

ESTCP Cost and Performance Report

(CP-9606)



Heavy Metals Analyzer

January 2003



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TECHNOLOGY CERTIFICATION PROGRAM

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LIST OF ACRONYMS

ATMA	Automated Trace Metal Analyzer
CRADA	Cooperative Research and Development Agreement
DoD	Department of Defense
EPA	U.S. Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
ETG	Environmental Technologies Group
gpm	Gallons Per Minute
GF-AA	Graphite Furnace Atomic Absorption
HCl	hydrochloric acid
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IWTP	Industrial Wastewater Treatment Plant
µg/l	Micrograms per liter
ml	milliliter
MRT	Molecular Recognition Technology
NAS	Naval Air Station
ppb	parts per billion
PSA	Potentiometric Stripping Analysis
PSNS	Puget Sound Naval Shipyard
QA/QC	Quality Assurance/Quality Control
R ²	Measurement of Correlation (where R ² =1 equates to perfect correlation)
RCRA	Resource Conservation and Recovery Act
RSD	Relative Standard Deviation
SPAWAR	The Space and Naval Warfare Systems Center

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1.0 EXECUTIVE SUMMARY

In industrial process control and environmental compliance monitoring, Graphite Furnace Atomic Absorption (GF-AA) spectroscopy and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) have been traditionally used to measure trace metals. These instruments are large, expensive and require a high level of infrastructure support. Because of this, trace metal measurement usually involves sampling, preservation and transport to a centralized laboratory for later analysis. Current field tests for metals are difficult to use under industrial conditions, usually lack simultaneous multianalyte capability, and require significant operator intervention.

The Space and Naval Warfare Systems Center (SPAWAR) developed an Automated Trace Metals Analyzer (ATMA), which is based on Potentiometric Stripping Analysis (PSA). This automated instrument is designed for unattended collection and analysis of trace levels of heavy metals in water. PSA is capable of measuring multiple metals simultaneously at environmentally relevant concentrations. This instrument will allow users to make on-the-spot or continuous long-term measurements of metal contamination in an unattended automated mode. The ATMA can be set up to take measurements at timed intervals or in response to an external trigger. The ATMA enables near real-time (one sample/5 min), unattended on-site measurement of trace metals, such as lead, copper, mercury, arsenic and cadmium in aqueous media. It will reduce analytical costs over conventional monitoring and enable near real-time industrial process monitoring.

The ATMA's Windows-based interface enabled non-technical personnel to set up the instrument and collect data with minimal training. The instrument continually monitors performance and will automatically notify the operator and log any problems that it cannot correct. While in operation, the instrument is sealed from the external environment excluding the possibility of sample contamination. The instrument also allows non-technical personnel to operate it in an on-site, discrete analyses mode. This capability will permit expanded monitoring in support of efforts where diverse sources must be frequently monitored over extended periods at a low cost.

The ATMA was used in two types of wastewater treatment systems. The first was a traditional manual batch tank treatment process where flocculent is manually added to a tank of wastewater and the precipitates containing the metals are allowed to settle out. The second system was a continuous flow-through system utilizing advanced Molecular Recognition technology (MRT).

The objective of this demonstration was to provide performance, cost and field data for user acceptance. To meet these objectives, this project was divided into two major thrusts, field demonstration and laboratory validation. Validation of the instrument involved collecting data, which defined the accuracy, precision and sensitivity of the instrument. Field demonstrations gathered "actual" use data such as operator and expendable cost using the ATMA versus the traditional laboratory sample-and-ship method.

The ATMA was previously demonstrated for the Measurement of Lead in Drinking Water in Environmental Security Technology Certification Program (ESTCP) Project CP-199507. In the present demonstration, the ATMA was used to measure other trace metals levels at the North Island Naval Air Station (NAS) Industrial Wastewater Treatment Plant (IWTP) batch process and to measure online, in real-time, the metal concentrations of the MRT demonstration system at the Puget

Sound Naval Shipyard (PSNS) IWTP. These results were compared to the standard GF-AA and ICP-MS.

