**PERFORMANCE ACCEPTANCE TEST
OF A PORTABLE INSTRUMENT
TO DETECT URANIUM IN WATER
AT THE DOE
ADVANCED WASTE WATER TREATMENT PLANT
FERNALD, OHIO**

Report Date
March 28, 1997

Prepared by:

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

M.S. Anderson¹ and S.J. Weeks²
Characterization, Monitoring, and Sensor Technology, Crosscutting Program
Office of Science and Technology, U.S. Department of Energy
Ames Laboratory, Iowa State University, Ames, IA 50011

R.J. Scheper
Technology Programs
Fluor Daniel Fernald, Inc.
P.O. Box 538704
Cincinnati, OH 45253-8704

MASTER

¹ Author to whom correspondence regarding the report should be sent.

² Current Address, CMST-CP, Special Technologies Laboratory, 5520 Ekwil St. Suite B, Santa Barbara, CA 93111

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, expressed 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.

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

TABLE OF CONTENTS

	Page
ABSTRACT.....	i
FIGURES.....	iv
TABLES.....	v
I. INTRODUCTION.....	1
Background.....	1
II. TEST FACILITY.....	2
III. SAMPLING PLAN.....	3
Raw Water samples collected for on-site analyses:.....	3
Acid-Preserved samples for on-site, and off-site confirmatory laboratory analyses:.....	3
IV. THE EPPENDORF-BIOTRONIK IC 2001-2 TECHNOLOGY.....	3
Description.....	3
Operating Parameters.....	4
Method of Operation (standard procedure).....	4
Cost.....	6
V. RESULTS AND DISCUSSION.....	6
Performance Evaluation Sample.....	7
Evaluation of Data Quality.....	7
Precision.....	7
Accuracy.....	8
Data Acquisition and Results.....	8
EB-IC Analyses.....	8
Fernald, July 10-11, Raw Water Sample Analyses.....	8
EB Laboratory Germany, July 25, Raw Water and Acid-Preserved Sample Analyses.....	12
EB-IC Precision and Accuracy.....	12
Confirmatory Laboratory, Argonne National Lab, ICP-MS.....	16

KPA Analyses at Fernald.....	16
Fernald, July 10-11, Raw Water Sample Analyses.....	17
Fernald, July 16, Acid-Preserved Water Sample Analyses.....	17
KPA Precision and Accuracy.....	17
Scintrex Analyses at Fernald.....	17
Summary of Analytical Results	18
Comparison with the Confirmatory Laboratory "true value"	19
VI. SUMMARY	24
Conclusions.....	24
Advantages and Limitations of the IC	24
Recommendation.....	25
Lessons Learned.....	26
APPENDIX A.....	A-1
Analytical Magnetics, Inc., price quotation for an Eppendorf-Biotronik IC 2001-2	
APPENDIX B.....	B-1
Confirmatory Laboratory Analytical Report from Argonne National Laboratory	
APPENDIX C.....	C-1
Distribution List for IS-5124	

FIGURES

1. COMPARISON BETWEEN THE RESULTS FROM THE EB LABORATORY (GERMANY) ANALYSES OF THE RAW WATER AND ACID-PRESERVED SAMPLES. THE ACID-PRESERVED SAMPLE RESULTS WITH ERROR BARS (STANDARD DEVIATION) ARE PLOTTED ON THE X-AXIS AND OFF-SET BY ± 1 PPB TO AVOID CONFUSION OF OVERLAPPING ERROR BARS. THE BROKEN LINES, SHOWN FOR REFERENCE, REPRESENT A CALCULATED ERROR OF $\pm 2\%$ 15
2. AGREEMENT BETWEEN THE KPA AND EB-IC RAW WATER SAMPLE ANALYTICAL RESULTS, TAKEN AT FERNALD, AND THE "TRUE VALUES" REPORTED BY ANL. A SECOND SET OF EB-IC RESULTS (REVISED) ARE ALSO SHOWN. THESE REVISED RESULTS WERE SUPPLIED BY AMI AFTER REVIEWING THE ORIGINAL EB-IC CHROMATOGRAMS. WHERE THERE ARE OVERLAPPING ERROR BARS, THE RESULTS HAVE BEEN OFFSET BY ± 1 PPB ON THE X-AXIS TO AVOID CONFUSION. 20
3. COMPARISON OF THE EB-IC ACID-PRESERVED AND RAW WATER SAMPLE RESULTS, TAKEN IN GERMANY, AND THE "TRUE VALUES" REPORTED BY ANL..... 21
4. THE KPA, SCINTREX, AND EB-IC (LABORATORY IN GERMANY) ACID-PRESERVED SAMPLE RESULTS COMPARED WITH THE "TRUE VALUES" REPORTED BY ANL. 22
5. THE ANL "TRUE VALUE" RESULTS SHOWN AS A BASELINE FOR COMPARING BOTH THE RAW WATER AND ACID-PRESERVED SAMPLE RESULTS FOR THE THREE INSTRUMENTS PROVIDING DATA TO THIS PROJECT..... 23

TABLES

1. FEMP-AWWT PERFORMANCE ACCEPTANCE TESTING SAMPLING MATRIX	5
2. RESULTS FOR BOTH THE RAW WATER AND ACID-PRESERVED SAMPLE ANALYSES FOR THE FERNALD KPA AND SCINTREX INSTRUMENTS, EPPENDORF-BIOTRONIK IC 2001-2, AND THE CONFIRMATORY LABORATORY ICP-MS. THE RAW WATER SAMPLES (NOT ACID PRESERVED), WERE ANALYZED ON JULY 10-11 AT FERNALD. THE REVISED RESULTS (JULY 14) WERE PROVIDED BY AMI AFTER REVIEWING THE CHROMATOGRAM FOR EACH EB-IC ANALYSIS. THE ACID PRESERVED SAMPLES WERE ANALYZED APPROXIMATELY THE SAME WEEK THAT THE SAMPLES WERE ANALYZED BY THE CONFIRMATORY LABORATORY (ANL).....	9
3. THE CALCULATION OF THE MEASUREMENT AVERAGE, <i>M</i> , THE STANDARD DEVIATION, <i>S</i> , AND THE DEVIATION D/ <i>S</i> FOR THE EB-IC FERNALD QUADRUPLICATE ANALYSES OF THE RAW WATER SAMPLES AND REVISED RESULTS.	13
4. THE CALCULATION OF THE MEASUREMENT AVERAGE, <i>M</i> , THE STANDARD DEVIATION, <i>S</i> , AND THE DEVIATION D/ <i>S</i> FOR THE EB LABORATORY ANALYSES OF BOTH THE RAW WATER AND ACID-PRESERVED SAMPLES. THIS TABLE ALSO INCLUDES THE RESULTS FOR THE QUADRUPLICATE ANALYSES OF SAMPLE AW-7508, THE PERFORMANCE STANDARD (IDC), AND THE SAMPLE BLANK.	14
5. THE CALCULATION OF THE MEASUREMENT AVERAGE, <i>M</i> , THE STANDARD DEVIATION, <i>S</i> , AND THE DEVIATION D/ <i>S</i> FOR THE FERNALD KPA QUADRUPLICATE ANALYSES OF SELECTED RAW WATER SAMPLES. STATED PRECISION OF THE METHOD USED BY FERNALD FOR THE KPA ANALYSIS OF DUPLICATE SAMPLES IS 4% AT 2 PPB U/L, AND 2% AT 50 PPB U/L (PRIVATE COMMUNICATION K. HUDSON).	18
6. A SUMMARY OF ANALYTICAL RESULTS FOR BOTH THE RAW WATER AND ACID-PRESERVED SAMPLES.....	19

I. INTRODUCTION

A number of Department of Energy (DOE) sites have an immediate need for a portable instrument that is capable of directly measuring the uranium content at the parts-per-billion level (ppb) in various classes of water found on a site and providing "real-time" results. These water analyses results will determine the level of treatment necessary, if any, to remove the uranium contamination to satisfy regulatory permits for the release of that water to the surrounding environment.

Several companies have recently developed portable instruments which are capable of directly analyzing water samples and quantitating the uranium in "real-time" (less than 10 minutes) at the parts per billion (ppb) detection level. This report provides the results from the Performance Acceptance Testing (PAT) project that evaluated the field performance of the Eppendorf-Biotronik portable ion chromatograph Model IC 2001-2 (EB-IC). The EB-IC analytical results for uranium content in aqueous samples are compared directly with those obtained from the off-site confirmatory laboratory, and the analytical results from the Kinetic Phosphorescence Analyzer (KPA), the current baseline technology used at Fernald by the site contractor, the Fluor Daniel Fernald, FD-FN. Also, analytical results from the Scintrex UA-3 phosphorescence analyzer, another FD-FN instrument, are presented.

Background

The impetus for developing instrumentation for directly measuring uranium contamination levels in water has existed since the Department of Energy's (DOE) forerunner, The Atomic Energy Commission (AEC), started mining, milling, and processing uranium during the early 1950s. An immediate need at a number of DOE sites is a "real-time" analytical capability for determining the uranium concentration in various classes of water found on a site.

The baseline analytical process is to draw a water sample and send it to either an off-site, or more recently, to an on-site laboratory for analysis. This is time consuming, and the analytical results required for decision making take from one day to several weeks, depending on the backlog at the laboratory. As hundreds of gallons of water are being processed per minute in water treatment plants, in the interest of public health it is imperative that rapid decisions be made concerning the quality of the treatment process, and whether or not the uranium level satisfies the regulatory permit requirements for release of the treated water into the surrounding environment.

