maturation and possible inclusion of this instrumentation in the WTP Analytical Laboratory can be included in the scope of a future assessment.

If you have any questions, please contact me, or your staff may contact Robert W. Griffith, Acting Director, WTP Project Engineering Division, (509) 372-2821.

Sincerely,

John R. Eschenberg, Project Manager
Waste Treatment and Immobilization Plant Project

WTP:AAK

Attachment

cc w/attach:
W. S. Elkins, BNI
P. Schuetz, BNI
BNI Correspondence

U.S. Department of Energy, Office of River Protection

**U.S. DEPARTMENT OF ENERGY (DOE), OFFICE OF RIVER PROTECTION (ORP)
DESIGN OVERSIGHT ASSESSMENT REPORT**

REVIEW
BECHTEL NATIONAL, INC.
LASER ABLATION-INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY DESIGN

August 2007

Design Assessment: D-07-DESIGN-041

Team Lead:

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Engineering Division Reviewers

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Fred B. Hidden, Jr., Technical Expert

Concurrence:

Robert W. Griffith, Acting Director
Waste Treatment and Immobilization Plant
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Approval:

John Eschenberg, Project Manager
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EXECUTIVE SUMMARY

The U.S. Department of Energy, Office of River Protection conducted a design oversight assessment of the Waste Treatment and Immobilization Plant (WTP) Project Laser Ablation-Inductively Coupled Plasma-Atomic Emission Spectroscopy (LA-ICP-AES) design. Specific objectives of the design oversight were to:

1. Evaluate the design and performance of the LA-ICP-AES equipment in relation to the adequacy of the design.

2. Evaluate the design and performance of the LA-ICP-AES equipment in relation to the WTP contract design requirements.

3. Evaluate the design and performance of the LA-ICP-AES equipment in relation to whether the appropriate safety and performance requirements are incorporated into the design.

Overall Conclusions

The development of the laser ablation (LA) technique for WTP support is still in the early discovery stages. Preliminary studies have demonstrated that LA-ICP-AES is viable and, with further development, capable of supporting WTP vitrification activities as a production control instrument. The methodology incorporated by WTP in developing and validating this instrumentation and technique has been thorough and direct. The next phase of development includes further testing and development with actual high-level waste samples in a hot cell. The prototype instrument is to be installed at the Hanford 222-S Laboratory and has the same configuration as proposed for application in the WTP Analytical Laboratory.

No Findings or Observations were noted by this Assessment Team at this stage of LA-ICP-AES development. The maturation and possible inclusion of this instrumentation in the WTP Analytical Laboratory can be included in the scope of a future assessment.

TABLE OF CONTENTS

LIST OF ACRONYMS

AES	atomic emission spectroscopy
ALARA	as low as reasonably achievable
BNI	Bechtel National, Inc.
DOE	U.S. Department of Energy
HLW	high-level waste
ICP	inductively coupled plasma
IHLW	immobilized high-level waste
LA	laser ablation
MDL	minimum detection limit
MFPV	melter feed preparation vessel
MRQ	minimum reportable quantity
ORP	Office of River Protection
PNNL	Pacific Northwest National Laboratory
RSD	relative standard deviation
SRNL	Savannah River National Laboratory
TAT	turnaround time
WTP	Waste Treatment and Immobilization Plant

1.0 INTRODUCTION

The U.S. Department of Energy (DOE), Office of River Protection (ORP) conducted a design oversight assessment of Waste Treatment and Immobilization Plant (WTP) Project Laser Ablation-Inductively Coupled Plasma-Atomic Emission Spectroscopy (LA-ICP-AES) design-basis requirements. The purpose of this assessment was to evaluate the physical equipment/components of the LA-ICP-AES system in relation to functional and operational requirements. These physical components were evaluated in relation to the objectives identified in Section 1.3 of the assessment plan (Appendix B). This assessment included an analysis of equivalency of method compared to traditional wet chemical techniques. Additionally, this assessment included an evaluation of the LA-ICP-AES in relation to melter throughput requirements.

2.0 BACKGROUND

ORP's mission is to retrieve and treat Hanford Site tank waste and close the tank farms to protect the Columbia River. In order to complete one major component of this mission, ORP awarded Bechtel National, Inc. (BNI) a contract for the design, construction, and commissioning of the WTP at the Hanford Site in Richland, Washington. In order to meet the requirements of the WTP contract, DE-AC27-01RV14136, and support the continuous vitrification process, BNI is designing a LA-ICP-AES system that requires remote operations with highly radioactive samples. The LA-ICP-AES method is applied for quantification of multiple elements. The ultraviolet laser ablates a small amount of the glass sample and the ICP-AES measures characteristic emission spectra by optical spectrophotometric methods. The ablated material is transported in a carrier gas to the plasma torch where element-specific emission spectra are produced by the high-temperature plasma. The spectra are dispersed by a grating spectrophotometer, and the intensities of the emission lines are monitored by an electro-optical detector. Laser-induced ablation of the sample is matrix dependent and the efficiency of ablation is known to vary from sample to sample.

3.0 OBJECTIVES, SCOPE, AND APPROACH

3.1 Objectives

The objectives of this assessment were to evaluate the design and performance of the LA-ICP-AES equipment. The LA-ICP-AES equipment and analytical technique were evaluated in relation to: (1) the adequacy of the LA-ICP-AES design; (2) the WTP contract and BNI design requirements; and (3) whether the appropriate safety and performance requirements are incorporated into the design.