The arsenic response was linear with an $R^2 > 0.95$ for concentrations ranging from 0-368 $\mu\text{g/l}$. Fifteen metals at 635 $\mu\text{g/l}$ and 1,250 $\mu\text{g/l}$ significantly suppressed the sensitivity of the ATMA to arsenic. The chromium response was linear with a $R^2 > 0.95$ $\mu\text{g/l}$ for concentrations ranging from 0-65 $\mu\text{g/l}$. Of the 15 metals tested two, antimony(III) and iron(III) interfered with chromium measurements. Both occurred at the 1,490 $\mu\text{g/l}$ level. The copper response was linear with an $R^2 > 0.99$ for concentrations ranging to 225 $\mu\text{g/l}$. Of the 15 metals tested, 9 interfered with copper measurements at the 635 $\mu\text{g/l}$ level. At the 2,979 $\mu\text{g/l}$ level there were 10 interferents. The mercury response was linear with an $R^2 > 0.99$ up to 400 $\mu\text{g/l}$. Of the 15 metals tested two, bismuth(III) and selenium(IV) interfered with mercury measurements. Bismuth(III) was at the higher 2,976 $\mu\text{g/l}$ level and selenium(IV) was at both levels tested.

On October 6, 1997 U.S. Environmental Protection Agency (EPA) published a notice [Federal Register: October 6, 1997 (Volume 62, Number 193, pages 52098-52100)] that it plans to adopt a fundamentally different approach to environmental monitoring, known as a “performance-based measurement system.” Rather than requiring that a prescribed analytical method be used for a particular measurement, under the new approach, any method could be used provided that it is demonstrated to meet required performance standards. EPA believes that this approach will be more flexible and more cost-effective for the regulated community and that it will encourage innovation in analytical technology and improve data quality. This approach will allow the use of technology such as the ATMA in monitoring without costly and time-consuming method approval previously required under the old system.

In these demonstrations the ATMA was used as a process monitor to ensure that regulatory requirements were met. The ATMA did not substitute for the permitted measurements.

The capital cost estimate for the ATMA is \$25,000. Cost per sample was reduced from \$64 for GF-AA to \$15 to the ATMA, resulting in an approximate payback period of six months.

Metal contaminations has been observed at more than 900 military sites.

The ATMA was licensed commercially to Environmental Technologies Group (ETG) Commercial Products Division and was produced in 1997 under the name Metalizer 5000™. Transition of ATMA technology and ongoing developments were subject to a Cooperative Research and Development Agreement (CRADA) with Environmental Technologies Group. The Navy maintains a laboratory, a portable and a survey ship instrument for demonstration.

Unfortunately, the Commercial Products Division of ETG was closed and production of the Metalizer 5000™ was discontinued. In 2002, negotiations are ongoing for a licensing agreement with Trace Detect Inc. for the technology. Trace Detect Inc. wants to use the technology with their existing commercial microelectrodes and miniaturized electronics. This would result in a less expensive and more compact package with no loss in features.

2.0 TECHNOLOGY DESCRIPTION

2.1 DESCRIPTION

SPAWAR developed a prototype automated laboratory trace metals analyzer based on the electrochemical technique of PSA pioneered by D. Jagner in the early 70's. Recent advances in electronics now enable the technique to perform completely automated copper, mercury or arsenic metal analyses in about five minutes. The system (Figure 1) consists of: (1) a computer; (2) custom control and data acquisition and analysis software; (3) a custom computer-controlled potentiostat and data acquisition circuitry; and (4) a custom flow-through electrochemical cell module and sample handling components.



Figure 1. The Trace Metals Analyzer Computer and Electronic Boards (Left) and a Wet Chemistry Section (Right).