Several companies have recently developed portable instruments which are capable of analyzing water samples immediately after they are drawn and provide the level of uranium in "real-time", with a low ppb detection limit. The objective of this project was to identify the portable instruments which are ready to be deployed and capable of rapidly and directly detecting low ppb levels of uranium in water samples, and rigorously test and evaluate their analytical capabilities using "real-world" samples. Two portable instruments which satisfy the above stated requirements were identified as candidates to participate in this project. The Test Plan

was written to test and evaluate the analytical capabilities of these two instruments. However, prior to the start of the test, one of the instruments was withdrawn from the project.

This report presents the results and evaluation of the Eppendorf-Biotronik IC 2001-2 (EB-IC), a portable Ion Chromatography instrument. In addition, the analytical results from the on-site Chemchek KPA-11, and another on-site phosphorescence analyzer instrument, Scintrex UA-3, will be presented. The analytical results from these three instruments are compared with the analytical results from an off-site confirmatory laboratory, Argonne National Laboratory (ANL). The ICP-MS technique was used to analyze the set of samples sent to ANL. The ANL report also provides isotopic information about the uranium in the water samples.

This project was jointly sponsored by the U.S. Department of Energy's, Office of Environmental Management (EM), Office of Science and Technology (OST), Office of Technology Integration, and the Characterization, Monitoring, and Sensor Technology Crosscutting Program (CMST-CP) from the Ames Laboratory; and FD-FN at the Fernald site.

Other participants in this project include: Analytical Magnetics, Inc. (AMI), Goffstown, NH and Eppendorf-Biotronik (EB) providing the instrument; the Fernald Advanced Waste Water Treatment (AWWT) plant providing the samples and the on-site low level radiometric laboratory providing baseline analysis; and Argonne National Laboratory (ANL), providing the off-site confirmatory analysis of the water samples.

II. TEST FACILITY

The AWWT plant was constructed at the Fernald site for the expressed purpose of removing elevated levels of uranium from various site wastewater streams. The AWWT contains two ion exchange treatment systems; one system treats 400 gallons of water per minute (gpm), and the second system treats 700 gpm. The final level of uranium in the plant effluent satisfies regulatory permit requirements, allowing the treated water to be released into a nearby river.

The water requiring treatment enters the AWWT from various sources including surface water retention basins, process water, and ground water from the regional aquifer. The influent first passes through clarification and filtration equipment to remove suspended solids. Any uranium in solid form in the wastewater is removed during this process. The influent then enters the ion exchange process where dissolved uranium (uranyl carbonate) is removed. The ion exchange resin changes the uranyl carbonate into uranyl chloride or uranyl sulfate ions and retains these chloride or sulfate ions. The treated water is sampled daily and evaluated for compliance with effluent permit requirements before being released into a nearby river.

The ion exchange resin used in the treatment systems has a limited capacity (number of exchange sites) for removing uranium. When all sites have been filled, the resin will be regenerated and used again. It is extremely important to monitor the effluent from the ion exchange process to maintain treatment system efficiency and ensure compliance with regulatory requirements.

Various water sampling ports have been installed throughout the treatment process to monitor the operating status of the AWWT plant.

III. SAMPLING PLAN

Seventeen half-liter water samples were drawn from various selected sampling ports in the AWWT's 400 and 700 gpm treatment systems. These sampling port locations and the respective sample designation are given in Table 1. Recent historical data trends were used to select ports where uranium concentrations were expected to be in the ranges of: 5-12 ppb, 17-25 ppb, 30-40 ppb, and 130-170 ppb. Quadruplicate analyses of these four samples were used to evaluate an instrument's precision, and accuracy (see Table 1). A Sample Blank, a performance evaluation standard, and a matrix-spiked sample were also provided. These raw water samples were delivered to the laboratory where they were analyzed using the baseline KPA technique and the EB-IC. A set of seven sample splits were preserved with nitric acid and sent off-site to the ANL laboratory for confirmatory analysis of total uranium content and isotopic makeup. In addition, a set of acid-preserved samples was retained at Fernald for KPA and Scintrex analysis, and a set along with a set of raw water samples was sent to the EB laboratory in Germany for analysis.

Raw Water samples collected for on-site analyses:

- 6 samples drawn from 5 sampling points in the 400 gpm water treatment system;
- 10 samples drawn from 8 sampling points in the 700 gpm water treatment system;
- 4 of the above sixteen samples were selected and split into 4 samples each - these quadruplicate sample splits provided the basis for determining instrument accuracy, precision and reproducibility;
- 4 QC samples: 1 sample blank, 1 NIST SRM standard sample, 1 matrix spiked sample, and 1 performance evaluation sample

Acid-Preserved samples for on-site, and off-site confirmatory laboratory analyses:

- 4 samples, 1 each of the samples analyzed on-site in quadruplicate for the determination of precision and accuracy;
- 3 QC samples: 1 sample blank, 1 matrix spiked sample, and 1 performance evaluation sample

IV. THE EPPENDORF-BIOTRONIK IC 2001-2 TECHNOLOGY

Description

The Eppendorf-Biotronik IC 2001-2 is a field-portable ion chromatography instrument made in Germany and distributed in the United States by Analytical Magnetics Inc. (AMI). This instrument measures anions and cations in aqueous samples. The instrument is light weight (approximately 30 lb.) and is powered by either a rechargeable battery pack or 110 V AC. The

EB-IC used the following configuration for this test: two pumps, one for transfer of the mobile phase sample (eluent), and one for pumping the uranium complexing agent; a uranium separation column; a UV-Vis detector; and a Notebook computer running the WinPeak Light Chromatography software.

Operating Parameters

Separation Column	BT Uran-1 50x4.6 nm
Eluent	dilute inorganic acids
Eluent flow rate	1.4 ml/min.
Injection volume	1 ml
Complexing agent	0.03% v/v Arsenazo III
Flow rate - complexing agent	0.15 ml/min
Uranium retention time	4.8 min
Detection	UV-Vis @ 660 nm

Method of Operation (standard procedure)

Note: The method of operation described here is suggested for the analysis of aqueous samples containing uranium and was the outcome of the PAT project at Fernald.

The EB-IC is calibrated using six standard solutions having a uranium concentration ranging from 5-200 ppb. These standard solutions were prepared by diluting an aqueous uranium standard reference material (SRM). A proprietary ion stabilization agent is added to both the samples and standards (4% v/v). The addition of the stabilizing agent ensures that the many uranium ionic forms which may exist in the sample are converted to a single anion form.

A syringe is used to load 5 ml of an aqueous sample into the instrument sample injection loop. Operating the sample introduction valve introduces 1 ml of sample into the eluent flow which passes through the ion exchange column where the uranium anions are separated from the aqueous matrix. The eluent then gradually moves the uranium through the column. After the uranium anions have passed out of the column (post column) Arsenazo III is mixed with the eluent producing a uranium complex which will absorb light at 660 nm. A single time dependent peak which is directly proportional to the uranium concentration in the sample, is detected by the UV-Vis detector.

Nitric acid-preserved samples are handled in a similar manner (see the discussion below on the method development that took place during the this project). The capability of analyzing nitric acid-preserved archived samples at a later date is essential.

AWWT System Sampling

400 gpm system

SAMPLE POINTS	Influent	Clarifier Discharge	Multi Media Filter	Lead IX Effluent	Lag IX Effluent
Number of Samples	1	1	1	2	1
Sample Identifier	AW-7495	AW-7496	AW-7497	AW-7498	AW-7499
Comment			400 IX Influent		

700 gpm system

SAMPLE POINTS	Influent	Clarifier Discharge	Multi Media Filter	Lead IX N. Effluent	Lag IX N. Effluent	Lead IX S. Effluent	Lag IX S. Effluent	Combined Effluent	Spit FV-990
Number of Samples	1	1	1	2	1	2	1	1	1
Sample Identifier	AW-7500	AW-7501	AW-7502	AW-7503	AW-7504	AW-7505	AW-7506	AW-7507	AW-7508
Comment			700 IX Influent	North D	North F	South A	South C	1100 Effluent	

Four of the above samples were split for quadruplicate analysis as a measure of precision and reproducibility. These samples were chosen in the following approximate representative ranges: (1) 5-12 ppb U (sample 7505), (2) 17-25 ppb U (sample 7501), (3) 30-40 ppb U (sample 7507), and (4) 130-170 ppb U (sample 7499).

QC Samples

SAMPLES	Blank	Standard	Matrix Spike	Performance Evaluation
Number of Samples	1	1	1	1
Sample Identifier	VAI-4245		Matrix Spike	IDC
Comment	Spit IX #3 Effluent	20 ppb NIST SRM	AW-7508 spike/w 50 ppb U	April IDC ERA control ~100 ppb U

The matrix spike was prepared in the approximate range 15-45 ppb U.
The performance evaluation sample was in the approximate range 10-200 ppb U.