3.2 Scope

The scope of this assessment included review of BNI and subcontractor design documents, instrumentation, and control features related to the LA-ICP-AES equipment in support of rapid quantification of high-level waste (HLW) samples to meet the requirement of less than nine hours turnaround time (TAT) for design (i.e., nameplate) production rates of immobilized high-level waste (IHLW). Included in the document review were drawings, specifications, calculations, test results, datasheets, and design change documentation.

3.3 Approach

This oversight was conducted within the guidelines of ORP M 220.1, *Integrated Assessment Plan*, and the ORP Desk Instruction DI 220.1 "Conduct of Design Oversight," Rev. 1, as revised January 13, 2006.

During ORP's evaluation, lines of inquiry were documented and given to BNI's point of contact for resolution. BNI's responses (Appendix A) were utilized as reference information during the Assessment Team's evaluation of the LA-ICP-AES design per the approved design oversight assessment plan, *Laser Ablation-Inductively Coupled Plasma-Atomic Emission Spectroscopy Design*, provided in Appendix B.

4.0 RESULTS

4.1 Evaluation of the Physical Equipment/Components

The physical equipment/components of the LA-ICP-AES system were evaluated in relation to functional and operational requirements. Both the equipment and the technique were evaluated in relation to: (1) the adequacy of the LA-ICP-AES design; (2) the WTP contract and BNI design requirements; and (3) whether the appropriate safety and performance requirements are incorporated into the design.

4.1.1 Adequacy of LA-ICP-AES Design

Early on in the project, laser ablation (LA) needed to be investigated and proven to be a viable alternative to liquid sampling. BNI awarded two subcontracts to national laboratories that had proven technical skills with HLW slurry and glass analysis, Savannah River National Laboratory (SRNL) and Pacific Northwest National Laboratory (PNNL). Both laboratories worked in parallel to develop and optimize the LA technique with different instruments. BNI supplied simulant samples of HLW feed and HLW melter feed to both laboratories as well as analytical reference glasses. Improved conventional non-dilute dissolution studies were also being performed concurrently at both laboratories facilitating the comparison of data between conventional wet chemistry-liquid sampling-ICP-AES analysis and LA-ICP-AES analysis. The results of the HLW simulant, HLW melter-feed simulant, and reference glass experiments agreed very well between both laboratories for both wet chemistry dissolution-ICP-AES analysis and LA-ICP-AES analysis. The laboratories shared their techniques, results, and lessons learned with BNI and each other during the experiments.

After testing was competed by both laboratories, results were reviewed by a panel of three external reviewers, who are experts in their respective fields. The external reviewers included: an expert in LA and ICP analysis, Dr. Detlef Günther of the Swiss Federal Institute of Technology in Zurich, Switzerland; Dr. Robert Houk, an expert in sample dissolution and ICP analysis from the DOE Ames Laboratory in Iowa; and Dr. Carol Jantzen, the glass expert from DOE SRNL. All three external reviewers independently agreed that the LA showed good promise, the methodology was sound, and that further testing was needed and should be conducted. Each reviewer provided feedback and guidance for instrument and method improvements that could be incorporated in the next phase of development.

The next phase of LA-ICP-AES development will be performed in a hot cell of the Hanford 222-S Laboratory with actual HLW samples. The method will be fine-tuned and the effects of spectral interferences from the actinide elements can be investigated. The additional data generated will be used to establish better measures of precision and accuracy for the technique.

The prototype system consists of the LA sample stage being installed within a hot cell and interfaced to a custom ICP-AES assembly in the adjacent glovebox. This configuration is planned for installation into the WTP Analytical Laboratory. The laser unit, water chiller, and power supply are located outside of the hot cell so maintenance and repair can be conducted easily on non-contaminated units. The laser path will be directed to the samples through a quartz window in the hot cell by using mirrors and will be completely sealed and enclosed. Because the laser removes only a small amount of material from the sample, the ICP torch assembly is being located in a glovebox to protect the operator from radiological dose or exposures. The ICP nebulizer, spray chamber, and torch assembly can be broken down and cleaned within the glovebox through the glove ports without difficulty.

4.1.2 WTP Contract and BNI Design Requirements

The LA-ICP-AES equipment and analytical technique was evaluated in relation to requirements of the WTP contract, DE-AC27-01RV14136. The LA-ICP-AES and/or conventional ICP-AES will provide the means to determine that products (i.e., IHLW and immobilized low-activity waste glasses) produced from a continuously fed melter produce glass that meets project specifications (Section C, Standard 2, paragraph (a)(3)(vi)(F), "IHLW Process Testing") and the product's chemical properties (Section C, Standard 3, paragraph (b)(1)(ii)).

The LA-ICP-AES equipment and analytical technique, as it stands in the prototype development stage and expected to be implemented in the WTP Analytical Laboratory, have been specified in the appropriate BNI system descriptions, specifications, and operations requirements documents. The analytical equipment requirements are contained in 24590-LAB-3PS-AELE-T0002, *River Protection Project – Waste Treatment Plant Engineering Specification for Inductively Coupled Plasma Atomic Emission Spectrometer with Laser Ablation*, Section 3, "Design Requirements." The method of analysis, as optimized by SRNL and PNNL, has been consolidated into 24590-WTP-RPT-OP-06-001, *LA-ICP-AES Analysis Method for Hanford Vitrification Process*.