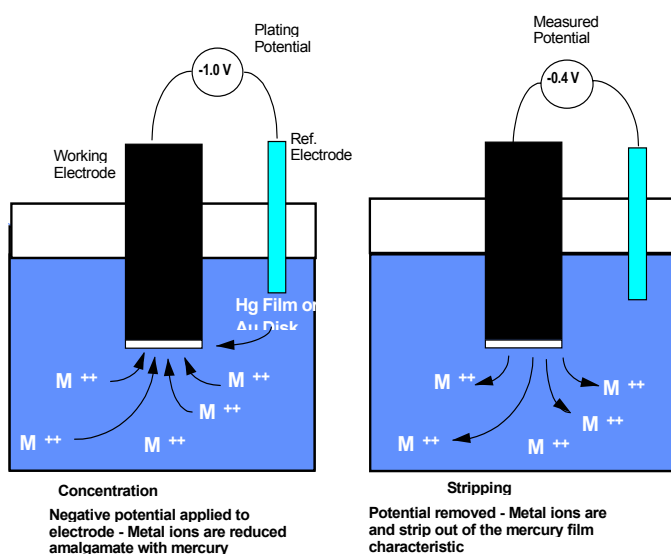


Figure 2. Potentiometric Stripping of Trace Metals.

concentrations in the range of 1-30 $\mu\text{g/l}$, a 30-second plating time is sufficient. In Step 2, the voltage is removed and the potential of the electrode is measured. The potential drops until it reaches the characteristic value for metal oxidation. At this voltage the metal is oxidized and stripped off the electrode. The potential remains constant until all the metal is oxidized producing a plateau in the voltage versus time graph (Figure 3). While a metal is oxidizing and stripping off of the electrode, the potential remains constant. The width of this plateau is proportional to the original concentration of metal ion in solution. The width of the plateau is proportional to the concentration of a specific trace metal originally in solution.

The high sensitivity of PSA can be attributed to the unique coupling of effective preconcentration steps and advanced measurement procedures. The electrode consists of a glassy carbon rod, on which is deposited a thin mercury film, or a thin gold disk. The electrode is exposed to the sample and a voltage potential is applied (Figure 2). PSA is a two step process consisting of a concentration step where the metal ions are amalgamated on the electrode and a stripping step where the metals are removed. In Step 1, the metal is reduced and forms an amalgam on the electrode. This concentration phase can last from 1 to 120 seconds depending on the amount of metal in solution. Typically, for metal

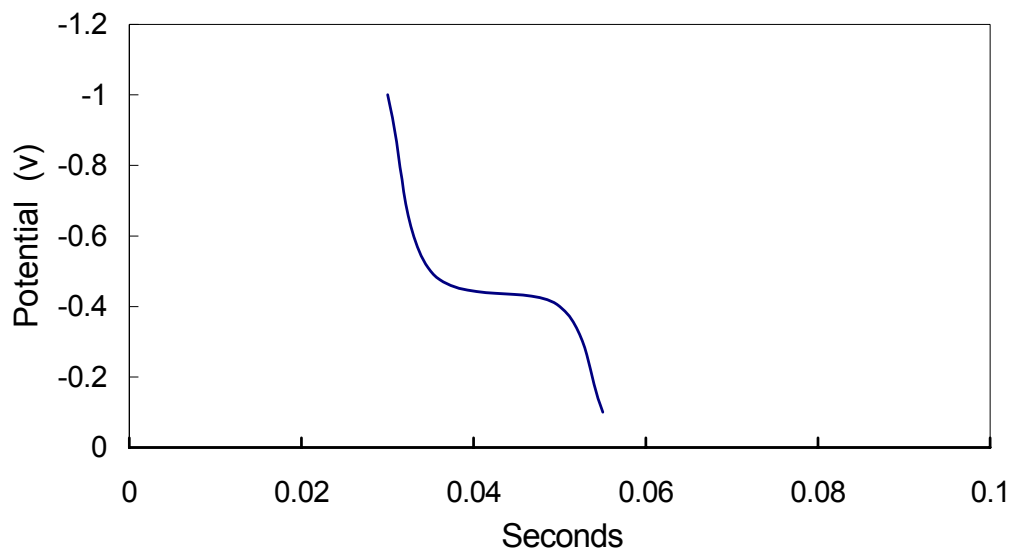


Figure 3. Potentiometric Stripping Curve.