Cost

A requested quote for an IC 2001-2 from Analytical Magnetics, Inc., is provided in Appendix A. The Eppendorf-Biotronik Model IC 2001-2 (item 5701-2) instrumentation package is complete and only needs the addition of the uranium separation kit (item 6903-U) to be ready for analysis at a total cost of \$20,400.00. This package is completely self-contained and has enough reagent for 1000 injections. Eppendorf-Biotronik suggests installing a new uranium column each time more reagent is ordered. This cost to replace the column and purchase enough reagent for 1000 injections is \$1500.00. Thus, the per sample cost is \$1.50. The options listed on the quote are not necessary for field work. However, if the instrument will be used in a site laboratory setting, the autosampler (item 8001) might be a labor saving addition.

The EB-IC portable instrument set up for uranium analysis and equipped with an autosampler costs less than 50% of the currently used KPA, a non-portable laboratory instrument, similarly equipped with an autosampler. The EB-IC instrument autosampler combination has an analytical productivity similar to a KPA autosampler combination.

V. RESULTS AND DISCUSSION

This section discusses the EB-IC method development, data acquisition, and presents the analytical results for: a) selected raw water samples at Fernald on July 10-11, b) the revised results from the re-examination of the chromatograms by AMI on July 14, c) the analyses of the selected raw water and nitric acid-preserved samples at the EB laboratory in Germany on July 25, d) the KPA analytical results for all of the raw water samples taken, and e) the confirmatory laboratory, KPA, and PA (Scintrex) analytical results for the set of selected acid-preserved samples.

Fourteen raw water samples (unpreserved) from the AWWT, a sample blank, a standard sample, a matrix spiked sample, and a performance evaluation sample were delivered to the Fernald laboratory in half-liter polypropylene bottles. Each sample was assigned a distinct number (see Table 1). FD-FN lab technicians prepared the sample splits for analysis by the different instruments participating in the PAT. Four samples, AW-7499, AW-7501, AW-7505, and AW-7507 were selected for quadruplicate analyses. The results from the analyses of these samples is used to estimate the precision and accuracy of the EB-IC and the KPA analyses.

FD-FN lab technicians also prepared three sets of sample splits and preserved them with nitric acid, sample pH=2. This addition of acid to water samples containing uranium follows a standard laboratory procedure and protocol for preserving water samples that will not be immediately analyzed, or that will be shipped off-site for analysis. Each set of acid-preserved water samples included the four samples selected above for quadruplicate analyses plus sample AW-7508, the performance evaluation sample, and a sample blank. These sets of acid-preserved samples were distributed as follows: one set was sent to the confirmatory laboratory (ANL), one set was retained at Fernald, and one set was sent to the EB laboratory in Germany. In addition, a

set of the same raw water samples was sent to the EB laboratory in Germany for analyses. The acid-preserved samples were analyzed the same week that the confirmatory laboratory analyzed their set of samples.

Performance Evaluation Sample

FD-FN participates in the Interlaboratory Data Comparability (IDC) program. The purpose of this program is to use data comparability to evaluate contract laboratories that are used to analyze samples off-site for the FD-FN laboratory. The IDC program requires each contract laboratory to analyze a set of samples, at least one per analyte group per month performing 5 replicate analyses, and return the results, the standard deviation, and the population mean percent recovery to FD-FN. FD-FN uses the percent recovery of the true value and deviation from the population mean for each analyte group to rate each contract laboratory. These ratings provide a guide for determining which contract laboratories will be used for future off-site analysis.

The IDC program samples are specially made by the FD-FN Quality Control Laboratory using certified standards traceable to a NIST SRM's (Standard Reference Materials) and ACS grade reagents. One of these IDC program samples (No. 200219437, April 1996) was selected as the performance evaluation standard sample for this project. The "True Value" for this sample is given as 100.00 ppb ($\mu\text{g/L}$) of uranium. Five contract laboratories have reported a 96.16 mean percent uranium recovery for this April IDC sample. This sample is simply called IDC in the Tables, Figures, and text that follows.

Evaluation of Data Quality

Two parameters, precision and accuracy, were used to evaluate the quality of the analytical results obtained from the EB-IC and KPA. The precision was determined from the quadruplicate analyses of the set of selected samples, both raw water and acid-preserved, and the accuracy was determined from the comparison of a technology's analytical results with the "true value" provided by the confirmatory laboratory.

Precision

Precision refers to the level of agreement between the results from replicate analyses of the same sample by each technology. Precision is an estimate of the random error that is expected when only one measurement of a sample is made.

To determine the precision of the measurements made during this PAT, four replicate analyses were made for each of four selected samples. By experimental design, the four samples were selected to cover the range of uranium concentrations of interest to the AWWT. Specifically, samples 7505, 7501, 7507, and 7499 were selected to provide information about the technology's precision in the 5-12 ppb range, 17-25 ppb range, 30-40 ppb range, and 130-170

ppb range respectively. However, since the samples were selected using recent analytical data as being representative of a particular range, all samples selected did not represent the ranges as planned. However, they are adequate to evaluate the capabilities of the portable EB-IC instrument and provide a comparison with the results from the KPA.

Precision is determined by first calculating the average of the quadruplicate measurements for each sample using the following equation:

$$\text{Measurement Average} = m = \sum x_i / n \quad \text{where } i = 1 \text{ to } n \quad (\text{Equation E-1})$$

where x_i is the measured value and n is the number of measurements.

Next, the standard deviation is calculated for each sample using:

$$\text{Standard Deviation} = s = [\sum d_i^2 / n - 1]^{1/2} \quad (\text{Equation E-2})$$

where $d_i^2 = (x_i - m)^2$. Finally, the differences, d , are divided by the standard deviation, s , to indicate the level of error expected in terms of the standard deviation.

Accuracy

Accuracy refers to the agreement between a technology's measured result and the "true value" obtained from an analysis of the same sample by a confirmatory laboratory, using standard laboratory practices and approved analytical methods and protocols. For this project the Eppendorf-Biotronik IC 2001-2 is the instrument being evaluated. Thus, the analytical results obtained by the EB-IC are directly compared with the "true value" reported by the confirmatory laboratory. The analytical results reported for the Fernald KPA and Scintrex instruments are also compared with the reported "true values" from the confirmatory laboratory.

Data Acquisition and Results

EB-IC Analyses

Fernald, July 10-11, Raw Water Sample Analyses

The first step was to calibrate the EB-IC using the EB uranium standard solutions that were preserved in hydrochloric acid (HCL). A direct comparison between the EB-IC and KPA analytical results was tried. This was simply done by using the EB-IC to analyze the KPA calibration standard solutions. This comparison would quickly identify any discrepancies between the calibration solutions. Unfortunately, this quick simple comparison failed. The EB-IC was not able to obtain the correct uranium values for the KPA standard solutions. Also, the KPA was unable to quantify the uranium level in the EB-IC calibration standard solutions. At this point it was not understood why the EB-IC was unable to analyze the KPA standard

solutions, but later on (discussion below) the problem surfaced again and was solved. The chloride in the EB HCL- preserved standard solutions affected the KPA uranium phosphorescence decay sufficiently to provide false uranium values, and in some cases no values at all. A FD-FN laboratory technician prepared a 20 ppb uranium standard in a deionized water matrix and both technologies were able to analyze this standard solution and obtain good agreement, see Table 2.

Table 2. Results for both the raw water and acid-preserved sample analyses for the Fernald KPA and Scintrex instruments, Eppendorf-Biotronik IC 2001-2, and the confirmatory laboratory ICP-MS. The raw water samples (not acid preserved), were analyzed on July 10-11 at Fernald. The revised results (July 14) were provided by AMI after reviewing the chromatogram for each EB-IC analysis. The acid preserved samples were analyzed approximately the same week that the samples were analyzed by the confirmatory laboratory (ANL).

Sample	Fernald		Eppendorf-Biotronik				Argonne National Laboratory	Fernald
	KPA		ion chromatography				ICP-MS	Scintrex
	7/10/96	7/16/96	7/11/96	7/14/96	7/25/96	7/25/96	7/24/96	7/23/96
	Raw Water	Acid-Preserved	Raw Water	Revised	Raw Water	Acid-Preserved	Acid-Preserved	Acid-Preserved
	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
N- 7495	652		713					
N- 7496	469							
N- 7497	462							
N- 7498	332							
N- 7499-1	117	116	111.9	121	127	127	109	116.5
N- 7499-2	116	115	114.8	123	127	127		
N- 7499-3	111		110.6	127	128	126		
N- 7499-4	110		113.8	125	128	125		
N- 7500	216							
N- 7501-1	28	34	30.3	29.1	30.2	29.4	32	32.5
N- 7501-2	29		28.6	32.2	31.4	30.8		
N- 7501-3	31		28.3	31.8	29.7	30.8		
N- 7501-4	30		31.4	29.0	31.0	30.0		
N- 7502	31							
N- 7503	2.5							
N- 7504	1.1							
N- 7505-1	10.2	10.1	8.8	7.74	9.8	9.8	9.5	11.8
N- 7505-2	9.8		8.7	8.08	10	9.6		
N- 7505-3	10.1		9.1	6.86	9.9	9.8		
N- 7505-4	9.8		8.8	8.12	9.9	9.9		
N- 7506	0.5							

Table 2. (Cont.)