4.1.3 Safety and Performance Requirements

LA was investigated as a means to: (1) support rapid turnaround time; (2) minimize procedural steps; (3) reduce waste generation; (4) maintain sample representativeness; (5) show equivalency to existing techniques; and (6) facilitate sample introduction. Through the initial studies at SRNL and PNNL, LA meets or has the potential to meet all of these requirements. The requirements to support rapid TAT and equivalency will be discussed in later sections in this report.

The number of procedural steps is greatly reduced by forming glass coupons for sampling by LA. Samples of HLW feed slurry are dried, weighed, and then mixed with glass-forming chemicals and an internal standard to fuse into glass coupons for LA-ICP-AES analysis. Melter feed samples can be directly fused after the addition of the internal standard.
Two separate dissolutions (peroxide fusion; rapid acid leach for sodium and nickel only) are

required for conventional wet-chemistry sample preparation and it is very unlikely that one dissolution method can be developed based on the work at PNNL and SRNL and the elemental coverage required. This leads to increased glassware and sampling equipment, secondary waste, and an increased number of process steps. LA of glass coupons reduces the time spent working with manipulators in front of hot cells and reduces operator fatigue. Additionally, LA eliminates concerns with dilution errors and additional preparation steps required for dilutions. The preparation of glass coupons addresses as low as reasonably achievable (ALARA) concerns by minimizing the potential for unnecessary exposures to operators from transferring diluted samples in shielded containers from the hot cell into the glovebox or radiochemical fume hoods for instrument analysis.

Sample representativeness was proven by PNNL and discussed in Section 6.0, "Confirmatory Wet Chemistry/ICP-AES Analysis," in their laser ablation study (WTP-RPT-140). Three fused glass samples (one HLW feed, one HLW melter feed, and one reference glass) that were used in the TAT study were submitted for confirmatory wet-chemical analysis. A small portion of material was removed from the glass coupons, crushed, and digested in acid for subsequent ICP-AES analysis. The results were compared with the ICP-AES results that were generated before fusion into glass samples. Given that the glass fusion process uses lithium borate flux, elemental concentrations of lithium and boron could not be determined. The results agreed to ± 25% (except for calcium and nickel in the HLW feed sample, which were 30% and 26% high, respectively), demonstrating excellent recovery. A more detailed study could determine better agreement by using larger sample volumes and multiple replicate analyses. Sample representativeness will be further investigated and refined in future development studies.

4.2 Equivalency of Method

ICP-AES is a widely used and very accepted technique for elemental determinations. There is no change in the determinative portion of LA-ICP-AES compared to the conventional ICP-AES method. The sample material is introduced via argon carrier gas to the ICP-AES from the LA unit instead of being nebulized from a wet-chemistry prepared solution. In order to test the equivalency of method, reference glasses, simulant samples of HLW feed, and HLW melter feed were independently analyzed by SRNL and PNNL by conventional liquid sampling ICP-AES and LA-ICP-AES methods. In the preliminary studies, minimum reportable quantities (MRQ), precision, and accuracy for a few elements were outside the expected limits. Precision measurements for most of the elements in the sampled glasses were less than 7% relative standard deviation (RSD). A quantitative comparison of ICP-AES and LA-ICP-AES techniques cannot be performed at this time due to the small sampling dataset. Qualitatively, LA-ICP-AES accuracy is very promising since the majority of elements were within ± 20% of the true values in all three glasses. Further improvements to accuracy can be gained through the use of better, matrix-matched standards. Also, normalizing the results to an internal standard spike added to the samples has shown great promise in the preliminary testing. Both of these improvements are currently being investigated and developed by BNI. Minimum detection limits (MDL) are instrument and method specific. The MDLs of elements on the prototype instrument that is being installed at the 222-S Laboratory in the next stage of testing need to be investigated and further refined to determine if they will meet the MRQs required. At this stage of development, equivalency of method cannot be accurately determined. Preliminary testing at SRNL and

PNNL has shown that LA-ICP-AES is a viable technique for determining elemental compositions of WTP waste as a process control measurement.

4.3 Evaluation of the LA-ICP-AES in Relation to Melter Throughput Requirements

The LA-ICP-AES is being developed to provide process control data for HLW in the melter feed preparation vessel (MFPV) before and after the addition of glass formers. Analyses need to be completed in less than nine hours to avoid impacting the HLW plant throughput.
As demonstrated by SRNL in the Phase I of LA-ICP-AES development (WSRC-TR-2005-00260), complete analysis is in the order of eight hours. PNNL obtained similar results in their TAT study as documented in their LA-ICP-AES study (WTP-RPT-140). PNNL found that by overlapping preparation and analysis operations, overall turnaround times for subsampling to analysis required about 9 hours for a batch of four HLW samples, and 12 hours for a batch of 8 melter feed samples. Further time-in-motion studies in the next stage of development may find that TAT can be reduced further by identifying efficiencies in sample preparation and handling, and by further optimization of instrument acquisition parameters (i.e., decreasing the number of integrations per replicate analysis).