To calculate the true concentration of the metal, a multi-point standard curve is generated by adding known quantities of metal to the test sample and repeating the measurement. This entire process is totally automated and proceeds without any intervention. When the concentration of metal has been determined (usually in less than 5 minutes) the instrument displays and logs the concentration and the relevant measurement statistics, pumps out the test sample, rinses the cell and waits for operator command.

2.2 STRENGTHS, ADVANTAGES AND WEAKNESSES

The strengths of the PSA method are accuracy, sensitivity, versatility and simplicity. Increasing the duration of the concentration or plating phase of PSA allows the instrument, in many cases, to measure metal concentrations in the single-digit $\mu\text{g/l}$ range. However, at these low levels, representative sampling becomes such a dominant factor that field use becomes impractical. The instrument is very versatile, allowing the user to operate the instrument in single-sample mode for multiple runs on a single sample.

As with all trace metal measurement techniques, the major weakness is in metal matrix effects interfering with the measurement. Interference for metal measurements include high concentrations of organics, solids or, in some cases, other metals. In samples containing interferences, greater than 10-fold reduction in signal will result. Therefore, it is not recommended to run samples for which the makeup, or potential make up, is not known, at least within an order of magnitude, without initial confirmation using standard analysis.

2.3 FACTORS INFLUENCING COST AND PERFORMANCE

There are three factors that influence the cost and performance of the ATMA. These are the startup capital equipment costs, the operation and maintenance costs, and the demobilization cost. The capital equipment costs will vary depending on the useful life of the equipment. The operation and maintenance costs are mainly dependent on the cost of labor as the material maintenance costs are minimal. The demobilization costs are minimal as there are no hazardous materials associated with the instrument.

2.4 PREVIOUS TESTING OF THE TECHNOLOGY

PSA technology is capable of measuring over 40 different metals with enough sensitivity in many cases to detect concentrations in the low parts-per-billion (ppb) range. It has been used to detect metals in such diverse fluids as drinking water¹, wine², sediment³, and blood⁴. An excellent summary of the technology can be found in *Stripping Analysis: Principles, Instrumentation and Applications*⁵.

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3.0 DEMONSTRATION DESIGN

3.1 PERFORMANCE OBJECTIVES

At the North Island NAS Wastewater Treatment Plant, when a plating bath waste load arrives, usually by bulk carrier, samples are collected and taken to the plant laboratory. In the laboratory a process plan to treat the waste is developed and tested. Analyzing the results of these small-scale treatment processes is the limiting step in large-scale treatment. Currently, off-site laboratory tests are used to determine the level of contamination that remains after small-scale treatment. Often, there is a three-day turn around time for the results. If the resulting levels are too high, the treatment process is adjusted and a new sample is sent to the laboratory.

This demonstration compared the results between the ATMA, and standard laboratory analysis. The main performance objective of this demonstration was to achieve chromium, mercury and arsenic measurements equivalent in accuracy and precision to the standard laboratory test currently used, without requiring a higher technical skill level and with results immediately available in the field at a lower cost.

The performance objective of this demonstration was to show the feasibility of using the ATMA to monitor outflow of the MRT system being demonstrated under ESTCP Project CP-199805: MRT and allow operators to easily determine, in real time, when filter breakthrough occurred. To meet that objective, the ATMA monitored the copper concentrations at a rate of 5 samples per hour for concentrations ranging from 10-100 µg/l.

3.2 SELECTION OF TEST PLATFORMS/FACILITIES

Two locations were selected for this demonstration. The sites were selected in consultation with Myron Anderson, USAF Wastewater Systems Program Manager, Headquarters Air Force Civil Engineering Support Agency and Katherine Ford and Nick Stencil, Pollution Prevention Technical Development Branch Code 421 at the Naval Facilities Engineering Service Center, Port Hueneme, CA. Site selection criteria included a high volume output of waste containing the demonstration metals, a permit allowing discharge of the demonstrated metals, on site treatment capability of the demonstration metals and availability and willingness of IWTP personnel to test this new method.

