WSRC-TR-2002-00447, REV. 0
SRT-RPP-2002-00219. REV. 0

FINAL REPORT: TECHNETIUM MONITOR (U) LONG TERM RUNS WITH ICPES SPECTROMETER

January 7, 2003

Westinghouse Savannah River Company
Savannah River Technology Center
Analytical Development Section
Aiken, SC 29808

UNCLASSIFIED
DOES NOT CONTAIN
UNCLASSIFIED CONTROLLED
NUCLEAR INFORMATION

ADC & Reviewing Official: R.E. Filpus-Luyckx Mgr., Analytical & Radiochem. Research
(Name and Title)

Date: 1/13/03

ADDITIONAL APPROVAL:

Official:
R&T Manager, RPP Hanford

Date: 4/17/2003

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

Prepared for the U.S. Department of Energy Under Contract Number DEAC09-96SR18500

SRS
savannah river site

WSRC-TR-2002-00447, REV. 0
SRT-RPP-2002-00219. REV. 0

Key Words:
ICP Emission Spectroscopy
On-line Monitor
Analyzer

Retention:
Permanent

Key WTP R&T References:
Test Specification:
2450-WTP-TSP-RT-01-018
Task Plan
WSRC-TR-2001-00576 /
SRT-RPP-2001-00217
Plan Modification
"Tc Monitor Down Selection"
May 1, 2002, Meeting with Al Pajunen,
David Sherwood, WTP, Hanford, WA
Follow-up instructions from Reid Peterson, WTP, to James Marra, WSRC, May 7, 2002, [stopped further development of an emission based monitor]

FINAL REPORT: TECHNETIUM MONITOR (U) LONG TERM RUNS WITH ICP SPECTROMETER

William A. Spencer, William D. King, and F. M. Pennebaker
Westinghouse Savannah River Company
Bldg 773-41A
Aiken, SC 29808

Issue Date: January 7, 2003

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

Prepared for the U.S. Department of Energy Under Contract Number DE-AC09-96SR18500

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161,
phone: (800) 553-6847,
fax: (703) 605-6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/help/index.asp

Available electronically at http://www.osti.gov/bridge
Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062,
phone: (865)576-8401,
fax: (865)576-5728
email: reports@adonis.osti.gov

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ACRONYMS

DOE	United States Government, Department of Energy
ICP	Inductively Coupled Plasma
ICPES	Inductively Coupled Plasma Emission Spectroscopy
ICPMS	Inductively Coupled Plasma Mass Spectroscopy
nm	Wavelength in nanometers
RF	Radio Frequency
RPP	River Protection Project, Hanford Site
SRTC	Savannah River Technology Center
SRS	U.S. Department of Energy, Savannah River Site, Aiken, SC
UV	Ultraviolet emissions
WSRC	Westinghouse Savannah River Company, LLC
WTP	Waste Treatment Plant, Hanford Site, Richland, Washington

ABSTRACT

The Hanford River Protection Project Waste Treatment Plant (WTP) is required by the current contract to remove radioactive technetium from stored caustic nuclear waste solutions. The Savannah River Technology Center (SRTC) has worked with typical envelopes of these wastes to optimize the removal process. To support the studies, SRTC developed a rapid on-line remote analyzer to monitor technetium and rhenium levels in solutions as well as track other metals in the solutions through the process operations. Rhenium was used as a non-radioactive substitute for technetium in process development studies. The remote monitor was based on inductively coupled plasma emission spectroscopy (ICPES). Fiber optic cable and extended RF cabling removed the plasma source from the spectrometer and instrument electronics.

The Waste Treatment Plant instructed SRTC to terminate further development of the ICPES monitor. The on-line ICPES system discussed in this report was developed in parallel with a beta scintillation system. Oleg Egorov at PNNL developed an automated beta scintillation system for possible on-line use. WTP personnel reviewed both systems on May 1, 2002. After that meeting WTP decided to stop development for the ICPES system and continue to develop the less expensive and more sensitive beta-scintillator system for their on-line application. They planned to include an ICPES in the supporting laboratory facilities. After the review, the existing ICPES instrument was perceived as a supporting tool rather than a developmental one and little effort was made to enhance performance for on-line applications or resolve the Inductively Coupled Plasma Mass Spectroscopy (ICPMS) versus ICPES measurement bias.

The SRTC ICPES monitor ran 24 hours a day for five days during each experimental run. Nine experimental process runs were completed. Data were taken automatically every 15 minutes. The system tracked real-time emission from five elements: technetium, rhenium, aluminum, chromium, and argon. Data for 27 other elements were stored for post processing. Multiple emission lines were monitored for each element to check for inter-elemental interference. Yttrium was added to the sample transport stream and served as an internal standard on sampling performance. Pneumatic and electrical sampling systems were evaluated in 1/16 and 1/8-inch sizes. The system was observed under rugged conditions such as argon feed failure, room temperature control failure, torch coolant failure, and sampling feed pump outages. Overall the system worked well; however tracking of trace rhenium levels (< 1 ppm) during column breakthrough was marginal due to light losses of the deep UV ion lines at 221 and 227 nm in the optical fiber. Rhenium could be monitored using the weaker 345 and 346 nm emission lines but with detection limits higher than desired.

1.0 SUMMARY OF TESTING

The inductively coupled plasma emission spectrometer (ICPES), discussed in this report and used as an on-line monitor for ^{99}Tc and Re isotopes, was described in detail in earlier reports[1-4]. The basic goal of the current work was to demonstrate instrument performance during process optimization studies conducted at SRTC over an extended period[5, 6]. The effects of thermal conditions on SuperLig® 639 column loading and elution were also studied.

The monitor was successfully used as described in the Task Plan to support thermal elution studies. In those studies synthetic process solutions contained rhenium as a non-radioactive substitute for technetium. Experiments included over 45 days of 24-hour on-line use. This report summarizes our experiences with the analyzer.

WTP personnel evaluated the monitor system May 2002 at Hanford. At WTP direction, several phases of the original Task Plan were terminated including the pilot-scale testing experiments and the laboratory method development. The support for the thermal elution experiments was continued because the monitor helped to lower total analytical costs for that study.

WTP instructed SRTC to terminate further development of an emission based on-line instrument. Al Pajunen of WTP wrote a summary report covering both the beta-scintillator and ICPES technetium monitors, (see 24590-PTF-RPT-PT-02-002, Rev. 0). The document describes the basis for the project recommendation to prefer pursuing Beta Scintillation as an on-line monitor[9]. This work was performed in accordance with NQA-1 1989.

1.1 OBJECTIVES

The objective of this task was to evaluate an ICPES system as a means to monitor ^{99}Tc on-line in the Hanford WTP. The system should produce accurate results when compared to the ICPMS method; operate for extended periods without maintenance (including recalibration) and without introducing undue risks to WTP personnel or equipment. In particular:

The following objectives from the Task Plan were performed:

1. Demonstrate the capability of the monitor to reveal thermal elution profiles.
3. Demonstrate the automated sample delivery step for the ICPES system. Integrate the automated sample delivery system with the ICPES.
4. Determine the timing and flow characteristics of the sampling system.
7. Demonstrate a level of precision of 10% relative standard deviation.
8. Operate the technetium monitoring system continuously, analyzing new samples once every 15 minutes during a 30-day trial period.

The following objectives were dropped when the scope was reduced after the May review meeting.

2. Clarify analytical differences between ICPES, ICPMS, and beta scintillation methods, and explore methods for oxidation and complexation of technetium.
5. Demonstrate analytical sensitivity in the range 0.1 – 0.5 µg /mL. 0.1 µg /mL sensitivity is desired for final column effluent monitoring. If this sensitivity cannot be consistently achieved, then on-line monitoring of the feed to the final ion exchange column combined with historical data from laboratory analyses of final column effluent will be used to guide operators in predicting final column breakthrough. For the purpose of this test, the detection limit will be defined as three times the standard deviation of 10 matrix blank measurements. The slope as a gain in intensity will be reported.
6. Demonstrate an accuracy of 20% compared to the reference ICPMS.
9. Test the effectiveness of using laser-induced breakdown spectroscopy (LIBS) to measure the concentration of ^{99}Tc.