Sample	Fernald		Eppendorf-Biotronik				Argonne National Laboratory	Fernald
	KPA		ion chromatography				ICP-MS	Scintrex
	7/10/96	7/16/96	7/11/96	7/14/96	7/25/96	7/25/96	7/24/96	7/23/96
	Raw Water	Acid- Preserved	Raw Water	Revised	Raw Water	Acid- Preserved	Acid- Preserved	Acid- Preserved
	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
AW- 7507-1	34	35	28.2	28.9	30.9	29.8	32	36.1
AW- 7507-2	34		29.8	34.3	31.3	30.7		
AW- 7507-3	35		29.7	34.1	29.8	30.6		
AW- 7507-4	34		29	33.2	30.3	30.0		
AW- 7508-1	14	13			11.1	10.1	12	12.3
AW- 7508-2					10.9	10.1		
AW- 7508-3					10.9	10.1		
AW- 7508-4					10.1	10.7		
IDC-1	100	98			105	107	89 ^b	106.8
IDC-2		98			106	106		89.1
IDC-3					106	106		
IDC-4					106	107		
BLANK-1	0	0.9	^a	0.3	0.82	0.39	0.8	1.11
BLANK-2					0.44	0.32		
BLANK-3					0.29	0.32		
BLANK-4					0.44	0.42		

Controls (acidified)

3.0	3.1							
4.0	4.0							
8.0	8.2							
30	30.1							
60	60.8							
AW-7508 spike/w 50 ppb U	64							
20 ppb std (Performance Std.)	20.7		19.7	20.8				

^a - This result was near zero but was not recorded in the notebook. (private communication with AMI)

^b - See IDC sample discussion in text.

While the EB-IC is capable of operating from a rechargeable battery, this capability was not evaluated since this work was carried out in a laboratory where line voltage was available. After the calibration of the EB-IC was finished, the instrument was ready to start analyzing samples from the AWWT.

The first AWWT sample analyzed using the EB-IC was AW-7495, the Influent to the 400 gpm treatment system, returned a uranium concentration of 713 ppb. This EB-IC value is 10% higher than the 652 ppb KPA result for the same sample. This difference is acceptable, but surprising since 200 ppb of uranium was the greatest standard solution value used to generate the EB-IC calibration curve. Thus, the 713 ppb is obtained from an extrapolation of the EB-IC calibration curve. This suggests that the EB-IC calibration curve for uranium is a smooth function, within 10%, through 713 ppb.

The second sample, AW-7508, was drawn from the Spit FV-990 in the 700 gpm system, returned an initial uranium value of 9.9 ppb; each succeeding replicate analysis resulted in a lower uranium value until after the sixth replication the result stabilized at a value of 3.7 ppb. Since a new injection of sample was used for each replicate analyses, neither the EB nor AMI scientists participating in the PAT could explain this lack of reproducibility or each succeeding reduction in value. This reproducibility problem was not previously observed while using the EB-IC to analyze environmental water samples, (i.e., ground water, river water, sea water, or tap water) in preparation for participation in this project.

The next sample, AW-7501 drawn from the Clarifier Discharge in the 700 gpm treatment system, and repeatedly analyzed with similar decreasing results as seen for sample AW-7508. The initial analysis yielded a U value of 10.3 ppb, and after two additional replicate analyses the values were 6.6 and 6.2 ppb respectively. The KPA analysis of sample AW-7501 reported a U value of 29 ppb. EB and AMI scientists concluded that the EB-IC instrument was not able to quantitate the uranium in the raw water samples reproducibly. The scientists suggested that the ionic form of the uranium in the various water matrices was not being converted and buffered to match the calibration standard solutions. These two samples, AW-7508 and -7501, were drawn from the treatment process at two very different points almost ensuring that the water matrix and uranium ionic forms would be different for each of the samples. However, why was the result decreasing in magnitude for each succeeding replicate analysis of the sample? The scientific staff discussed these results and decided there must be something wrong with either the column in the instrument or in the complexing solution. The 20 ppb uranium standard solution in deionized water, prepared by the Fernald laboratory, was analyzed several times and reproducibly returned a uranium value of 19.2 ppb. This suggested that EB-IC was operating properly. The AWWT samples were re-analyzed and the reproducibility problem reappeared. The following discussion provides an insight into the resolution of the reproducibility problem and suggests an analytical method for sample analysis.

Since the AWWT uses an ion-exchange treatment process, the raw water samples drawn from different points in the process are not expected to have the same nor a constant water matrix or metal ion stoichiometry. Specifically of interest in this project are the uranium-complex ions. This problem was not present in the analysis of the prepared 20 ppb uranium standard in deionized water. The forms of the uranium-complex ions vary at different points in the treatment process. The forms of these ions depend on the ionic content of the water, for example, sample AW-7508 was drawn from a point after the ion-exchange columns where most of the

uranium has been removed. A similar problem was seen for sample AW-7501 taken from the Clarifier Discharge near the front end of the 700 gpm treatment process. The change in the uranium-complex ions at this point may be explained by the addition of additives to help the clarification process (ionic adjustment of the metal-complex ions to cause precipitation). From the foregoing discussion and evaluation of the results for the samples already analyzed, the following method evolved for analyzing samples with unknown water matrix and/or metal ion stoichiometry.

Reproducible results were achieved by adding 2 ml of 20 mM H_2SO_4 to 48 ml of sample prior to analysis. Four replicate analyses of sample AW-7501 after the addition of the acid resulted in values of 30.3, 28.6, 28.3, and 31.4 ppb of uranium (ave. = 29.7 ppb). The results for the quadruplicate analyses prior to the acid addition were; 30.2, 18.0, 17.9, and 16.8 ppb. The KPA analysis of AW-7501 gave an average value for four replicate analyses of 29.5 ppb uranium. Thus, all raw water samples analyzed at Fernald were prepared by the addition of 2 ml of 20 mM H_2SO_4 prior to EB-IC analysis.

Developing the EB-IC analysis method for the AWWT samples required the complete first day of the two day project. Previous commitments by the EB scientists required them to leave the Fernald site before noon on the second day. Thus, knowing that there would not be time to analyze all the samples in the Test Plan (Table 1), the decision was made to analyze only those samples (AW- 7499, -7501, -7505, and -7507) which would provide information about the EB-IC's precision and accuracy, the prepared 20 ppb uranium standard in deionized water, and the sample blank. These samples, with the exception of the 20 ppb uranium standard and the sample blank, were each analyzed four times. The results from these analyses are reported in Table 2 in the Eppendorf-Biotronik, raw water column. The values listed under the Revised column, Table 2., were provided the next week by AMI after re-evaluating the chromatogram for each analysis. The value for the sample blank at Fernald unfortunately was not recorded in the data book, and could not be located in the computer file.

EB Laboratory Germany, July 25, Raw Water and Acid-Preserved Sample Analyses

A set of both raw water and acid-preserved (nitric acid) samples was sent to the EB laboratory in Germany for analysis using the EB-IC instrument. The methodology used to analyze the samples is described above under the instrument description and is slightly different than the one that was developed and demonstrated at Fernald. Quadruplicate analyses were performed on all the AW- samples, the performance standard, and sample blank. The results from these analyses are presented in Table 2.

EB-IC Precision and Accuracy

The results from the calculation of the Measurement Average, m , the Standard Deviation, s , and the deviation, d/s , (equations E-1 and E-2) for the quadruplicate analyses are given in Table 3 for the EB-IC Fernald raw water sample analyses and revised results, and Table 4 the EB German

Table 3. The calculation of the Measurement Average, m , the Standard Deviation, s , and the deviation d/s for the EB-IC Fernald quadruplicate analyses of the raw water samples and revised results.

Sample	Eppendorf-Biotronik (at Fernald) ion chromatography							
	Raw Water (7/11/96)				Revised (7/14/96)			
	ppb	ppb	ppb	σ	ppb	ppb	ppb	σ
	Meas.	Meas. Ave. m	Std Dev. s	d/s	Meas.	Meas. Ave. m	Std Dev. s	d/s
AW- 7499-1	111.9	112.8	1.88	-0.5	121	124	2.58	-1.2
AW- 7499-2	114.8			1.1	123			-0.4
AW- 7499-3	110.6			-1.2	127			1.2
AW- 7499-4	113.8			0.5	125			0.4
AW- 7501-1	30.3	29.65	1.46	0.4	29.1	30.53	1.71	-0.8
AW- 7501-2	28.6			-0.7	32.2			1.0
AW- 7501-3	28.3			-0.9	31.8			0.7
AW- 7501-4	31.4			1.2	29.0			-0.9
AW- 7505-1	8.8	8.85	0.17	-0.3	7.74	7.70	0.59	0.1
AW- 7505-2	8.7			-0.9	8.08			0.6
AW- 7505-3	9.1			1.4	6.86			-1.4
AW- 7505-4	8.8			-0.3	8.12			0.7
AW- 7507-1	28.2	29.18	0.74	-1.3	28.9	32.63	2.53	-1.5
AW- 7507-2	29.8			0.8	34.3			0.7
AW- 7507-3	29.7			0.7	34.1			0.6
AW- 7507-4	29			-0.2	33.2			0.2

laboratory results for both the raw water and acid-preserved samples. Table 4 also includes the calculated results for the quadruplicate analyses of sample AW-7508, the performance standard (IDC), and the sample blank. These last three samples were not analyzed in quadruplicate by any of the other instruments.

The d/s value for both the raw water and acid-preserved samples, Tables 3 and 4, show good agreement, with maximum error of 1.5σ (standard deviations) between the replicate measurements for any sample. There does not appear to be any correlation between the magnitude of the error and the level of uranium concentration being measured, thus, there is no evidence of cross-contamination between samples. And, most importantly, the EB-IC has a very high degree of precision (reproducibility) down to the very low ppb region.