5.0 FINDINGS

The development of the LA technique for WTP support is still in the early discovery stages. Preliminary studies have demonstrated that LA-ICP-AES is viable and, with further development, capable of supporting WTP vitrification activities as a production control instrument. The methodology incorporated by BNI in developing and validating this instrumentation and technique has been thorough, well thought out, and direct. The next phase of development includes further testing and development with actual HLW samples in a hot cell. The prototype instrument that is being installed at the 222-S Laboratory has the same configuration as proposed for application in the WTP Analytical Laboratory.

No Findings or Observations were noted by this Assessment Team at this stage of LA-ICP-AES development. The maturation and possible inclusion of this instrumentation in the WTP Analytical Laboratory should be the subject matter for the scope of a future assessment.

6.0 PERSONNEL CONTACTED AND REFERENCES

6.1 Personnel Contacted

WTP

- C. Albert
- A. Arakali
- D. Burks
- J. Jain
- D. Jantosik
- D. Kammenzind
- T. Lane
- D. Perkins
- D. Pisarcik

- K. Wells

Hanford Analytical Laboratory (222-S)

- L. Lockrem
- C. Seidel

6.2 References

24590-LAB-3PS-AELE-T0002, *River Protection Project – Waste Treatment Plant Engineering Specification for Inductively Coupled Plasma Atomic Emission Spectrometer with Laser Ablation*, Rev. 0, October 25, 2005

24590-WTP-RPT-OP-06-001, *LA-ICP-AES Analysis Method for Hanford Vitrification Process*, Rev. 0, August 10, 2006

DE-AC27-01RV14136, *Bechtel National, Inc., Design, Construction, and Commissioning of the Hanford Tank Waste Treatment and Immobilization Plant*, August 31, 2000

ORP DI 220.1, "Conduct of Design Oversight," Rev. 1, January 26, 2006

ORP M 220.1, *Integrated Assessment Plan*, Rev. 4, January 3, 2006

WSRC-TR-2006-0003, 2006, *The Development of Laser Ablation-Inductively Coupled Plasma-Atomic Emission and Mass Spectroscopy for the Analysis of Hanford High Level Waste: Phase II (U)*, Westinghouse Savannah River Company, Aiken, South Carolina

WSRC-TR-2005-00260, 2005, *The Development of Laser Ablation-Inductively Coupled Plasma-Atomic Emission Spectroscopy for the Analysis of Hanford High Level Waste: Phase I*, Westinghouse Savannah River Company, Aiken, South Carolina

WTP-RPT-140, 2005, *Laser Ablation Study for High-Level Waste and Melter Feed Characterization*, Pacific Northwest National Laboratory, Richland, Washington

6.3 Other Documents

24590-LAB-3YD-AHL-00001, *System Description for the Analytical Hotcell Laboratory Equipment (AHL)*, Rev. 1, August 5, 2005

DOE O 226.1, *Implementation of Department of Energy Oversight Policy*, September 15, 2005

ORP M 412.1, *Consolidated Action Reporting System*, August 8, 2001

WTP-RPT-139, 2005, *Conventional Non-Dilute Wet Chemistry Dissolution/ICP-AES Time Study*, Pacific Northwest National Laboratory, Richland, Washington

WTP Test Plan; Graves, W.L., "CCN 091850, 2004, 'WSRC – SRNL NTP Wet Chemistry & Laser Ablation Testing, Maximum $100,000'," (email to R.E. Edwards), Bechtel National, Inc., Richland, Washington

APPENDIX A. LA-ICP-AES FUNCTIONAL AND OPERATIONAL DESIGN LINES OF INQUIRY AND ASSESSMENT

LA-ICP-AES FUNCTIONAL AND OPERATIONAL DESIGN LINES OF INQUIRY AND ASSESSMENT

Layout:

The mock up diagrams do not show where the high-purity Argon cylinders are to be located. They should be in an easily accessible place. Are they going to be close to the instrument? Also, matching high purity regulators and lines should be used.

> The hot cell facility at 222S lab has piped-in lines with regulators for Argon supply. This is a standard item for the lab because of other ICP instruments in use. The lab is working out the final configuration and proximity of the supply lines for supporting the LA-ICP-AES prototype testing.

Is a drop tube from the glove box still being considered for the optional introduction of liquid samples/standards?

> Yes, drop tube for introduction of liquid samples, standards, and dilute acids has been designed and is part of the glove box fabrication.

Follow up question: How are liquid samples going to be introduced from the hot cell?

> Liquid samples from hot cell would be transferred using a shielded transfer can that locks into the base of glove box for sample access and introduction to aspiration tube going into the ICP nebulizer. In WTP lab, samples would be transferred after appropriate dilutions (and dose-rate check) through transfer glove box (attached to Hot Cell#1) for designated analysis.

Are the electronics going to be connected to an Uninterruptible Power Supply? Some thought should be given to ensuring that an entire run worth of data isn't lost if the computer locks up or is accidentally reset.

> It is not feasible to have UPS for analytical equipment and computers in hot cell area because of space constraint and power load. Data acquisition systems have built-in saver for back-up data files in the event of power surge or computer glitch. The only data that might be lost would be, for the sample that was being analyzed at that time. And this recovery requires rerun of calibration, QC and the sample.

Are there high-voltage instruments or machinery nearby that could induce EMF fields or cause power fluctuations or vibrations that might affect the instrument?

> No.