1.2 CONDUCT OF TESTING

EXPERIMENTAL EQUIPMENT AND FACILITY DETAILS

The experimental setup matched closely that described in the Task Plan[6]. Figure 1 shows a photo of the thermal elution studies apparatus as set up in C139. The plasma torch box of the analyzer is on the right. One of the sampling valves used in the study is shown. Figure 2 shows the plasma torch box after ignition.

Primary equipment for the on-line monitor was:

- Advanced Energy Products, Model 16 L, 40 MHz, 1600 W RF power supply
- Porter Instruments Flow Controllers for Argon with:
    - 4 Port Digital Display and Control Adjustment Panel;
    - 0-20 L/min controller;
    - 0-2 L/min mass flow controllers for plasma, nebulizer, auxiliary, and spectrometer purge.
- Pentium 233 MHz Computer including:
    - Thermo Jarrell Ash Software Thermo Spec v2.10
    - Keithley Relay control – 16 digital relay ports, 0-120 V, 3 amps;
    - National Instruments DIO-32F board for Charge Injection Device (CID) Camera Spectrometer detector.
- Echelle Spectrometer – Thermo Jarrell Ash,
    - 0.02 nm resolution at 250 nm;
    - 190-800 nm coverage with CID digital camera;
    - Flexicool two-stage compressor cooler for cooling CID to –85°C;
    - Camera frame grabber and sensor control board with embedded 386 controller.

An automated Valco Cheminert sampling valve was used to divert effluent from a research column containing SuperLig 639 resin to the nebulizer of the on-line ICPES system. The diverted sample was precisely pumped with an Altec HPLC pump using an aqueous feed with 2 ppm of yttrium as an internal standard. A script program running on the 233 MHz personal computer delayed timing for injections and ran the ICPES analyses. The optical emission from the plasma was collected using a 4-meter fiber optic cable. Emission intensities were determined using a Thermo Jarrell Ash IRIS echelle spectrometer running ThermoSpec software.

On-line analyses were made for 65 to 85 hours during column loading and up to 48 hours while flushing the column to remove the collected rhenium. Column samples were automatically taken at 15 minute intervals to monitor the operations. Rhenium, argon, and aluminum were trended in real-time on the computer screen in graphic charts. Concentrations of all monitored wavelengths could be read from a table on the computer screen for the current sampling instance. The software allowed individual line profiles to be viewed on demand while the analyzer program ran in the background.

Laboratory samples were collected at 3-hour intervals using a fraction collection system that was in-line with the column effluent and located after the on-line monitoring sampling valve. Laboratory samples were taken more frequently if indicated by the on-line signal. This was especially important during the rhenium elution.

The current on-line instrument design used a 40 MHz, 1600-watt RF power supply requiring three-phase 208-volt power. An alternative design, with a 27 MHz and 208 V single-phase power requirement, was purchased for pilot operations but not used. Three laboratory ICPES systems were used to support the studies including a 27 MHz ARL 3580, a 40 MHz JY Ultima, and a 40 MHz PE Optima system. Instrument calibrations were checked with standards from High Purity Standards, Charleston, SC.

Connections to the on-line ICPES included a 25-foot RF coax cable, two water lines [in and return], three argon lines, RF tuner controller line, and a grounding strap. A 4 meter solarized resistant deep UV quartz fiber-optic cable from Polymicro transferred the emission signal from the torch to a Thermo Jarrell Ash echelle spectrometer. The automatic sampler was a Valco Cheminert 6 port valve. A Valco stainless steel pneumatic 1/8” sampling port was used for the larger column. For the small column studies Teflon™ and PEEK tubing was used. The larger column used 1/8” tubing.

The Thermo Jarrell Ash echelle was taken from an IRIS ICP spectrometer. The echelle was modified to work with fiber optic input rather than directly coupled to the plasma via optical lenses. The echelle used a charge-injection-device detector chilled to –85 degree C, which allowed coverage of the 190-800 nm spectrum in a single reading. [A simpler grating instrument would work if just rhenium were monitored]. For the R&D studies, multiple elements were monitored to improve process knowledge. An Electro-Technic Tesla probe was used to provide ions to ignite the torch.

Thermo Jarrell Ash ThermoSpec software was used to control the spectrometer and select emissions lines to monitor. Emission lines were corrected for background and multiple lines were monitored for the same element to help detect matrix interference. Each monitored emission line was corrected for background level on each side of the emission peak and scaled by an intensity factor for quantitative measurements. Wavelengths below 250 nm were significantly hampered by light loss in the fiber optic cable when compared to a direct ICPES that used lenses to couple the spectrometer to the torch. This made measurement of rhenium lines at 221.4 and 227.5 nm difficult. Technetium lines were at 254.3, 261.0, and 264.7 nm. The technetium 264.7 line was monitored in all experiments including those with out technetium so we could determine if matrix interference would occur had technetium been present. Data are shown in a real-time trend plot on the computer screen during the runs as shown in the screen image. Post analysis of the trend data was used to determine detection limits and compare data to off-line samples sent to the laboratory.

The argon flow lines were controlled using Porter Instruments mass flow controllers. A Keithley Instruments relay rack with a Metrabyte I/O card provided computer-controlled contact closures for signaling the automatic sampling valve.

The plasma box contained a double-pass spray chamber with a Burgener high-solids nebulizer, a standard concentric torch, induction coil and impedance-matching network. The impedance match and induction coil was cooled with water circulation from a Neslab water chiller set at 25°C. The induction coil was three and one half turns of 1/8” copper tubing. Coil diameter was approximately one and one quarter inches. The torch was ignited using a small Electro-Technics Tesla coil probe.

The system had several safety interlocks including a gas flow sensor on the main coolant gas and interlocks on the water flow and plasma door. The plasma box was coupled to the spectrometer via 600-micron fiber optic cable [Polymicro]. The fiber was optimized for UV and non-solarization. RF cable was 25 feet of RG 217 military grade 50-ohm cable.

Originally a 1/16” 6 port VICI Cheminert electronic sampling valve was used. When the column size changed from the small 1-cm ID column to the larger 2.5-cm id column a change in the sampling valve was made to a pneumatically driven 1/8” stainless steel version. This later valve allowed the flow rate to be increased without creating a significant line pressure. Adapter fittings reduced the ICP nebulizer and HPLC feed lines down to 1/16” tubing.

1.3 RESULTS AND PERFORMANCE AGAINST OBJECTIVES

Table 1 lists the runs for the thermal elution studies. The starting date for each run is shown as well as the associated name for the Excel spreadsheet. The data for each run are included on the enclosed CD. Table 1 lists the experimental solutions and conditions for the thermal analysis runs. Table 2 gives the concentration for the feed solutions used to load the column and indicates the wavelengths used to monitor the concentrations. Table 2 lists the primary emission lines used for on-line and laboratory ICPES systems**.**

TABLE 1 COLUMN RUN SUMMARY

Tests involved processing app. 2500 mL of caustic feed (loading time app. 65 hours) followed by elution with water at 65 °C ***(app. 24 hours).***

10-12 ml resin bed

Test Date	Simulant	Temp.	Flow Rate (BV/hr)	Column ID (cm)	DataFile
1/8/2002	AN-105	25°C	3	1.5	wkjan7b.xls
1/15/2002	AN-105	45°C	3	1.5	wkjan14a.xls
1/22/2002	AN-105	35°C	3	1.5	wkjan21a.xls
2/5/2002	AN-105	25°C	3	1.5	WKFeb5Run4.xls
7/17/2002	AN-105	25°C	3	1.5	k071702a.xls
7/29/2002	AN-105	35°C	3	1.5	wkjul29.xls
8/19/2002	AN-105	45°C	3	1.5	wkAug18_2002run1.xls

Tests involved processing 15-18 L of caustic feed (loading time 65-85 hours) followed by elution with water at 65 C (app. 24 hours).