Prior to using the confirmatory laboratory "true values" to evaluate the raw water results, it is necessary to compare the sets of raw water and acid-preserved results to determine whether a systematic difference exists. If a systematic difference is observed then the confirmatory

Table 4. The calculation of the Measurement Average, m , the Standard Deviation, s , and the deviation d/s for the EB laboratory analyses of both the raw water and acid-preserved samples. This table also includes the results for the quadruplicate analyses of sample AW-7508, the performance standard (IDC), and the sample blank.

Eppendorf-Biotronik (Laboratory in Germany) ion chromatography								
Sample	Raw Water (7/25/96)				Acid-Preserved (7/25/96)			
	ppb	ppb	ppb	σ	ppb	ppb	ppb	σ
	Meas.	Meas. Ave. m	Std. Dev. d	d/s	Meas.	Meas. Ave. m	Std. Dev. s	d/s
AW- 7499-1	127	127.5	0.58	-0.9	127	126.3	0.96	0.8
AW- 7499-2	127			-0.9	127			0.8
AW- 7499-3	128			0.9	126			-0.3
AW- 7499-4	128			0.9	125			-1.3
AW- 7501-1	30.2	30.58	0.77	-0.5	29.4	30.25	0.68	-1.2
AW- 7501-2	31.4			1.1	30.8			0.8
AW- 7501-3	29.7			-1.1	30.8			0.8
AW- 7501-4	31.0			0.6	30.0			-0.4
AW- 7505-1	9.8	9.90	0.08	-1.2	9.8	9.78	0.13	0.2
AW- 7505-2	10			1.2	9.6			-1.4
AW- 7505-3	9.9			0.0	9.8			0.2
AW- 7505-4	9.9			0.0	9.9			1.0
AW- 7507-1	30.9	30.58	0.66	0.5	29.8	30.28	0.44	-1.1
AW- 7507-2	31.3			1.1	30.7			1.0
AW- 7507-3	29.8			-1.2	30.6			0.7
AW- 7507-4	30.3			-0.4	30.0			-0.6
AW- 7508-1	11.1	10.75	0.44	0.8	10.1	10.25	0.30	-0.5
AW- 7508-2	10.9			0.3	10.1			-0.5
AW- 7508-3	10.9			0.3	10.1			-0.5
AW- 7508-4	10.1			-1.5	10.7			1.5
IDC-1	105	105.8	0.50	-1.5	107	106.5	0.58	0.9
IDC-2	106			0.5	106			-0.9
IDC-3	106			0.5	106			-0.9
IDC-4	106			0.5	107			0.9
BLANK-1	0.82	0.50	0.23	1.4	0.39	0.36	0.05	0.5
BLANK-2	0.44			-0.3	0.32			-0.8
BLANK-3	0.29			-0.9	0.32			-0.8
BLANK-4	0.44			-0.3	0.42			1.1

laboratory “true values”, obtained by analyzing only acid-preserved samples, cannot be used to evaluate the raw water analytical results.

The EB laboratory (Germany) analytical results for both the raw water and acid-preserved samples, Table 4, were chosen for this important comparison since quadruplicate analyses were

performed on both sets of samples. The results from this comparison are shown in Figure 1. In this figure the results for the acid-preserved samples are subtracted from the raw water results and the differences are plotted in ppb vs. the acid -preserved results. The $\pm$ error bars represent the standard deviation. To show the level of agreement between the two sets of data and avoid the confusion of overlapping error bars, the acid preserved sample results are plotted on the x-axis with a ± 1 ppb off-set. A $\pm 2\%$ calculated error is shown for reference (broken line).

Figure 1. Comparison between the results from the EB laboratory (Germany) analyses of the raw water and acid-preserved samples. The acid-preserved sample results with error bars (standard deviation) are plotted on the x-axis and off-set by ± 1 ppb to avoid confusion of overlapping error bars. The broken lines, shown for reference, represent a calculated error of $\pm 2\%$.

Figure 1 shows excellent agreement between the results from the raw water and acid-preserved sample analyses. Also, Figure 1 shows the consistency of the EB-IC calibration, and the order of

sample analyses suggests that no apparent cross-contamination, carryover, or retention of uranium by the instrument column exists. Thus, preserving the raw water samples by adding nitric acid does not present any detection or quantitation problems for the EB-IC instrument, and the confirmatory laboratory results can be confidently used to evaluate the raw water sample results.

Confirmatory Laboratory, Argonne National Lab, ICP-MS

One set of the selected acid-preserved samples was sent to ANL for confirmatory analyses. These samples were analyzed on July 24 using the inductively coupled plasma mass spectrometer (ICP-MS) technique. The results from this analyses are shown in Table 2. A discussion of the analyses procedure and comments about the data quality are given in the analytical report, see Appendix B .

The confirmatory laboratory results reported in Table 2 were reported as average values for five replicate measurements. The estimated error for these measurements is stated as $\pm 5\%$.

The confirmatory laboratory also provided information on the isotopic content of the uranium in the water samples. An initial spectral scan of sample AW-7399 showed the uranium content to be of near-natural isotopic composition. Aliquots from each sample were analyzed directly versus a 2% (v/v) high-purity nitric acid blank to determine the ratios of U-234, 235, 236 and other minor isotopes. These isotopic composition results for each sample are given in the analytical report, see Appendix B.

KPA Analyses at Fernald

The Chemchek KPA-11, kinetic phosphorescence analyzer, is the primary baseline laboratory instrument used at Fernald to analyze environmental water samples for uranium content. The KPA instrument uses a pulsed nitrogen dye laser, 0.1 - 0.5 mW with a 3 nano-sec pulse width operating at 20 pulses/sec, to excite the complexed-uranium ions in the aqueous sample. The detector measures the intensity of the light emitted (phosphorescence) with respect to time. The integrated area under this intensity vs. time curve is directly proportional to the number of uranium ions in the aqueous sample.

Both raw water and acid-preserved samples were analyzed by the KPA during this project. Quadruplicate analyses were performed on the selected set of raw water samples, but were not performed on the set of acid-preserved samples. Thus, only the results from the quadruplicate analyses of the raw water samples were used to provide an evaluation of the precision and accuracy of the KPA analyses. The analytical results from the KPA analyses of both sets of samples are reported in Table 2.

Fernald, July 10-11, Raw Water Sample Analyses

The KPA was first calibrated using standard calibrating solutions. Then each of the raw water samples collected from the sampling ports in the AWWT (Table 1) were loaded into individual sample vials, buffer solution was added, the vials were placed in the autosampler, and the automatic analysis program started. The analytical results for all samples were printed out. The selected set of samples were analyzed in quadruplicate. The results from the KPA analyses are reported in Table 2.

Fernald, July 16, Acid-Preserved Water Sample Analyses

A selected set of acid-preserved samples was analyzed at Fernald on July 16 using the KPA. Unfortunately, these samples were not analyzed in quadruplicate. The results from this analyses of the acid-preserved samples are given in Table 2. Very good correlation is seen when comparing the KPA raw water and acid-preserved sample results (Table 2).

KPA Precision and Accuracy

Quadruplicate analyses were only performed on the selected set of raw water samples during the PAT. Thus, only the results from these measurements were used to evaluate the precision and accuracy of the KPA analyses and provide an estimate of the expected measurement error. Equations E-1 and E-2 were used to calculate the Measurement Average, m , the Standard Deviation, s , and the deviation, d/s for the KPA results. These calculated results are given in Table 5. The d/s values for these raw water samples (Tables 5) show good agreement, maximum error of 1.5σ (standard deviations), between the replicate measurements for any sample. There does not appear to be any correlation between the magnitude of the error and the measured level of uranium concentration, thus, there is no evidence of cross-contamination between samples.

The KPA is the baseline technology that Fernald uses to analyze water samples from the AWWT to determine uranium concentrations. The method that Fernald uses to determine these uranium concentrations states an accuracy of 3% when measuring standard solutions as low as 1 ppb U/L, and a precision of 4% and 2% for measuring duplicate samples with concentrations of 2 ppb and 50 ppb U/L respectively (private communication K. Hudson).

Scintrex Analyses at Fernald

Before the KPA was purchased for analysis of water samples at Fernald, the Scintrex UA-3 was the baseline technology. This instrument also works on the phosphorescence analyzer principle. A pulsed nitrogen laser excites the uranium ions and the intensity of the emitted light is proportional to the uranium concentration. The UA-3 measures the peak light intensity only, not a time resolved measurement like the KPA.

On July 23, a set of acid-preserved samples including the performance standard and sample blank were analyzed using the Scintrex instrument. The results from the analyses are shown in Table 2. Since these analyses were not performed in quadruplicate the determination of the precision and estimated error can not be made. However, these results can be compared with the confirmatory laboratory's "true value" to provide an indication of the accuracy of the measurements.

Table 5. The calculation of the Measurement Average, m , the Standard Deviation, s , and the deviation d/s for the Fernald KPA quadruplicate analyses of selected raw water samples. Stated precision of the method used by Fernald for the KPA analysis of duplicate samples is 4% at 2 ppb U/L, and 2% at 50 ppb U/L (private communication K. Hudson).