If the hot-cell operator is required to wear laser-safety eyewear, what will be the means for protecting bystanders/passers-by from stray laser light?

> Laser Safety eye-wear not required as the ablation unit is inside the hot cell and the laser beam from encapsulated source is aligned and focused towards the sample cell. The alignment and

focusing is checked out and tested in the factory before the unit is shipped, retested at the time of installation for any possibility of stray light.

Where is the water chiller unit for the laser located? What protection is in place for potential leaks?

The chiller unit would be located on top of hot cell at 222S facility. Inspection, monitoring of water level and periodic draining/refills are protective measures for leak checks and proper functioning of the chiller.

Follow up question: Where is the chiller located in the WTP lab?

Since WTP lab hot cell layout is in design/modeling stage, two options are being considered for chiller location. One option is to secure next to the laser power supply unit on the same platform and the other is to separate and place the chiller on the floor below the glove box.

Where exactly will the assembly be located?

The location of the assembled units will be in Hot Cells 12 & 13. Please refer to AHL System Description 24590-LAB-3YD-AHL-00001 pages 36 through 38. The attached drawing shows the location of Hot Cells 12 & 13 within the Hot Cell complex.

Has the locations/fit/function been reviewed with start-up/operations?

Operations, represented by Tom Lane and Aruna Arakali at the kick-off meeting, have been intimately involved in all aspects of defining the location/fit/function for the equipment.

ORP Comment on the BNI response: The maturation and possible inclusion of this instrumentation in the WTP Laboratory should be the subject matter for the scope of a future assessment.

<u>Method</u>:

Are the platinum crucibles going to be cleaned and reused? How is it expected to be accomplished? Platinum lids are also going to be used in the Hot Cell correct?

Pt crucibles to the extent possible would be cleaned and reused. Standard acid cleaning procedure would be used. Lids were used for fusions done in the development work. Hence, plan on using lids for hot cell testing to minimize cross contaminations.

Can the [laboratory control sample] LCS button be used for multiple batches? Has any thought been given to how it is to be resurfaced for additional use if it can be reused?

LCS button can be used for multiple batches. Resurfacing not required because of rastering scans. For WTP work, we plan to prepare batch QC and blank glass coupons with every batch to account for sample prep variations.

ORP Comment on the BNI response: Scanning over previously ablated areas is not recommended due to non-representative debris at the crater boundaries. Fresh LCS buttons are prepared per batch so resurfacing is not necessary.

I was concerned about the amount of native copper in the unknown samples and how it is determined beforehand so it can be subtracted from the response before the Internal Standard (IS) normalization calculations were performed. Is scandium going to be pursued as the IS instead of copper as they did in the Phase II LA study at SRNL? Is there any likelihood of native Sc in the samples?

> Sc will be pursued in the method optimization after completing the prototype testing at hot cell facility (222S lab). Based on characterization data, native Sc is expected to be a trace constituent in HLW feed for WTP operations

ORP Comment on the BNI response: Sc or another trace level constituent will suffice.

I am concerned with a statement made on page 18 of the Phase II LA study (WSRC-TR-2006-00003, rev. 0).... "One issue with these standards for use with the ICP-MS is that many of them are very high in concentration and saturate the detector. With the ICP-AES, only three of the elements saturated the detector at their highest concentration; however, it does appear that the high concentrations for some of the elements may be out of the linear dynamic range of the instrument." Dr. Detlef Gunther also states, in his peer review, that "the upper and lower limit of the linear dynamic range should be determined for each selected emission line." Looking at the data for the standards in the Phase II study, Table 4 on page 19, it shows that SiO_2, Na_2O, and Fe_2O_3 are present at the approximately 20 wt% oxide (or greater) level. Does the detector become saturated at levels near 20 wt% oxide or greater? All three of the simulant glasses also tested have components in the low-teens plus silicon-dioxide in the mid-forties, so it is plausible for samples to have some high value constituents.

> Detector saturation is a concern with simultaneous (catch-all) analyses. We plan to address this concern by selecting less sensitive wavelength for quantitating elements in high concentrations. As Gunther has recommended, we will establish the linear dynamic range limits for selected emission lines for each element prior to implementing the method for WTP support.

ORP Comment on the BNI response: Thorough method development will minimize the effects of detector saturation. Alternate emission lines that are less sensitive can be used for quantifying elements with high concentrations. Over-saturation can occlude nearby wavelengths. This will be investigated further in the prototype testing and method development.

Follow up question: The use of the phrase "quantitating elements" is unclear, please reword. Is this to mean "quantitative analysis of"?

> Yes, refers to quantitative analysis of elements

The LCS data can be used as an indicator to monitor instrument drift for the full ICP, torch, and laser ablation assembly. Liquid standards can be run to monitor ICP and torch process drift. In the two models of laser assemblies used in the studies, the laser power was measured differently and an energy density at the sample surface had to be estimated. How is process drift going to be measured for the laser ablation assembly? Are there plans to measure the laser power directly that is independent of the gauge on the laser unit itself?

Per the vendor, the laser power and performance of the prototype would be monitored through the PC program. Also, there will be energy meters to provide the information on laser power at the point of sample ablation.

Follow up question: PC stands for Personal Computer and not Process Control, correct?

PC - Personal Computer

Are the simulant glasses WV-205 and CVS IS being explored as other LCS candidates?