75 mL resin bed

Test Date	Simulant	Temp.	Flow Rate (BV/hr)	Column ID (cm)	DataFile
9/4/2002	AZ-102	25°C	3	2.54	RunSept42002wkdata.xls
9/16/2002	AN-107	25°C	3	2.54	wksep162002.xls

TABLE 2 FEED SIMULANT COMPOSITIONS

	AN105	AZ102	AN107	Wavelength [A]
	mg/L	mg/L	mg/L	
Na	109000	112000	134000	Na_3302
Al	14700	1290	241	Al_2567, Al_2652
K	3310	5590	1390	K_7689
Cr	590	1350	.20	Cr_2677,Cr_2835
S	198	10300	1760	S_1807*
Si	105	6.8	9.70	Si_2516, Si_2881
P	71.7	288	302	P_1774*
Mo	36.5	98	21	Mo_2816
B	24.0	9.5	21	B_2496
Pb	20.4	<1.4	<1.4	Pb_2207*
Re	11.5	36.3	5.7	Re_2275,Re_3451
Zn	4.83	<. 74	17.2	Zn_2133*
Fe	1.82	.54	17.5	Fe_2382
Ca	0.67	65.1	143	Ca_3933
Cd	0.55	<. 03	<.03	Cd_2265*
Ba	0.24	.23	<.03	Ba_4554*
Cu	0.15	<.25	2.3	Cu_3273
Zr	0.12	<0.1	.86	Zr_3391*
Sr	0.05	.61	90.8	Sr_4077
La	<1.4	<1.4	<1.4	La_3949*
Sn	<0.52	<1.0	<.52	Sn_2840*
Ti	<0.28	<0.3	<0.3	Ti_3349*
V	<0.26	<.26	<.26	V_3202*
Li	<0.2	<0.2	<0.2	Li_6103*
Mg	<0.17	<.17	<.18	Mg_2795
Ni	<0.12	<.12	306	Ni_3414
Co	<0.088	<.088	<.088	Co_2286*
Mn	<0.018	<.04	1.2	Mn_2593

* Lines were monitored on lab ICPES but not on-line. Values less than the detection limit are reported as < the detection limit.

The spectrum contained major emissions from the argon used for the plasma, the water matrix – hydrogen and hydroxide lines, air – nitrogen, oxygen, and nitrate/nitrite anions in the water. The nebulizer feed was water with a 2 µg/mL of yttrium. The Y served as an internal check on both the plasma response and consistency of the sample injection. If the sample injection were poor, the yttrium level would increase indicating that less sample had diluted the yttrium feed. That is, the response was inversely proportional to injection.

1.4 QUALITY REQUIREMENTS

This work was performed in accordance with NQA-1 1989. This work was conducted in accordance with the RPP-WTP QA requirements specified for work conducted by SRTC as identified in DOE IWO MOSRLE60. SRTC has provided matrices to WTP demonstrating compliance of the SRTC QA program with the requirements specified by WTP. Specific information regarding the compliance of the SRTC QA program with RW-0333P, Revision 10, NQA-1 1989, Part 1, Basic and Supplementary Requirements and NQA-2a 1990, Part 2.7 is contained in these matrices. The Task Plan[4] included a copy of the QA matrix with applicable sections marked. The research used equipment that was already acquired so procurement controls were limited and operating procedures were already written. The research supported W. King's Task Plan[6] which addressed calibration issues. Therefore, the main QA requirements in the matrix were reduced to maintaining research notebooks for the study. The research notebooks were audited by WSRC and WTP QA personnel during the course of the work.

1.5 ISSUES

The on-line ICPES system discussed in this report was developed in parallel with a beta scintillation system. Oleg Egorov at PNNL developed an automated beta scintillation system for possible on-line use[8]. WTP personnel reviewed both systems on May 1, 2002. After that meeting WTP decided to stop development of the ICPES system and continue to develop the beta-scintillation system for their on-line application. Al Pajunen of WTP wrote a detailed report detailing the selection process and information about the analyzer[9].

After the review, the existing ICPES instrument was perceived as a supporting tool rather than a developmental one and little effort was made to enhance performance for on-line applications or resolve the ICP-MS versus ICP-ES measurement bias. The instrument was used "as is" for what information it could provide. An instrumentation failure in mid June was only partially repaired for the runs in the 735-11A laboratory. This limitation was noted above in the experimental details.

The ICP-ES monitor is currently in stand-by mode and could be deployed to support other studies for RPP. A commercial version of a torch box was purchased for the pilot scale operations and is available for use. The box is currently in storage.

Newer echelle spectrometers with higher resolution and improved detector cameras are available and would improve performance. The new echelles do not require an external camera chiller and have a smaller instrument package. The TJA echelle spectrometer used to support these studies was 10 years old. TJA makes an improved version of the camera electronics. The upgrade costs approximately $15K to convert the current system to the new standard. The optics in the echelle should be replaced or re-coated as the mirrors have aged and no longer have optimum UV transmittance.

2.0 CD-ROM ENCLOSURES

The raw data from the analyzer were stored in a Dbase-compatible format by Thermo Jarrell Ash software. The data were exported to ASCII data format and then imported into a Microsoft Excel spreadsheet for post-run data analysis and charting. The enclosed CD-ROM contains copies of the Microsoft Excel data workbooks for the experiments. The file names for the runs are given in Table 2.

An electronic copy of this report, in Adobe “pdf” format, is included on the CD-ROM along with cleared pdf files from the earlier reports. A report from Argonne West that was found on the OSTI Energy Portal is also included as it describes how they measured technetium using an ICPES system. That report is not readily available from government documents.

3.0 DISCUSSION

The basic ICPES instrumentation for on-line monitoring of technetium was developed during previous studies and described in earlier reports. The current set of experiments sought to build experience with the instrument in continuous usage while helping on-site researchers study the proposed technetium removal process.

W. D. King in our laboratories planned a series of thermal elution experiments using synthetic mixtures of tanks AN105, AZ102, and AN107. Rhenium was used as a non-radioactive analog for technetium in the synthetic tank mixtures. Previous studies showed that rhenium behaved similarly to technetium in the process. Solutions were pumped through a SuperLig 639 column at 25, 35, and 45°C and then eluted with water at 65°C. King pulled samples from the column every 3 hours and sent them for laboratory analyses. Our analyzer was used to fill in the gaps taking samples every 15 minutes.

Laboratory samples were analyzed on a Perkin-Elmer Optima 3000 ICPES. This system enabled analyses of deep UV emission lines including sulfur, phosphorous, lead, zinc, and cadmium. Those elements were impossible or difficult to do on the on-line monitor system because the fiber optic cable blocked the emission. The PE ICPES was at least 10 times more sensitive for Re compared to the on-line system because of the fiber. It readily measured trace breakthrough concentrations at 221.4 and 227.5 nm emission lines. Samples were diluted approximately 20 fold prior to analyses, which decreased the matrix effect. A scandium internal standard worked well with the dilution. Results of the diluted samples compared closely with the results obtained on a VG Plasma QUAD ICP-MS system for the King test matrices. That is, we had little bias with these samples between the ICPES and ICPMS instruments. The PE ICPES had a rhenium detection limit of approximately 20 ppb versus 200 ppb for the on-line fiber system.

Laboratory results for Re were similar to on-line results. The optic fiber in the on-line system allowed the plasma to be isolated from the instrumentation. This allowed the spectrometer to be put in a convenient location while still analyzing samples rapidly with total automation. However, much better sensitivity was obtained if a non-fiber optical system was used. As mentioned in a previous report, the difference between laboratory and on-line ICPES is less for technetium than for rhenium. Technetium is measured at a higher wavelength using the 264.7 nm line and less signal loss from the fiber occurs.

In the last two thermal runs the column size was changed from a 10-mL bed to a 7-mL one. Flow rate in both cases was set to 3 bed volumes per hour. That is in the first set of experiments the actual flow rate was approximately 30 mL/hr and in the second the flow rate increased to 225 mL/hr. To cause minimal backpressure from the sampling system, the sampling valve was changed from a 1/16" valve to a 1/8" valve. The 1/8" valve was pneumatically driven rather than electrically turned. The injection loop was changed to 1/8" tubing. Adapter fittings were used to connect the 1/16" feed pump and nebulizer lines to the valve. These changes appeared to have little effect on the data and analyzer use. A slight increase in the pulsing of the nebulizer was noticed.