Fernald KPA					
Raw Water Samples					
7/10/96					
Sample	ppb	ppb	ppb	Percent	σ
	Meas.	Meas. Ave. m	Std. Dev. s	s/m	d/s
AW- 7499-1	117	113.5	3.51	3.1%	1.0
AW- 7499-2	116				0.7
AW- 7499-3	111				-0.7
AW- 7499-4	110				-1.0
AW- 7501-1	28	29.5	1.29	4.4%	-1.2
AW- 7501-2	29				-0.4
AW- 7501-3	31				1.2
AW- 7501-4	30				0.4
AW- 7505-1	10.2	9.98	0.21	2.1%	1.1
AW- 7505-2	9.8				-0.8
AW- 7505-3	10.1				0.6
AW- 7505-4	9.8				-0.8
AW- 7507-1	34	34.25	0.50	1.4%	-0.5
AW- 7507-2	34				-0.5
AW- 7507-3	35				1.5
AW- 7507-4	34				-0.5

Summary of Analytical Results

A summary of the analytical results from all of the instruments that participated in this project, and the confirmatory laboratory results are given in Table 6.

Table 6. A summary of analytical results for both the raw water and acid-preserved samples

Sample	Argonne National Laboratory	Fernald		Eppendorf-Biotronik ion chromatography				Fernald
	ICP-MS	KPA ^f		at Fernald		Laboratory in Germany		Scintrex
	7/24/96	7/10/96	7/16/96	7/11/96	7/14/96	7/25/96	7/25/96	7/23/96
	Acid-Preserved	Raw Water	Acid-Preserved	Raw Water	Revised	Raw Water	Acid-Preserved	Acid-Preserved
	Meas. ^d ppb	Meas. Ave. ppb	Meas. ppb	Meas. Ave. ppb	Meas. Ave. ppb	Meas. Ave. ppb	Meas. Ave. ppb	Meas. ^a ppb
AW- 7499	109	113.5	116/115 ^c	112.8	124.0	127.5	126.3	116.5
AW- 7501	32	29.5	34.0	29.7	30.5	30.6	30.3	32.5
AW- 7505	9.5	9.98	10.1	8.85	7.70	9.90	9.78	11.8
AW- 7507	32	34.3	35.0	29.2	32.6	30.6	30.3	36.1
AW- 7508	12	14 ^a	13.0			10.8	10.3	12.3
IDC	88.6 ± 0.4 ^e	100 ^a	98/98 ^c			105.8	106.5	106.8/89.1 ^e
BLANK	0.8	0 ^a	0.9	- ^b	0.3	0.50	0.36	1.11
AW-7508 spike/w 50 ppb U		64 ^a						
20 ppb U Standard		20.7 ^a		19.7 ^a	20.8 ^a			

^a - Result not determined from quadruplicate analyses.

^b - This result was near zero, but was not recorded in the notebook. (private communication with AMI)

^c - The results for two separate analyses of the sample.

^d - Data based upon atom % data and isotope dilution with ²³⁶U. Estimated uncertainty is ± 5%.

^e - Separately calculated mean and standard deviation for three separate analyses of the sample.

^f - Stated KPA method accuracy is 3% for measurements of standard solutions as low as 1 ppb U/L. Stated precision for duplicate samples is 4% at 2 ppb U/L, and 2% at 50 ppb U/L (private communication K. Hudson).

Comparison with the Confirmatory Laboratory “true value”

Difference plots are used to show agreement between the ANL confirmatory laboratory “true values” and the analytical results from each instrument that analyzed water samples for this project. The difference plots are constructed by subtracting the ANL reported “true value” from the analytical results reported by each instrument for each sample, and plotting this difference, in ppb, vs. the “true value”. Where quadruplicate analyses were performed on a sample, the average measured value is used for the sample result (see Table 6), and error bars are drawn representing the standard error (standard deviation). Broken lines are drawn on each graph representing the ± 5% estimated error in the “true value” as reported by ANL. The ANL “true

values” were used to evaluate the analytical results for both the raw water and acid-preserved samples.

Figure 2 shows the agreement between the KPA and EB-IC results for the raw water samples analyzed during the PAT at Fernald and the “true value” results. The EB-IC revised results, reevaluation of the EB-IC Fernald data chromatograms, are also shown. These revised results show poor agreement, 14% error, for the highest value. The lowest values of the EB-IC results are just outside the 5% estimated error of the ANL “true values”, however, they appear to scatter randomly about the “true values”. The KPA results are outside the 5% estimated error of the “true value” results except at for the highest value which lies within the estimated error. All KPA results except for the 12 ppb and IDC samples are within 10% of the “true value”. There is no explanation for the large error ($\approx 17\%$) seen for the 12 ppb sample. Possible reasons for the IDC discrepancy are discussed later. The overall agreement between the ANL “true values” and the results from both technologies is within 10%. The order in which the samples were analyzed suggests that there is no cross contamination between analyses.

The April 1996 IDC (performance evaluation) sample, 100.00 ppb ($\mu\text{g/L}$) of uranium, was chosen to provide certification of instrument operation and method parameters during this

Figure 2. Agreement between the KPA and EB-IC raw water sample analytical results, taken at Fernald, and the “true values” reported by ANL. A second set of EB-IC results (revised) are also shown. These revised results were supplied by AMI after reviewing the original EB-IC chromatograms. Where there are overlapping error bars, the results have been offset by ± 1 ppb on the x-axis to avoid confusion.

project. Table 6, shows the analytical results from all instruments for the IDC sample to be within 7% of 100 ppb except for the ANL confirmatory laboratory. ANL reported an initial result of 89 ppb (11% low) for the IDC. Because of this low IDC value, ANL performed two additional analyses, 5 replicates each. A value of 88.6 ± 0.4 ppb was the resulting mean and standard deviation for the three analyses. It is not clear why this value is low, but this is the “true value” that was used to evaluate the IDC results for all the technologies participating in this project. The differences seen between the comparisons of the IDC sample results for the various instruments and the ANL “true value” lie significantly outside the “true value” estimated error. See Figures 2, 3, and 4. Five contract laboratories reported a 96.16% mean uranium recovery for this sample in April 1996.

Figure 3. Comparison of the EB-IC acid-preserved and raw water sample results, taken in Germany, and the “true values” reported by ANL.

The comparison between the EB-IC raw water and acid-preserved sample results (German laboratory) and the ANL “true value” results are shown in Figure 3. The agreement for the low ppb values are within the 5% estimated error of the “true value” results except for the 14% deviation at 12 ppb. The IDC sample deviation is discussed above. The large deviation, $\approx 14.7\%$, at 109 ppb is not understood; however, it maybe traceable to the different standard solutions that are used to calibrate the instruments or caused by other systematic errors. Of

primary importance however, is the good agreement within the 5-40 ppb uranium concentration range, which is of primary interest for process control at the AWWT.

The comparison between the KPA, Scintrex, and EB-IC (laboratory in Germany) acid-preserved sample results and the ANL "true value" results are shown in Figure 4. The KPA results lie systematically high by a constant $\approx 6.5\%$, and the Scintrex results scatter randomly about this offset. This systematic offset suggests that a possible discrepancy may exist between the different standard solutions used to calibrate the various instruments. To identify the cause of this problem we look to the results obtained for the QC samples.

The project Test Plan identified the QC samples (a sample blank, a matrix-spiked sample, and a performance evaluation sample) that were to be provided for analysis by each instrument and the confirmatory laboratory. All of the QC samples were analyzed by the Fernald KPA instrument (see Table 2), unfortunately, the matrix spiked sample (AW-7508 spiked with 50 ppb uranium) was accidentally left out of the QC sample set provided to EB and the confirmatory laboratory for analysis. This unfortunate oversight was not discovered until much later when comparisons

Figure 4. The KPA, Scintrex, and EB-IC (laboratory in Germany) acid-preserved sample results compared with the "true values" reported by ANL.

with the results from the confirmatory laboratory were being made to determine the accuracy of each instrument (Figure 4). The 6.5% offset was discovered, and an effort was made to determine the cause of the offset. At this point the missing matrix-spiked sample results were discovered.

Using the results reported by EB and the confirmatory laboratory for the two QC samples (the sample blank and the performance evaluation sample (IDC)) analyzed are not sufficient to determine the cause of the 6.5% offset. The earlier comments made about the EB-IC sample comparison with the ANL results and shown in Figure 3 apply here as well. Thus, for this evaluation, the uncertainty in the accuracy for each instrument cannot be stated any better than 6.5%, even though it maybe much better than this.

And finally, Figure 5 shows a composite of both the raw water and acid-preserved sample results for the three instruments providing data in this project with the ANL results as a baseline for the comparison. Again, the good agreement over the uranium concentration range of interest for AWWT process control and compliance measurement should be noted. Disregarding the uncertainty discussed above, the EB-IC, KPA and Scintrex instruments provide operationally

Figure 5. The ANL “true value” results shown as a baseline for comparing both the raw water and acid-preserved sample results for the three instruments providing data to this project.

acceptable accuracy for the determination of the uranium concentration in both raw water and acid-preserved water samples.

VI. SUMMARY

Conclusions

This project identified one commercially available portable instrument capable of rapidly and directly detecting low ppb levels of uranium in water. This instrument was rigorously tested and its analytical capabilities evaluated using “real-world” samples from the Fernald AWWT. Scientists from Eppendorf and its vendor AMI teamed to demonstrate the Eppendorf-Biotronik model IC 2001-2, a portable (battery powered) ion chromatography instrument.