Several meetings were held with IWTP personnel to discuss the test plan. From these discussions it was found that of the various sources processed by the IWTP only the plating bath waste was routinely measured for the metals addressed by this demonstration. Plating bath waste is relatively consistent pollution source as all Department of Defense (DoD) plating shops follow military specifications when conducting plating operations.

The sites selected were the IWTPs located at North Island NAS and the Puget Sound Naval Shipyard. The North Island IWTP uses a conventional batch treatment process while the Puget Sound IWTP is demonstrating the advanced MRT system.

3.3 SITE/FACILITY DESCRIPTIONS

3.3.1 North Island Naval Air Station Wastewater Treatment Plant

The Industrial Wastewater Treatment Plant (IWTP) is located on the western end of the North Island Naval Air Station (NAS). It is operated by the Navy Public Works Center, Code 932. Processes contributing wastewater to this facility include: batch treatment of hauled wastewater, oil/water separation, paint stripping, steam cleaning, film processing, vehicle and aircraft washing, and cooling tower bleed. The total flow through this facility is approximately 184,000 gallons per day. This demonstration will concentrate on plating bath wastewater.

At the IWTP, plating bath wastewater arrives by bulk carrier and is placed in storage tanks. Samples are collected from the tanks and analyzed for metals at an off-site laboratory. Based on this analysis a treatment plan is developed. A small volume of the waste (~600 milliliter [ml]) is treated in the IWTP field laboratory and the treated sample is tested, at the off-site analytical laboratory, to assess the effectiveness of the treatment process. If the resultant metal levels are below discharge permit levels (Table 1) the treatment process is scaled up and used to treat the bulk waste. The bulk waste is treated then discharged into the San Diego municipal sewage system without further measurement.

Table 1. Metal Discharge Limits for the North Island NAS IWTP.

Metal	Maximum Concentration (mg/l)
Arsenic	0.8
Chromium	2.8
Copper	1.8
Mercury	0.8
Selenium	0.8

3.3.2 Puget Sound Naval Shipyard Wastewater Treatment Plant

The Puget Sound Naval Shipyard (PSNS) is engaged in extensive maintenance work on small and large Naval vessels. The work is heavy industrial and includes several metal plating and cleaning operations such as etching, passivating, plating, galvanizing and general cleaning. Many of these processes generate rinse water that must be processed before discharge.

In 1976, the PSNS constructed an Industrial Waste Pretreatment Facility (Building 871) to treat industrial wastes from several facilities throughout the Shipyard. Building 871 is located on the north end of the Shipyard facility and is part of the Public Works Department, operated by Code 910HZ. The waste treatment facility was built in a central location the shipyard with piping to transfer the wastewater. Today the only piping remaining is from the largest generator of wastewater, the Metal Preparation Facility. The IWTP still receives waste by tank delivery in minimal quantities from the sheet metal shop and the photo laboratory.

The building containing the treatment plant was design to process wastewater in a two level heavy concrete structure. The upper level covers a floor area of approximately 9,000 sq. ft. It is housed

in a prefabricated metal structure with masonry walls on the east and south sides. All process equipment is located within the building, and only external activity is unloading of the wastewater from portable tanks and process chemicals, and loading of sludge to be hauled to the Hazardous Waste Containing Storage Area in Building 944.

The PSNS IWTP operates under a Resource Conservation and Recovery Act (RCRA) “permit by rule” exempting it from requiring a Part B Permit. It now functions under the regulations of the Clean Water Act. Treated wastewater is discharged to the Shipyard sanitary sewerline, and eventually discharged to the City of Bremerton’s sanitary sewer plant. Sludge is dewatered, drummed, and transported to Building 944, then disposed as a RCRA-listed hazardous waste at an off-site, permitted Treatment, Storage and Disposal Facility.