Figure 3 shows the rhenium signal for all nine runs. Breakthrough signals are very small compared to the elution signal. The largest signal was for the AZ102 run which had nearly three times the rhenium concentration of the other runs. The AZ102 run shown in figure 4 shows typical instrument response for selected lines. During Sept 5, the column torch was exchanged after an argon outage and the plasma readjusted to a more ionizing position. That is, the overall sodium response decreases and the response for yttrium was improved after the adjustment. Rhenium sensitivity improved with improved sensitivity for yttrium. The system was stable from noon on Sept 6 through the elution cycle on the evening of Sept 7. The comparing the yttrium and sodium responses could identify the occasional bad injection or air bubble in the feed stream. If yttrium went up and the sodium down then the injection loop had not fully filled with sample. If both went down, then liquid had not been pumped or nebulized.

Figures 6 and 7 show the breakthrough curves for the on-line AN105 runs and the laboratory runs. As expected, the breakthrough was more noticeable when loading at higher temperature. The noise figures for rhenium were marginal for these runs, which suggests that a non-fiber system should be used for rhenium studies.

3.1 TECHNETIUM DEEP UV SCAN

W. F. Meggers reported technetium emission lines in several journal articles while working at the National Bureau of Standards[7]. He used a DC arc and spark source spectrometer that did not have deep UV capability for those studies.

A Jobin Yvon Ultima 2000 ICPES was recently set up in our laboratories for radioactive measurements. This system has a nitrogen-purged spectrometer and is able to scan from 120 nm to 800 nm. To check for deep UV emission lines we scanned a 400 mg/L pertechnetate standard in 0.1 M nitric acid. This system was set up to use the 2nd order spectrum, which improved the resolution. The plasma was set at 1250 watts.

Figure 8 shows the emission pattern that was observed. Major emission lines were observed at the wavelengths reported by Meggers[7]. The ICPES lines that we observed are listed in Table 3. Only weak emissions were observed in the deep UV. The strong emissions at the very low end are believed to be first order lines from the 254-264 group showing up at one half their actual wavelength. The line marked as 130.33 nm is most likely the same as the 260.985 line but first order instead of second order, which the spectrometer was set to read. Meggers reported that line as being 261.000 nm, which gives some indication of the accuracy of our spectrometer. The best ICP lines are those previously reported for ion lines at 254.3, 261.0, and 264.7 nm. One interesting emission is at 249.7 nm, which overlapped in our spectrometers one of the boron doublet lines often measured in some radioactive glasses. The boron 249.6 line did not have the interference. Technetium line libraries are rarely included in commercial software but we found that technetium can be readily measured with an ICPES. We have reported the lines as read on our spectrometer. The spectrometer was calibrated against common elemental and argon emission lines.

TABLE 3 MAJOR TECHNETIUM ICPES EMISSION LINES

As measured on a JY Ultima 2000
Spectrometer set up for 2nd order, 1250 watts

Tc Line	Wavelength (nm)	Intensity
1	130.422*	39257
2	130.691*	82000
3	130.775*	59500
4	132.333*	220000
5	136.323*	39257
6	180.449	13086
7	213.973	16476
8	229.779	7229
9	249.653	25894
10	254.314	144038
11	260.985	122542
12	264.702	68859
13	319.476	23792
14	321.16	29740
15	323.661	36878
16	346.541	19034
17	363.514	70000
18	371.811	30649
19	374.619	29740
20	403.123	74300
21	409.549	23400
22	426.193	42837
23	429.674	63292
24	423.788	28345
25	561.158	26171
26	696.507	15569
27	740.309	34500
28	763.51	14800

*We suspect the lines from 130-136 nm are most likely first order lines in the spectra and actually twice the wavelength reported by the spectrometer.

3.2 ALTERNATIVE – LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

In the course of these studies we considered using a laser as alternative method to stimulate the emission signal. The idea was that a laser probe coupled to an optical fiber to collect the emission signal might work well in a process environment and is a simpler and less expensive instrument compared to maintaining an ICP plasma in containment.

Because our laboratory did not have a full LIBS setup, we asked J.P. Singh at the Mississippi State Diagnostic and Instrumentation Laboratory to investigate the initial LIBS concept using their equipment and waste simulants[10]. Singh's group had demonstrated field process LIBS measurements on molten glass. DIAL worked with synthetic solutions and looked at rhenium, manganese, and chromium since their laboratory was not set up for radioactive materials. The primary challenge was to develop a method for direct analysis of rhenium. We wanted detection at sub parts per million levels in a high salt caustic liquid.

Singh's group developed a double pulse droplet method with encouraging results. The sample was converted to small droplets, which they then blasted twice with the laser. The first hit vaporized the sample and formed a micro gas sphere containing the sample. The second hit ionized the sample. Singh's data indicates that rhenium could be detected near 1 ppm. This level is adequate for monitoring the elution of rhenium or technetium from the process column. Singh's findings are being reported in a couple of papers, which they expected to be in print by Spring[9].

3.3 PROBLEMS IN THE MEASUREMENTS

3.3.1 Instrumentation Failure Modes

Continuous use of the on-line ICPES during the long data runs revealed technical problems with the on-line analyzer that required intervention. For the most part the fixes were simple and took only a few minutes to repair and return the unit to operation. Most of the technical problems can be avoided with a better design.

For example, the nebulizer feed solution had a 2 liter source bottle, which at 1 mL per minute should have lasted 33 hours between refills. However we learned that the inlet tubing and its inlet filter tended to lift in the bottle. Liquid could not be drawn when the inlet filter was not fully covered. If an air bubble formed the pump could lose its priming ability. The feed needed to be refilled about every 20 hours, which often happened in the middle of the night or early morning hours when the instrument was unattended. Our system ran dry several times during the experiments. We should have used a larger 5 liter feed source, located the feed solution above the pump to help self priming, and possibly degassed the solution prior to use. After about 6 weeks of operations we needed to service the HPLC pump to clear trace particles from the system and check valves.

A problem with the nebulizer feed was readily detected visually by looking at the nebulizer spray chamber, which would become clear rather than cloudy. The yttrium signal decreased, the argon signal generally increased slightly and there was a loss in almost all other elemental emission, as solution was no longer being pushed into the nebulizer. A poorly functioning nebulizer from a partially plugged nebulizer or from a faulty feed pump tended to pulse the spray chamber and could be readily observed. As one might expect, best performance occurred with a smooth feed and no pulsing.

The current generation of the plasma box mounted the glass nebulizer external to the torch shielding. This mode facilitated visual inspection of the spray chamber and nebulizer operation but made the torch more difficult to ignite. The small torch shielding changed the torch RF loading dynamics. In the earlier system the nebulizer was enclosed and not visible but torch lighting was easier.

We had some problems with the plasma wanting to run upstream rather than downstream especially during ignition. Occasionally, a small finger of plasma would flicker into the low-flow auxiliary line to the torch. This line was made of a silicon rubber and after several hours we noticed it would yellow. Apparently some of the tubing would off gas. A deposit formed a pale yellow film in the hotter part of the torch near the RF coil. The higher organic feed tanks likewise tended to form a yellow deposit on the torch. We found that the fiber optic lens needed to be cleaned between runs although a visible film was not always evident. Better UV response occurred after cleaning the lens.

Torches were generally good for about three weeks of runs. Torches that were improperly cooled such as occurred when the argon source ran out would crack and be easily broken if moved. Torch replacement was generally easy in our design and should be a feature in any on-line ICP system.

Most commercial companies have apparently solved the ignition problem for their systems but we found that our remote system was not always easy to ignite. We found that using a new torch made plasma ignition easy but a dirty one was often a challenge. A dirty torch had to be carefully centered in the plasma coil. We found that sometimes a dirty torch could be started by increasing the spread of the RF coil or by shifting the torch up or down a millimeter. Plasma ignition could be a major concern if the torch needs to be totally remote running dirty samples, frequently turned off and on, or the RF coupling is not well matched with a good fast auto-tuning network. We found that once the plasma was ignited with a well-shaped plasma then the plasma part of the system was stable for days.