Overall, the Eppendorf-Biotronik IC 2001-2 performed exceptionally well providing a detection limit in the low ppb region (<10 ppb) and giving rapid (less than 5 minutes) accurate, reproducible analytical results for process water samples with uranium concentrations in the region of interest (10-40 ppb). The IC 2001-2 has good analytical accuracy and precision. The per sample operating cost for this instrument is equivalent to the per sample cost for the currently used KPA. The time required to analyze a sample and provide a result is approximately the same for the IC 2001-2, KPA, and Scintrex instruments.

A systematic error giving $\approx 6.5\%$ offset was identified while comparing the KPA and Scintrex analytical results with the ANL (confirmatory laboratory) results. This error suggests a possible discrepancy between the different standard solutions used to calibrate the various instruments. It was not possible to determine the cause of this error since one of the QC samples, the matrix-spiked sample, was accidentally left out of the QC sample set that was sent to EB and ANL for analysis. Therefore, the uncertainty in the accuracy for each instrument used in this project cannot be stated any better than 6.5%, even though it maybe much better than this. Setting this offset aside, the IC 2001-2, KPA, and Scintrex instruments provided operationally acceptable accuracy for determining the uranium concentration in both raw water and acid-preserved water samples in the 10-40 ppb range.

Advantages and Limitations of the IC

The IC 2001-2 used manual sample introduction for this project, however, the measurement time per sample is similar to the KPA and Scintrex instruments. To enhance the productivity of the IC 2001-2 in a fixed laboratory setting, an autosampler package can be added. The cost of the basic manual IC 2001-2 is approximately 60% of a manual KPA, adding the autosampler package makes the total instrument package still less expensive ($\approx 60\%$) than the equivalent automatic Chemchek KPA-11 that includes the autosampler package.

The sample concentrating capability prior to analysis is a additional feature of the IC 2001-2. This concentration feature lowers the minimum detection limit to the ppt (parts per trillion)

range. This concentrating capability was tried and appeared to work successfully, but was not evaluated since the stated project objective, low ppb detection limit, was easily obtained without concentration.

The IC 2001-2 is a very versatile instrument. While the instrument that was demonstrated and evaluated at Fernald was specifically designed for uranium detection and quantitation, (having only the UV-Vis detector and uranium separation column), an option is available that provides a conductivity detector, the proper column and buffer solution to modify the instrument for water quality assessment using EPA Method 300. This method quantitates the chlorides, chlorates, phosphates, and sulfates in water. In addition, samples can be assayed for other analytes with the proper instrument setup.

The Eppendorf-Biotronik IC 2001-2 is currently the only fully portable, field ruggedized, commercially-available instrument for directly detecting low ppb of uranium in water samples. Overall, the IC 2001-2 performed exceptionally well during this rigorous testing providing detection limits in the low ppb region, and providing rapid reproducible analytical results for uranium in the region of interest (10-40 ppb) using AWWT water samples. The instrument can be modified to expand its measurement capabilities to a broader range of analytes, including those outlined in EPA Method 300 for determining water quality.

Recommendation

In the project proposal FD-FN identified the need for a portable instrument to provide near real-time assessment of the uranium levels in the water samples drawn from various points in the AWWT treatment process, and the analytical results were to have a high degree of accuracy and precision in the 10-40 ppb range. The rigorous testing of the IC 2001-2 during this demonstration shows that it more than adequately satisfies these stated requirements. This instrument is portable and ruggedized for field work. The IC 2001-2 could prove to be a valuable cost effective tool for assessing the uranium level of monitoring wells in the field by providing the real-time data need for making immediate decisions on whether or not water needs to be treated.

Additional possible applications were identified for the IC 2001-2 that could result in operational cost savings. One potential application is for an automated, real-time, total uranium ground water monitor and control system. This automated system might be installed in a well house to assay water as it comes directly from an extraction well to monitor the quality of the water in the aquifer. A second potential application is for the installation of a real-time water treatment process control to provide optimization of the treatment plant operation. This real-time process control is accomplished by installing an automated sampling, analysis, and water diverting system at various treatment stages. This process control could eliminate unnecessary water treatment by diverting the water directly to the effluent once it satisfies the uranium level specified in the regulatory permit. This real-time process control could also be used to closely monitor the ion-exchange column efficiency and identify when column regeneration is needed.

Lessons Learned

This project was designed to test and evaluate EB-IC'S analytical accuracy, precision, and performance criteria identified by the customer using actual samples. This evaluation was accomplished by obtaining meaningful analytical results within specific ranges using actual samples, and comparing these results with the values obtained by the confirmatory laboratory using the same samples. To obtain a quality assessment of the analytical capabilities for analytical instruments it is important that all potential sources of error be eliminated or at least minimized.

The Test Plan for this project specified that a standard set of QC samples, a sample blank, a matrix-spiked sample, and a performance evaluation sample, be evaluated by all instruments including the confirmatory laboratory. Unfortunately, the matrix-spiked sample (50 ppb uranium) was not included in the set of samples that were evaluated by the IC 2001-2 and the confirmatory laboratory. It is obvious from the comparison of the results that the sample blank and the performance evaluation sample (IDC) were not sufficient to identify the reason for the 6.5% offset in the data, and thus to provide the agreement necessary to evaluate an instrument's accuracy with a high degree of certainty. The addition of the matrix spiked sample may have provided the additional information needed. In addition, replicate analyses of these samples was not performed by all instruments.

The systematic relative error (6.5% offset) seen when comparing the analytical results from the various instruments with the results from the confirmatory laboratory affects the size of the error assigned to an instrument's accuracy. This added uncertainty in the accuracy is believed to be caused by the use of different sets of calibration standards by the various instruments. This uncertainty could be eliminated in future tests if a common set of calibration standards is used by all instruments tested including the confirmatory laboratory. If using a common set of standards for calibration is not possible, then at least include a set of calibration standards should be provided in addition to the three QC samples for evaluation by the confirmatory laboratory. This would either eliminate or identify errors that are introduced by the calibration standards. The result from the analyses of these additional samples would provide a truer measure of an instrument's accuracy with a high degree of certainty.

Additional time needs to be allocated prior to the start of the project to allow for instrument set-up, testing, and troubleshooting. The testing and evaluation program should not be started until each instrument developer has certified that their instrument is operating satisfactorily and they are ready to participate.

APPENDIX A.

Analytical Magnetics, Inc., price quotation for an Eppendorf-Biotronik IC 2001-2

analytical magnetics

Mr. Marvin Anderson
Ames Laboratory
Iowa State University
Ames, Iowa 50011

Date: Sept. 24, 1996
Quote Number: 62409
Terms: Net 30 Days
F.O.B.: Delivered

Quotation

<u>ITEM</u>	<u>QUANTITY</u>	<u>DESCRIPTION</u>	<u>AMOUNT</u>
5701-2	1 each	Eppendorf Model IC-2001-2 Ion Chromatograph with: <ul style="list-style-type: none">- UV-Vis Detector 660 nm- User Selected Flow Rates- A/D signal output- Internal Microcomputer- Internal Data Integrator- Integrated Printer- Keypad and Liquid Crystal Display- Two Dual Piston Pumps (sapphire piston)- 4 sensitivity ranges (1 to 1000μS)- RS-232 Interface- Coupled Gain and Polarity Control Switches- Three Rolls Printer Paper	\$ 18,900.00
6903-U	1 each	Uranium Separation Kit includes column and sufficient reagent for 1000 injections.	\$ 1,500.00
TOTAL			<u>\$ 20,400.00</u>

DELIVERY: Stock, A.R.O.

VALIDITY PERIOD: 60 days from issue date.

Options

7002	1 each	Everex 486DX/50 Notebook Computer with color dual scan monitor, 350MB HDD, 3.5"FDD, docking station and spare battery	\$ 3,000.00
7001	1 each	WinPeak Light Chromatography Software and A/D Interface board for real time data acquisition and chromatograph downloading from the IC-2001 to a computer.	\$ 3,500.00
8001	1 each	Alcott Autosampler 708 Series 128 position, positive displacement, programmable sampler with optional 0.45 u filter caps.	\$ 6,700.00

Notes: One year warranty parts with on-site labor. Five percent discount on multiple unit orders.

By: Jim Hannon
Title: Marketing Manager

Analytical Magnetics, Inc.

236 Bridle Path / No. Andover, MA 01845-2012 / (508) 682-1816 / (800) 828-0476 / FAX (508) 689-3868

APPENDIX B.

Confirmatory Laboratory Analytical Report from Argonne National Laboratory

ARGONNE NATIONAL LABORATORY

100 SOUTH CASS AVENUE, ARGONNE, ILLINOIS 60439-4831

TELEPHONE: (708)252-7399

FAX: (708)252-3146

E-MAIL: CRAIN@CMT.ANL.GOV

July 30, 1996

Dr. Stephan Weeks
Ames Laboratory
Iowa State University
125 Spedding Hall
Ames, IA 50011-3020

Dear Stephan,

As I reported to you previously via E-mail, my colleague Jim Kiely and I have completed, per Ames Laboratory P.O. A6-4342 (ANL Account 054F2, ACL Job 96-0380), the inductively coupled plasma mass spectrometric (ICP-MS) analysis of seven water samples. These samples were received from Fernald on July 15, and we completed our determination of total and isotopic uranium content on July 24. The results of this work are attached. I will use the remainder of this letter to describe our analysis procedure and comment upon the quality of the data.