Yes, WV-205 and CVS IS are being considered as good LCS candidates because they are similar to Hanford HLW tank matrices. Also, other standard glasses are being considered. A preliminary list was given to Fred Hidden for reference.

General Comments/Questions:

Have any general composition NIST glass standards been identified? Could additional samples from previous ASTM round-robin studies be used to show agreement between labs?

Yes, several NIST glass standards have been identified. Previous glass samples from round-robin studies are being considered. John Vienna from PNNL is supporting this effort.

Equation 11.5 in the Data Reduction section of the preliminary method is confusing because of the inclusion of the ug/g units. With the many subscripted g's and the g-prime, I had to look at it closely to insure the 'g' was a unit and not a variable. Perhaps move the x10E6 ug/g to the very end?

Will fix the equation as suggested in the next revision.

ORP Comment on the BNI response: Accepted, this qualifies as an administrative change.

Also in the Safety section of the preliminary method: OSHA recommends the use of a lab coat, chemical resistant gloves, and safety glasses in addition to an apron and face shield when working with concentrated acids.

The use of lab coat, gloves and safety glasses are minimum requirement for working in lab fume hood areas (part of lab safety procedures). Hence, not listed separately.

APPENDIX B. DESIGN OVERSIGHT ASSESSMENT PLAN

U.S. DEPARTMENT OF ENERGY (DOE), OFFICE OF RIVER PROTECTION (ORP) DESIGN ASSESSMENT PLAN

REVIEW
BECHTEL NATIONAL, INC.
LASER ABLATION-INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY DESIGN

July 2007

Design Assessment: D-07-DESIGN-041

Team Lead:	_original signed by_ Albert A. Kruger, Facility Area Engineer Waste Treatment and Immobilization Plant Engineering Division
Engineering Division Reviewers	_original signed by_ Paul R. Hirschman, BOF Facility Area Engineer Waste Treatment and Immobilization Plant Engineering Division
	original signed by Fred B. Hidden, Jr., Technical Expert
Concurrence:	_original signed by_ Robert W. Griffith, Acting Director Waste Treatment and Immobilization Plant Engineering Division
Approval:	_original signed by_ John Eschenberg, Project Manager Waste Treatment and Immobilization Plant

1.0 BACKGROUND, PURPOSE, AND OBJECTIVES

1.1 Background

The U.S. Department of Energy (DOE), Office of River Protection's (ORP) mission is to retrieve and treat Hanford Site tank waste and close the tank farms to protect the Columbia River. In order to complete one major component of this mission, ORP awarded Bechtel National, Inc. (BNI) a contract for the design, construction, and commissioning of the Waste Treatment and Immobilization Plant (WTP) at the Hanford Site in Richland, Washington. In order to meet the requirements of WTP contract, DE-AC27-01RV14136, and support the continuous vitrification process, BNI is designing a Laser Ablation-Inductively Coupled Plasma-Atomic Emission Spectroscopy (LA-ICP-AES) system that requires remote operations with highly radioactive samples. The LA-ICP-AES method is applied for quantification of multiple elemental analytes. The ultraviolet laser ablates a small amount of the glass sample and the ICP-AES measures characteristic emission spectra by optical spectrophotometric methods. The ablated material is transported in a carrier gas to the plasma torch where element-specific emission spectra are produced by the high-temperature plasma. The spectra are dispersed by a grating spectrophotometer, and the intensities of the emission lines are monitored by an electro-optical detector. Laser induced ablation of the sample is matrix dependent and efficiency of ablation is known to vary from sample to sample.

1.2 Purpose

The purpose of this assessment is to evaluate the physical equipment/components of the LA-ICP-AES system in relation to functional and operational requirements. These physical components will be evaluated in relation to the objectives identified in Section 1.3 of this plan. This assessment will include an analysis of equivalency of method compared to traditional wet chemical techniques. Additionally, this assessment will include an evaluation of the LA-ICP-AES in relation to melter throughput requirements.

1.3 Objectives

The objectives of this assessment are to evaluate the design and performance of the LA-ICP-AES equipment. The LA-ICP-AES equipment and analytical technique will be evaluated in relation to: (1) the adequacy of the LA-ICP-AES design; (2) the WTP contract and BNI design requirements; and (3) whether the appropriate safety and performance requirements are incorporated into the design.

2.0 SCOPE

The scope of this assessment will include review of BNI and subcontractor design documents, instrumentation, and control features related to the LA-ICP-AES equipment in support of rapid quantification of high-level waste (HLW) samples to meet the requirement of less than 9 hours turnaround time for design (i.e., nameplate) production rates of immobilized high-level waste (IHLW). Documents to review include drawings, specifications, calculations, test results, datasheets, and design change documentation.

This oversight shall be conducted within the guidelines of ORP M 220.1, *Integrated Assessment Plan*, and the ORP Desk Instruction DI 220.1 "Conduct of Design Oversight," Rev. 1, as revised January 13, 2006.

3.0 PREPARATION

a. Identify ORP Design Assessment Team.

b. Notify BNI that ORP will be conducting the LA-ICP-AES design assessment, number D-07-DESIGN-041.

c. Identify documents to review, including the results of previous contractor external or internal assessments.

d. Identify contract requirements and contractor design requirements.

e. Prepare and implement schedule of design assessment activities.