The MRT system designed for the ESTCP demonstration was intended to recover those metals found in the miscellaneous tank at PSNS’s IWTP. The waste stream from the miscellaneous tank has the range of metal ions shown in Table 2. The metal contaminants vary with in this range depending on the metal finishing activities of the Metal Preparation Facility and the time of analysis.

Table 2. Baseline Metal Concentration Range for PSNS IWTP.

Metal	Baseline Influent Range (mg/l)
Zinc	1.12-10.80
Lead	0.10-1.99
Copper	3.66-17.2
Silver	0.11-0.38
Cadmium	0.13-2.16
Nickel	1.15-7.93
Chromium (Total)	2.20-18.50

3.4 NORTH ISLAND NAS WASTEWATER TREATMENT PLANT

3.4.1 Physical Setup and Operation

The IWTP chemical technician at the plant laboratory used the ATMA and the standardized laboratory test was conducted at a certified independent testing laboratory.

3.4.2 Sampling Procedures

When a waste load arrived, usually by bulk carrier, samples before and after small-scale treatment was collected and split. Half of each split was taken to the plant laboratory and immediately measured by a wastewater treatment plant technician. Samples that were stored or shipped for later analysis were preserved. Holding time did not exceed seven days. Arsenic samples were preserved by adding 0.5% high-purity hydrochloric acid (HCl) to a pH <2 in metal-free fluoropolymer containers. Chromium samples were preserved in a 50% NaOH solution in metal-free polypropylene containers. Mercury samples were preserved by adding 0.5% high-purity HCl or 0.5% BrCl to a pH <2 in metal-free fluoropolymer containers.

3.4.3 Analytical Procedures

Chromium and arsenic were analyzed using EPA Method 200.8. Mercury was analyzed using EPA Method 7470. Equipment blanks, field blanks, and field duplicates were used in accordance with the Quality Assurance/Quality Control (QA/QC) plan. Chain of custody, shipping and holding times followed the QA/QC plan.

3.5 PUGET SOUND NAVAL SHIPYARD MRT WASTEWATER TREATMENT PLANT

3.5.1 Physical Setup and Operation

The ATMA was connected to sampling port 6 of the MRT system (see Figure 4). The ATMA was run during the Acid/Alkali MRT mixed bed column flow tests. In these tests, Column 1 and Column 2 are connected in series and the copper concentration exiting Column 2 were measured. The ATMA was used by the MRT operators to determine when filter breakout occurs. The ATMA was operated in a continuous mode at a frequency of not less than 5 samples per hour.

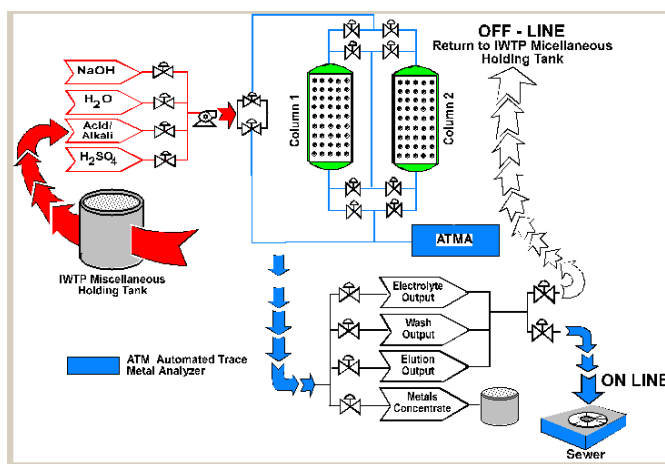


Figure 4. Application of the ATMA to the ESTCP Demonstration of MRT.