3.3.2 Diagnostic Lines

To improve control and provide feedback on performance, diagnostic emissions were routinely measured. Monitoring the argon emission indicated major problems with the plasma and helped identify spectral noise sources. Argon was monitored at the 415.8 and 404.4 nm emissions. The former was occasionally interfered with by high calcium in a nearby order on the echelle. As expected argon emission was stable compared to emission that came from nebulized sources.

Yttrium was added to the nebulizer water feed [sample carrier] at a 2 µg/mL concentration. Yttrium was monitored at three wavelengths, 324.2, 360.0, and 371.0 nm. All worked well without detectable interference at each line. The 371.0 nm was used for routine monitoring. Yttrium in the feed was used to detect injection failures and to adjust the timing between injection and analyses. Yttrium response was negatively correlated. That is the yttrium signal would be at the full response level for 2 ppm when a sample was not injected but would decrease as the carrier was displaced by the sample. The ratio of the measured yttrium signal to the full signal could be used as an indicator of the injection and the downstream mixing between the sample system and the plasma torch. Figure 6 for the AZ102 run illustrates the negative correlation of the yttrium line with sodium reading and could be used to reject invalid sampling.

One of the advantages of using a multiple wavelength simultaneous spectrometer was that single element emissions could be correlated with the other elements in the sample matrix. Instrumental problems could be distinguished from separations by examining the dependency of the lines. Elements would drift together in most instrumental problems.

Emissions from iron and silicon were used to indicate possible corrosion and dissolution problems. Occasionally, a silicon band appeared to elute during the water flush cycle. We suspected that a colloidal suspension or gel formed during the loading of the caustic feed solution. Glass wool or glass beads had been used to help retain the column resin. Once water removed the caustic the suspension around the silicon source became unstable and was removed. A similar phenomenon would likely occur if the feed contained sand. Dissolved silicon in the feed appeared to not be captured by the column indicating two possible types of silicon complexes.

4.0 FUTURE WORK

The on-line ICPES system described in this report has proven useful and cost effect in support of research and development activities for the River Protection Project. The system is not scheduled for future development. The existing equipment could be applied, where cost effective, for future studies involving the separation of metal ions. For example, a study on alternative separation methods for technetium is proposed for the Spring of 2003. The system could be applied in support of those studies. The Singh group at DIAL believes that their LIBS system could be made portable with an enclosed laser beam. They would like to try that system on actual technetium samples.

5.0 REFERENCES

1. Spencer William A., Pennebaker, F.M., D.M. McCabe, “Evaluation of Emission Spectroscopy for the On-Line Analysis of Technetium”, **BNF-003-98-0199, Rev. 1**, Feb. 7, 2000.

2. Spencer William A., Pennebaker, F.M., D.M. McCabe, “Supplemental Report: Evaluation of Emission Spectroscopy for the On-Line Analysis of Technetium”, **BNF-003-98-0233, Rev. 1**, Feb. 7, 2000.

3. Sherwood, David, RPP Task Specification, “Evaluation of Technetium Monitor Prototype”, **24590 WTP-TSP-RT-01-018, Rev. 0**.

4. Spencer, William A., “Evaluation of Technetium Monitor Prototype”, Task Technical and QA Plan, **WSRC-TR-2001-00576, SRT-RPP-2001-00217**, Savannah River Site, Aiken, SC, December 12, 2001.

5. RPP Task Specification: **TSP-W375-01-00023**, **Rev. 0**, “Evaluating Effects of Resin Particle Size and Solution Temperature on SuperLig® 644 and SuperLig® 639 Resins Performance with LAW Envelope A Simulant”.

6. “Task Technical and Quality Assurance Plan for Evaluating Effects of Resin Particle Size and Solution Temperature on SuperLig® 644 and SuperLig® 639 Resins Performance with LAW Envelope A Simulant”, **WSRC-TR-2001-0202, SRT-RPP-2001-0049**, July 13, 2001.

7. Meggers, W.F., “The Spectrochemistry of technetium and promethium”, Spectrochimica Acta, 1951, Vol. 4, pp. 317-326. Peragon Press Ltd., London.

8. Egorov,O.B., McNamara, B.K., “Development and Testing of the Automated ^{99}Tc Monitor. Fiscal Year 2001 Progress Report”, **WTP-RPT-025**, June 2002, Battelle, Pacific Northwest Division, Richland, Washington.

9. A. Pajunen, “Online Technetium Monitor Technology Selection Report”, **24590-PTF-RPT-PT-02-002, Rev. 0**.

10. F. Y. Yueh, R. C. Sharma, J. P. Singh and H. Zhang, “ Evaluation of the potential of laser induced breakdown spectroscopy for detection of trace elements in liquid,” J. Air & Waste Manag. Assoc. 2002 (In Press).

6.0 FIGURES

Figure 1: Thermal Elution Setup in C139 Laboratory

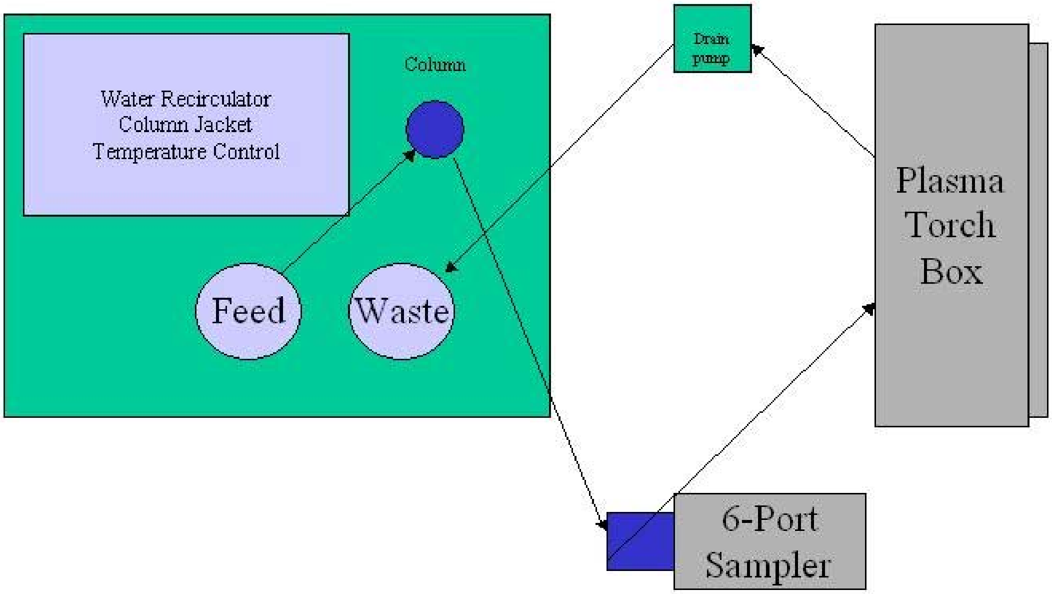

Figure 2: The Plasma Torch Box of the analyzer contains the radio frequency plasma used to create elemental emission. A fiber optic cable with lens assembly collected the emission signal and sent it to a high-resolution spectrometer. The nebulizer and spray chamber are shown mounted below the plasma.