4.0 EVALUATE AND IDENTIFY, RESOLVE, OR DOCUMENT ISSUES

The ORP Design Assessment Team will evaluate BNI documentation in relation to WTP Contract and BNI design requirements. During ORP's evaluation, lines of inquiry (LOI) will be documented and given to BNI's point of contact (POC) for resolution. BNI's responses to LOI questions will be utilized as reference information during the Design Assessment Team's evaluation of the LA-ICP-AES design.

5.0 REPORTING

The Design Assessment Team Lead will periodically brief ORP management and the Contractor POC during the assessment. The Team Lead, with assistance from the team, will prepare a design assessment report that summarizes review activities, results, conclusions, and recommendations.

6.0 SCHEDULE OF ACTIVITIES

Table 1 lists the schedule of assessment activities.

7.0 WTP CONTRACT REQUIREMENTS DE-AC27-01RV14136 AND WTP DESIGN DOCUMENTS

The documents provided by BNI, during this design assessment, will be reviewed in relation to WTP Contract requirements and BNI WTP design documentation, as follows:

REQUIREMENT	SECTION/PARAGRAPH (and as applicable)	
WTP Contract DE-AC27-01RV14136	• C. Standard 2 Research, Technology and Modeling, paragraph (a) (3) (vi) (F) IHLW Process Testing • C. Standard 3 Design, paragraph (b) (1) (ii) Functional Specification	• C. Standard 5 Commissioning, paragraph (f) (1) (ii) Design Capacity Performance Tests and paragraph (g) (4) (ii) Hot Commissioning Performance Tests • C.7 Facility Specification, paragraph (d) (2) (ii) High-Level Waste Vitrification
Systems Descriptions and Specifications Documents 24590-LAB-3PS-AELE-T0002 24590-LAB-3YD-AHL-00001	• Section 3.1, Analytical Equipment Requirements	
Operations Requirements Document 24590-WTP-RPT-OP-06-001		
Other Applicable References WTP SOW under CCN 091850, Test Plan WSRC-TR-2004-00447 and CCN 130232, and WSRC-TR-2006-0003		

8.0 DOCUMENTATION

The final report will be formally issued once the draft review comments have been resolved. Any findings, assessment follow-up items, or open issues identified in the report will be assigned a number, and tracked to resolution through Corrective Action Reporting System (CARS) by ORP. These assigned numbers shall also be tracked to resolution by the Contractor through the Correspondence Control Number (CCN) that will be assigned to the transmittal of the report from ORP to the Contractor.

9.0 CLOSURE

The Assessment Team Leader, with concurrence of the WED Division Director, shall confirm that findings, assessment follow-up items, and/or open items from this review are adequately resolved.

10.0 REFERENCES

24590-LAB-3PS-AELE-T0002, *River Protection Project – Waste Treatment Plant Engineering Specification for Inductively Couple Plasma Atomic Emission Spectrometer with Laser Ablation*, Rev. 0, October 25, 2005

24590-LAB-3YD-AHL-00001, *System Description for the Analytical Hotcell Laboratory Equipment (AHL)*, Rev. 1, August 5, 2005

24590-WTP-RPT-OP-06-001, *LA-ICP-AES Analysis Method for Hanford Vitrification Process*, Rev. 0, August 10, 2006

DE-AC27-01RV14136, *Bechtel National, Inc., Design, Construction, and Commissioning of the Hanford Tank Waste Treatment and Immobilization Plant*, August 31, 2000

DOE O 226.1, *Implementation of Department of Energy Oversight Poli*cy, September 15, 2005

ORP DI 220.1, "Conduct of Design Oversight," Rev. 1, January 26, 2006

ORP M 220.1, *Integrated Assessment Plan*, Rev. 4, January 3, 2006

ORP M 412.1 *Consolidated Action Reporting System*, August 8, 2001

WSRC-TR-2006-0003, 2006, *The Development of Laser Ablation-Inductively Couple Plasma-Atomic Emission and Mass Spectroscopy for the Analysis of Hanford High Level Waste: Phase II (U)*, Washington Savannah River Company, Aiken, South Carolina

WTP Test Plan; Graves, W.L., "CCN 091850, 2004, 'WSRC – SRNL NTP West Chemistry & Laser Ablation Testing, Maximum $100,000'," (email to R.E. Edwards), Bechtel National, Inc., Richland, Washington

Table 1. Schedule of Design Oversight Activities

Activity Description	Responsibility	Early Finish	Late Finish
Develop and Issue Design Oversight Plan	Kruger	07/17/07	07/24/07
Identify Team members	Kruger/Griffith	06/17/07	06/25/07
Advise BNI of Oversight; provide Review Plan for identification of BNI information/support	Kruger	06/14/07	07/24/07
Design Oversight Entrance Meeting	ORP Team/BNI	08/06/07	08/08/07
Obtain Information/Conduct Assessment	ORP Team/BNI	08/08/07	08/10/07
Complete Assessment	BNI and ORP Team Lead/Reviews	08/15/07	08/15/07
ORP Individual Team Reviewers Prepare Report to ORP Team Lead	ORP Team Reviewers	08/22/07	08/24/07
BNI Factual Accuracy Check of ORP Design Oversight Draft Report	ORP Team Lead and BNI	08/24/07	08/31/07
Resolve comments and issue Final Report	ORP Team	09/07/07	09/14/07

Notes:
(1) Schedule subject to change through Assessment Team Lead.
(2) Team Lead will notify BNI POC of schedule changes as applicable.