Upon receipt, the samples were unpacked and the bottles were inspected. All of the bottles were intact and leak free. No suspended or precipitated matter was observed in the samples and, as such, the samples were not filtered in advance of further preparation.

Our mass spectrometer has been described previously.¹ A preliminary mass spectral scan of sample AW-7399, diluted 20-fold in 2% (v/v) high-purity nitric acid (Optima™ grade, Fisher Scientific), led us to assume that all of the samples contained uranium of near-natural isotopic composition. Given the kinetic phosphorimetry (total uranium) data that accompanied the samples, aliquots from each sample were analyzed directly versus a 2% (v/v) high-purity nitric acid blank to determine the ^{234}U : ^{235}U and ^{236}U : ^{235}U (minor isotope) atom ratios. Each atom ratio was measured 5 times (30 seconds per replicate) in succession, and between samples, the instrument was rinsed with 10% (v/v) high-purity nitric acid. These atom ratios were not corrected for mass bias² as the bias was expected (and later found) to be small ($\leq 2\%$).

A second aliquot of each sample was drawn and mixed with 1 ng of dissolved uranium which was 99.8 atom % in ^{236}U . Then, each mixture was diluted with 2% (v/v) high-purity nitric acid to obtain a total uranium concentration of approximately 10 ng/mL. The diluted, spiked solutions were analyzed directly versus a 2% (v/v) high-purity nitric acid blank to determine the ^{238}U : ^{235}U and ^{236}U : ^{235}U atom ratios. A solution of New Brunswick Laboratory certified reference material (CRM) U-010 (10 ng/mL total uranium in 2% high-purity nitric acid) was also analyzed. Note that the purity of the ^{236}U spike was such that the spike did not contribute significantly to the ^{238}U or ^{235}U content of the samples. As such, the ^{238}U : ^{235}U atom ratio in the spiked sample was identical to that of the unspiked sample.

¹ Crain and Alvarado, *J. Anal. At. Spectrom.*, 9, 1223 (1994).

² Russ and Bazan, *Spectrochim. Acta, Part B*, 42B (1/2), 49 (1987).

The ^{238}U : ^{235}U atom ratios in the samples were calibrated by using the relative error in the CRM ^{238}U : ^{235}U atom ratio measurements as a correction factor. Then, the abundances (A_i) for each uranium isotope in the unspiked samples were determined using the equation:

$$A_i = \frac{R_{is}}{\sum R_{ns}}$$

where the numerator (R_{is}) is the atom ratio of a uranium isotope relative to ^{235}U , and the denominator is the sum of all uranium atom ratios relative to ^{235}U (including ^{235}U : $^{235}\text{U} \equiv 1$).

The atomic weight of uranium in the unspiked sample (M_U) was calculated using the equation:

$$M_U = \sum A_i M_i$$

where M_i is the exact atomic weight of each uranium isotope. Then, the uranium concentrations in each solution aliquot (C_U) were calculated by isotope dilution using the equation:

$$C_U = \frac{(n_6)_s(R_{i6})_{sp} - (n_i)_s}{A_i - A_6(R_{i6})_{sp}} \frac{M_U}{V}$$

where $(R_{i6})_{sp}$ is the ratio of some uranium isotope to ^{236}U in the spiked sample, $(n_6)_s$ and $(n_i)_s$ are the moles of each isotope added (via the spike) to the sample, A_6 is the abundance of ^{236}U in the unspiked sample, and V is the original volume of sample to which the spike was added.

The abundance and concentration data are given in the attachment. The uncertainty in the abundance data is estimated to be in the 1 to 5% range, based upon propagation³ of the random and systematic uncertainties associated with the isotope ratio measurements. The uncertainty in the concentration data is estimated to be on the order of 5 to 10%, based again upon propagation of the experimental uncertainties. These uncertainty estimates are consistent with our performance in blind interlaboratory comparisons,⁴ specifically QAP 41 (run by the DOE Environmental Measurements Laboratory) and RADQA (run by the EPA National Exposure Research Laboratory, Las Vegas). In each study, our results were within 6% of the interlaboratory mean, and were well within the uncertainty of the interlaboratory mean.

We hope that these data will facilitate progress in your sensor evaluation project. Should you wish to inquire further about our procedures or our interpretation of these data, please feel free to contact me by electronic mail or by telephone. My addresses (U.S. Mail and E-mail) and phone number (voice and FAX) are given in the letterhead. We appreciated the opportunity to analyze these samples for your project, and we would certainly welcome other opportunities to assist you in the future.

³ Miller and Miller, Statistics for Analytical Chemistry, 3rd Edition, Ellis Horwood (New York, 1993), ch. 2.

⁴ ANL Analytical Chemistry Laboratory Jobs 94-9518 and 95-9500.

Dr. Stephan Weeks

-3-

July 30, 1996

Sincerely,

Jeffrey S. Crain
Analytical Chemistry Laboratory
Chemical Technology Division

JSC:amb

Attachment

cc: w/attach:
J. Laidler (2)
D. Green
P. Lindahl
D. Graczyk
J. Kiely
M. Anderson (Ames Lab)

Subject: Determination of total and isotopic uranium in water (ACL Job 96-0380)

ANALYTICAL CHEMISTRY LABORATORY
Argonne National Laboratory
Argonne, IL 60439

REPORT OF ANALYTICAL RESULTS

Sample Material: Fernald Waste Water
Submitted by: S. Weeks, Ames Laboratory

Date Received: 7/15/96
Date Reported: 7/26/96

Submitter's Sample No.	ACL Sample No.	Atom % ^a				
		<u>U (ng/mL) ^b</u>	<u>U-238</u>	<u>U-236</u>	<u>U-235</u>	<u>U-234</u>
Blank	96-0380-01	0.8	99.21	nd ^c	0.79	nd
IDC	-02	88.6 ± 0.4 ^d	99.27	1.1 × 10 ⁻³	0.72	5.3 × 10 ⁻³
N-7499	-03	109	99.49	1.5 × 10 ⁻²	0.49	3.3 × 10 ⁻³
N-7501	-04	32	99.23	1.3 × 10 ⁻²	0.75	5.4 × 10 ⁻³
N-7505	-05	9.5	99.25	1.4 × 10 ⁻²	0.73	5.8 × 10 ⁻³
N-7507	-06	32	99.49	1.5 × 10 ⁻²	0.49	3.5 × 10 ⁻³
N-7508	-07	12.0	99.26	1.6 × 10 ⁻³	0.73	5.8 × 10 ⁻³
		^a Data based upon the means (n=5) of the ²³⁸ U: ²³⁵ U, ²³⁶ U: ²³⁵ U, and ²³⁴ U: ²³⁵ U atom ratios, determined in unspiked samples. Estimated uncertainty is ±5%. ^b Data based upon atom % data and isotope dilution with ²³⁶ U. Estimated uncertainty is ±5%. ^c Isotope not detected. ^d External mean and standard deviation for 3 separate analyses of the sample.				

Unused sample material will be returned to the Customer. Prepared samples will be discarded one (1) month from the date of this report unless other arrangements are made. When making future inquiries regarding this report, reference the ACL sample number(s) above. For further information about the results reported here, please call in _____ at 2- 7399 .

Reference(s): CMT Notebook No. 1390, pg. 41; ICP-MS experiment \Kiely\96-07-24 and 96-07-30

Submitted To: S. Weeks (Ames)
M. Anderson (Ames)
D. Green
mb P. Lindahl
6 D. Graczyk
1)

J. Crain
J. Kiely
ACL 200 File

Analyst(s): J. Crain
J. Kiely

APPENDIX C.

Distribution List for IS-5124

DOE

Tom Parker
Caroline Purdy
Rod Warner DOE-FN
John Kappa-DOE-FN
Rob Janke-DOE-FN
Paul Beam
Skip Chamberlain
Bob Cornish
Eric Lightner
John Mathur
Dave Shafer
Stephen Warren
Doug Maynor - DOE-OH
Frank DiSanza - DOE-NVO
John Jones - DOE-NVO

Fluor Daniel-Fernald

Paul Pettit
Larry Stebbins
Richard Schéper
Chris Sutton
Everett Henery
Jim Leslie
Kathy Hudson
Carl Bishop
Mark Durrrough
David Madsen
Cathy Glassmeyer
Grace Rusink

Ames Laboratory

Marvin Anderson (5)

Special Technologies Laboratory

Paul Wang (5)
Stephan Weeks (5)

Eppendorf-Biotronik/Analytical Magnetics

Hans Zimmermann
Daren Yan
Jim Hannon
Wayne Mozer

Argonne National Laboratory

Jeff Crain
David Green
Elaine Streets, IPEP

DOE Grand Junction Office

Ray Plienness
Craig Goodknight

GETF

Larry Burdge

Ohio EPA

Tom Ontko

FETC

Scott Renninger
Joe Paladino
Steve Cooke
C. Edward Christy

EML

Colin Sanderson
Isabel (Sue) Fisenne

INEL/RESL/MAPEP

Stan Morton
Dave Sill

EPA EMSL

George Dilbeck

RUST Federal Services, Inc.

Joe Bianconi

Corps of Engineers

Al Rosenkrantz