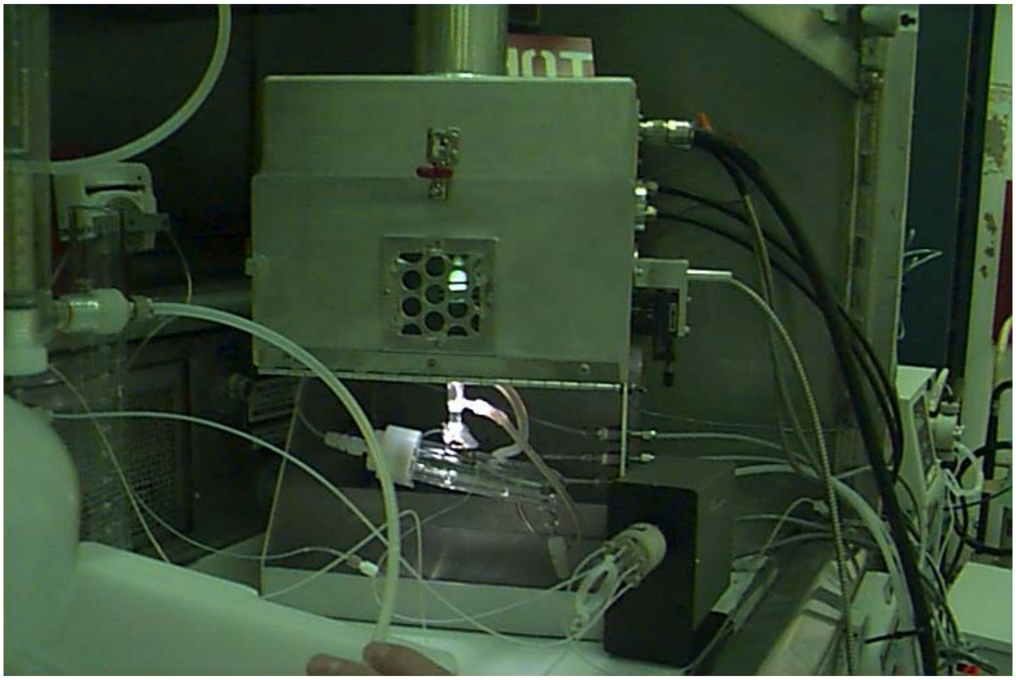

Figure 3: Data for nine thermal runs.

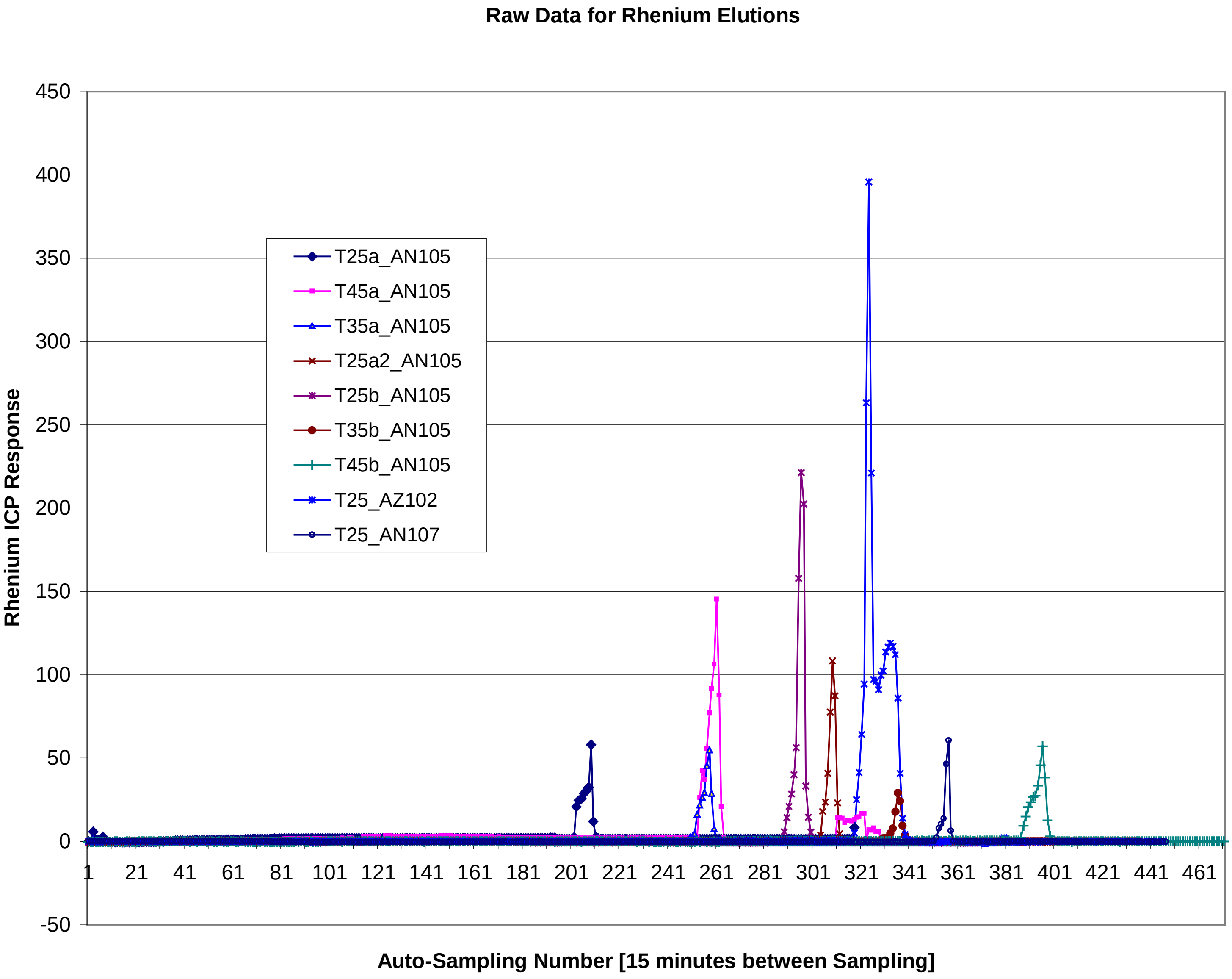

Figure 4: AZ102 column run had a higher concentration of rhenium and more potassium. Rhenium eluted in two bands. Yttrium and sodium lines gave opposite response when a bubble was in the sample loop but both decreased if bubble was in nebulizer feed supply.