Task# ORP-WTP-2007-0239

E-STARS[R] Report
Task Detail Report
09/10/2007 1202

TASK INFORMATION

Task#	ORP-WTP-2007-0239		
Subject	Concurrence: 07-WTP-237 TRANSMITTAL OF THE U.S. DEPARTMENT OF ENERGY, OFFICE OF RIVER PROTECTION (ORP) DESIGN OVERSIGHT ASSESSMENT REPORT NUMBER D-07-DESIGN-041: LASER ABLATION-INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY (LA-ICP-AES) DESIGN		
Parent Task#		**Status**	CLOSED 09/10/2007
Reference	07-WTP-237	**Due**	
Originator	Perez, Anez (Perez, Anez)	**Priority**	High
Originator Phone	(509) 373-0068	**Category**	None
Origination Date	08/29/2007 1537	**Generic1**	
Remote Task#		**Generic2**	
Deliverable	None	**Generic3**	
Class	None	**View Permissions**	Normal
Instructions	bcc: WTP OFF FILE WTP RDG FILE MGR RDG FILE T. M. WILLIAMS, AMD T. Z. SMITH, DEP-MGR J. R. ESCHENBERG, WTP R. W. GRIFFITH, WTP P. R. HIRSCHMAN, WTP A. A. KRUGER, WTP Correspondence is being routed for concurrence via hard copy instead of electronically. Once you receive the correspondence, please approve or disapprove electronically via E-STARS and route to the next person on the routing/concurrence list.		

ROUTING LISTS

1	Route List	Inactive
	• Kruger, Albert A - Review - Concur - 08/29/2007 1616 *Instructions:*	
	• Hirschman, Paul R - Review - Concur - 08/30/2007 1243 *Instructions:*	
	• Griffith, Robert W - Review - Concur - 09/06/2007 1700 *Instructions:*	
	• Eschenberg, John R - Review - Concur - 09/04/2007 1346 *Instructions:*	
	• Smith, Zack - Review - Cancelled - 09/10/2007 1202 *Instructions:*	
	• Olinger, Shirley J - Review - Concur with comments - 09/06/2007 1629 *Instructions:*	
	• Eschenberg, John R - Approve - Approved - 09/10/2007 1156 *Instructions:*	

ATTACHMENTS

No Attachments

Task# ORP-WTP-2007-0239

COLLABORATION

COMMENTS

Poster	Olinger, Shirley J (Mendoza, Stella) - 09/06/2007 0409
	Concur
	Zack has concurred for Shirley

TASK DUE DATE HISTORY

No Due Date History

SUB TASK HISTORY

No Subtasks

-- end of report --

Task# ORP-WTP-2007-0239

E-STARS[R] Report
Task Detail Report
08/29/2007 0404

TASK INFORMATION

Task#	ORP-WTP-2007-0239		
Subject	Concurrence: 07-WTP-237 TRANSMITTAL OF THE U.S. DEPARTMENT OF ENERGY, OFFICE OF RIVER PROTECTION (ORP) DESIGN OVERSIGHT ASSESSMENT REPORT NUMBER D-07-DESIGN-041: LASER ABLATION-INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY (LA-ICP-AES) DESIGN		
Parent Task#		**Status**	Open
Reference	07-WTP-237	**Due**	
Originator	Perez, Anez (Perez, Anez)	**Priority**	High
Originator Phone	(509) 373-0068	**Category**	None
Origination Date	08/29/2007 1537	**Generic1**	
Remote Task#		**Generic2**	
Deliverable	None	**Generic3**	
Class	None	**View Permissions**	Normal

Instructions

bcc:
WTP OFF FILE
WTP RDG FILE
MGR RDG FILE
T. M. WILLIAMS, AMD
T. Z. SMITH, DEP-MGR
J. R. ESCHENBERG, WTP
R. W. GRIFFITH, WTP
P. R. HIRSCHMAN, WTP
A. A. KRUGER, WTP

Correspondence is being routed for concurrence via hard copy instead of electronically. Once you receive the correspondence, please approve or disapprove electronically via E-STARS and route to the next person on the routing/concurrence list.

ROUTING LISTS

1	Route List	Active

- Kruger, Albert A - Review - ~~Awaiting Response~~ - Due Date
  Instructions: AAK 30·8·07
- Hirschman, Paul R - Review - Awaiting Response - Due Date
  Instructions: 8/30/2007
- Griffith, Robert W - Review - Awaiting Response - Due Date
  Instructions: 8/31/07
- Eschenberg, John R - Review - Awaiting Response - Due Date
  Instructions: 9/4
- ~~Smith, Zack - Review - Awaiting Response - Due Date~~
  ~~*Instructions:*~~ N/R
- Olinger, Shirley J - Review - Awaiting Response - Due Date
  Instructions: 9/6/07 09/06/07
- Eschenberg, John R - Approve - Awaiting Response - Due Date
  Instructions:

Rec'd 9/4/07
Rec'd 9/7/07

ATTACHMENTS

No Attachments

Task# ORP-WTP-2007-0239

COLLABORATION

COMMENTS

No Comments

TASK DUE DATE HISTORY

No Due Date History

SUB TASK HISTORY

No Subtasks

-- end of report --