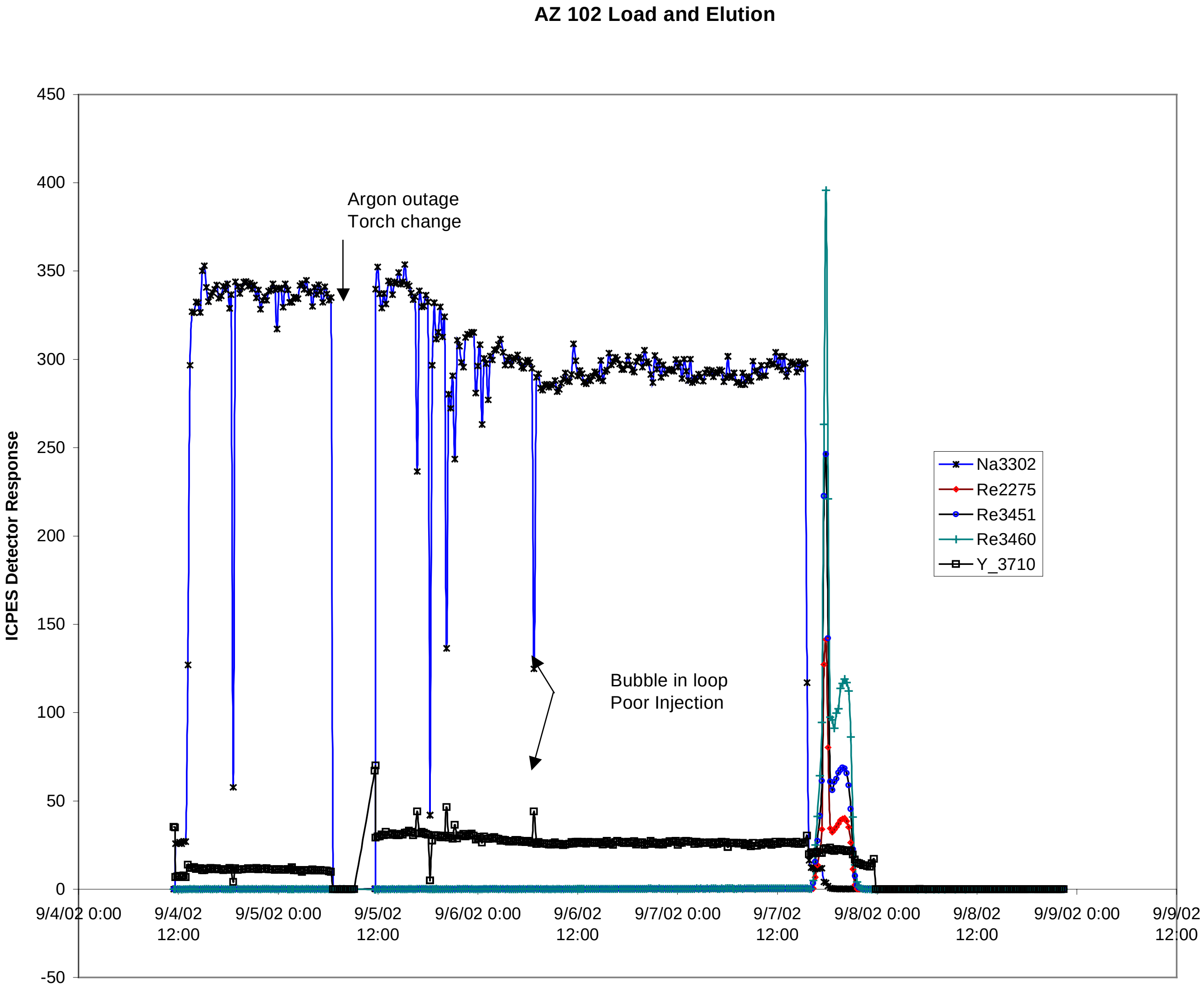

Figure 5: Enhanced view of the AZ102 elution shows that the second elution shoulder contained potassium.

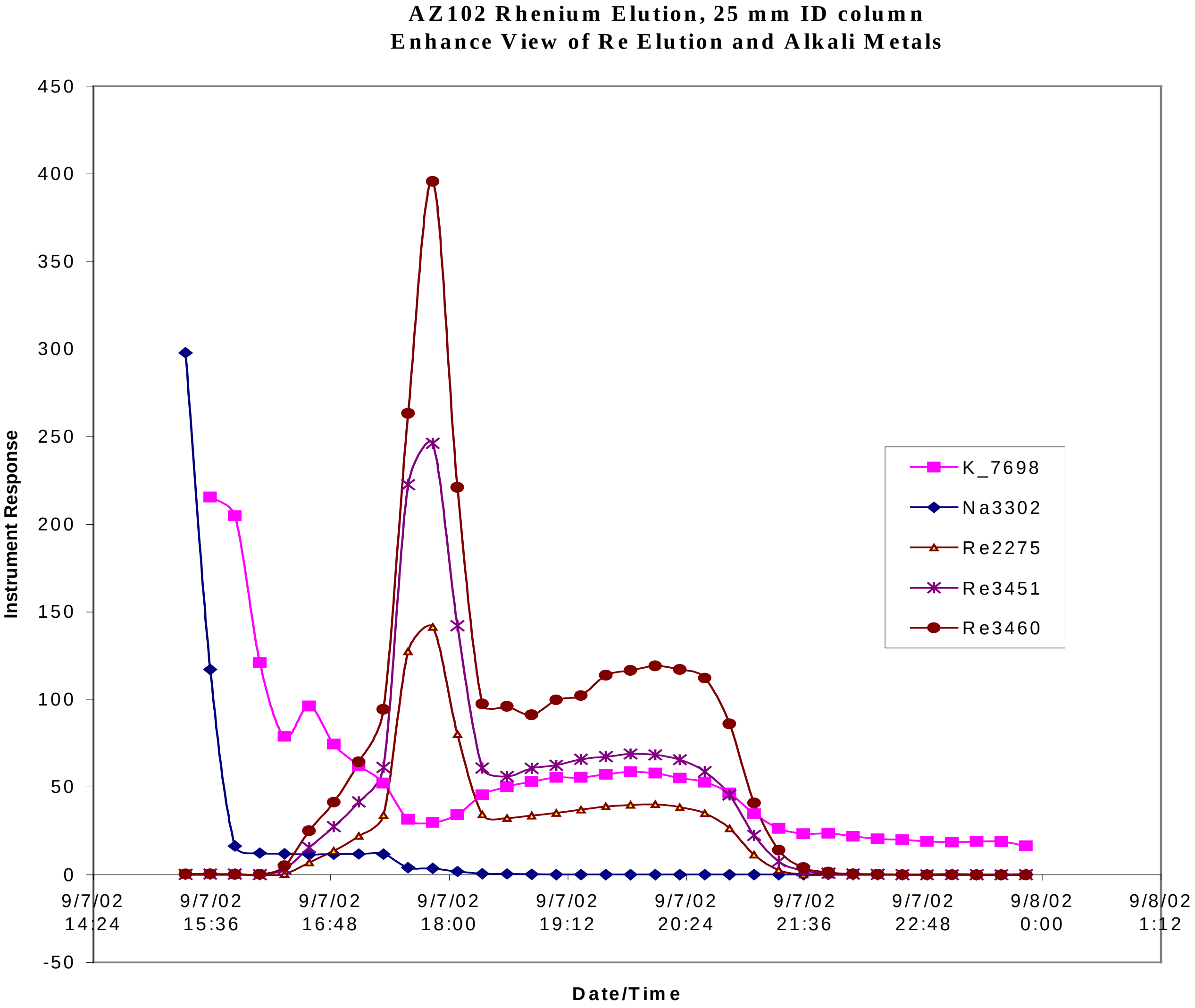

Figure 6: Enhanced view of the loading. Breakthrough was significant at the higher 45°C temperature but could be barely detected at 25°C using the on-line monitor.

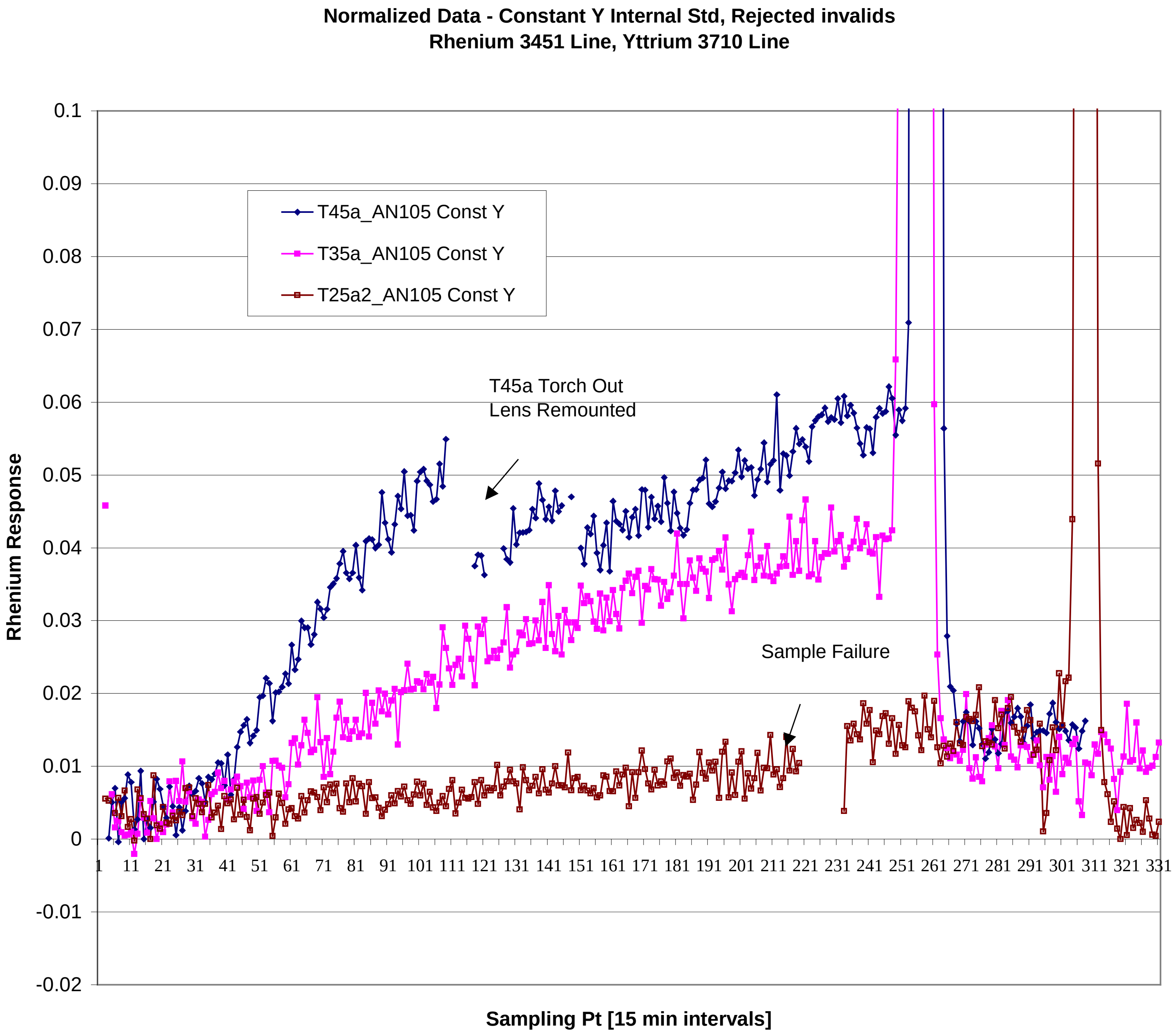

Figure 7: Breakthrough from laboratory samples taken every 3 hours was easily tracked. The lines were fit using the third order polynomial fit that comes with the Excel spreadsheet program.

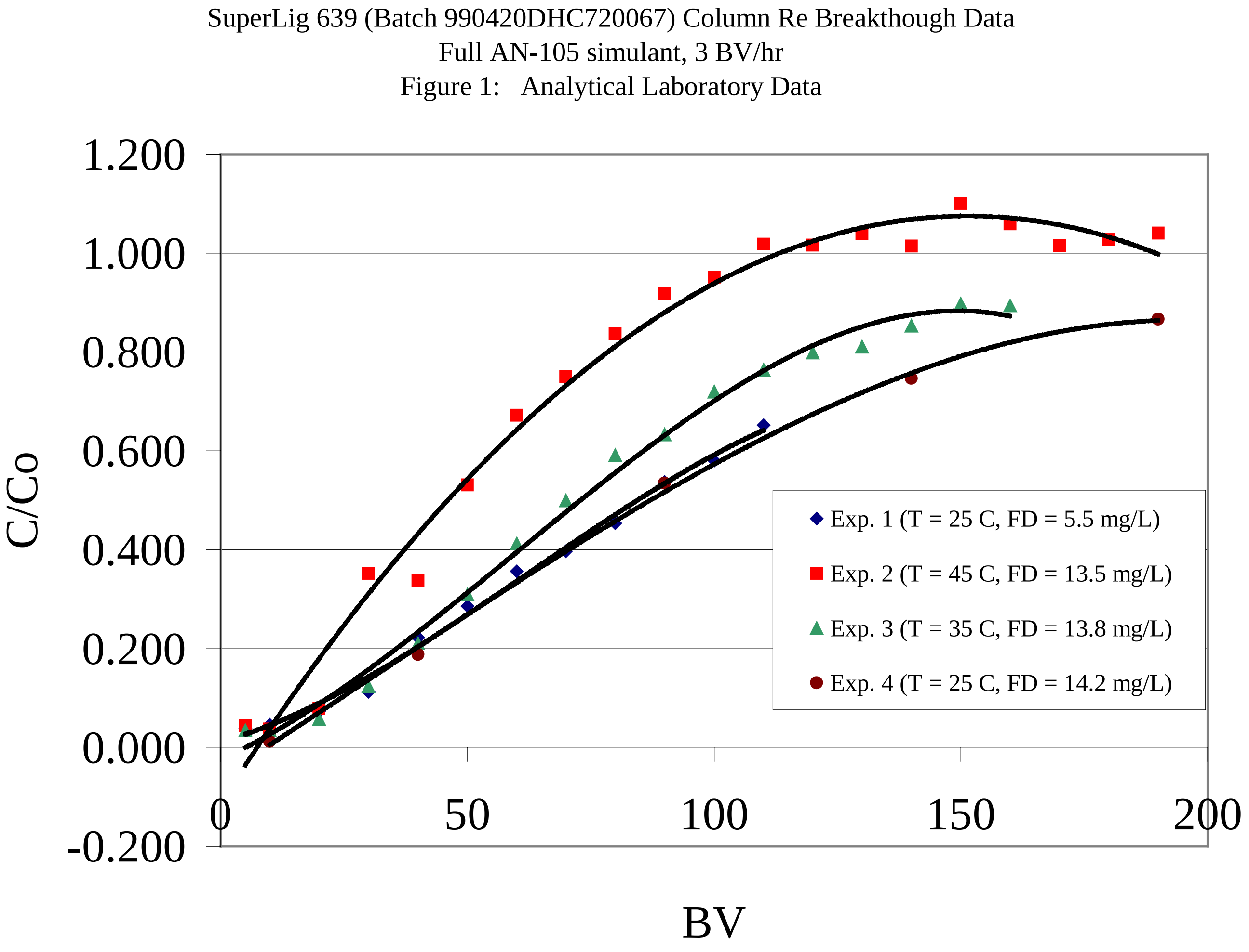

Figure 8: Deep UV emissions are shown in this technetium emission spectrum from 129 to 391 nm taken with a JY Ultima 2000 ICPES. We suspect that the lines below 140 nm were really first order spectral lines that had not been fully rejected by the spectrometer. That is the 132.3 nm is probably the 264.6 nm line but in a different order.

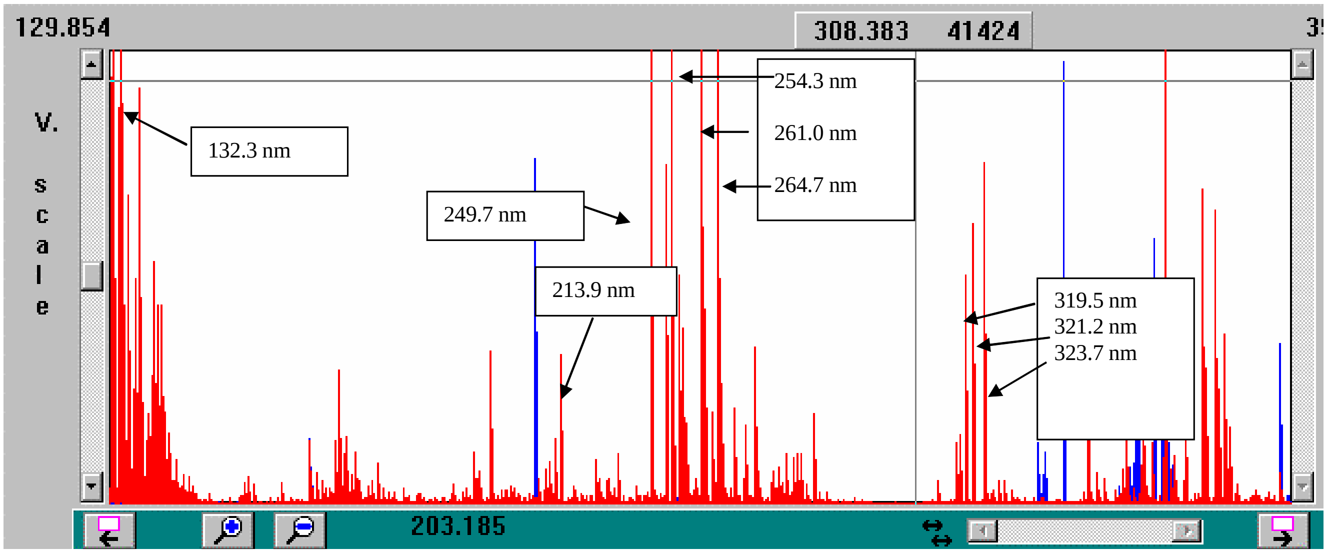

Figure 9: Temperature variation in lab 773A, C139 was small, generally less than a degree. In 735-11A, Rm130 variations of 10°F in a day were observed. In the lower 735-11A chart lines were offset to see weeks on same chart.