3.5.2 Sampling Procedures

The ATMA was located at Port 6. It measured copper ion concentrations in the effluent after the effluent had passed through the MRT columns. There were two demonstration runs using the ATMA. In the first run, samples were collected every thirty minutes in pre-cleaned, trace-metal-free polyethylene bottles and immediately hand-carried to the shipyard analytical laboratory for analysis. The ATMA was operated in a continuous mode at a rate of one sample every thirty minutes. The time and amount of waste processed was noted on the ATMA log and sample bottles. The second run demonstrated the ability of the ATMA to continuously monitor and plot metal concentrations in real-time. The operators used the concentrations to determine, in real-time, when the exact moment breakout of the filter bed occurred.

3.5.3 Analytical Procedures

Copper was analyzed using EPA Method 200.8 Equipment blanks, field blanks, and field duplicates were used in accordance with the MRT QA/QC plan.

3.6 DATA ARCHIVING

The raw and processed data for the ATMA and laboratory analysis were assembled and archived on CD-ROM. The raw data is in comma-separated values and the laboratory data is in Microsoft Excel spread sheets.

4.0 PERFORMANCE ASSESSMENT

4.1 PERFORMANCE DATA

A series of laboratory tests were conducted to assess the performance of the ATMA in measuring arsenic, chromium, copper, mercury and selenium. Three tests were performed on each metal to determine interferences, linearity and sensitivity response.

To determine the metal ion interferences, a study was conducted to assess the performance of the ATMA in the presence of 15 different metal ions at high and low concentrations. A decrease in instrument sensitivity greater than 50% was considered significant enough to impair the metal measurement.

Linearity was tested by measuring a range of known metal concentrations. The initial metal concentrations in the prepared base stock samples were determined using an ICP-MS. The base stock sample was then diluted to the required metal concentration using ultra-clean trace-metal-free water.

Placing the ATMA in an automated mode and repeatedly measuring a single sample allowed the observation of the change in sensitivity of the instrument over time. Ten measurements were taken and the relative standard deviation was calculated.

The ATMA performs standard addition calibrations after each measurement and calculates the concentration of the measured metal based on these calibrations. To accurately measure the interferences, linearity and sensitivity, the raw analog to digital converter output was used. This allowed examination of the performance before the ATMA automatically adjusted for any changes in sensitivity or linearity.

4.1.1 Arsenic

The original water sample was spiked with arsenic(III) to 32 µg/l and split three ways for each interfering metal tested. Aliquots Two and Three were spiked with the interfering ion to 635 µg/l and 1,250 µg/l respectively. The percent change in measured arsenic levels between the spiked samples and the original 32 µg/l sample was recorded. In Table 3, it can be seen that all 15 metals at 635 µg/l and 1,250 µg/l significantly suppress the sensitivity of the ATMA to arsenic. Given this performance, arsenic should only be measured using relatively clean, well-defined samples such as drinking water or relatively clean well water.

Table 3. Arsenic Interference Study of 15 Metals at 635 µg/l and 1,250 µg/l.

Arsenic Interference (32 µg/l concentration)			
Interfering Ion	635 µg/l Interfering Ion Added	1,250 µg/l Interfering Ion Added	Interference
	% Decrease in Instrument Sensitivity	% Decrease in Instrument Sensitivity	>50% Decrease in Sensitivity
Aluminum(III)	92.5	87.6	Yes
Antimony(III)	82.3	63.4	Yes
Bismuth(III)	<100	<100	Yes
Cadmium(II)	<100	<100	Yes
Copper(II)	<100	<100	Yes
Chromium(VI)	<100	<100	Yes
Iron(III)	85.4	69.7	Yes
Lead(II)	100.0	100.0	Yes
Magnesium(II)	94.0	87.6	Yes
Manganese(II)	89.7	83.5	Yes
Mercury(II)	<100	<100	Yes
Nickel(II)	95.7	83.5	Yes
Selenium(IV)	<100	<100	Yes
Tin(IV)	86.9	72.7	Yes
Zinc(II)	95.5	91.1	Yes

As seen in Figures 5 and 6, the arsenic response of the ATMA was linear with a $R^2 > 0.95$ for concentrations ranging from 0-368 µg/l.

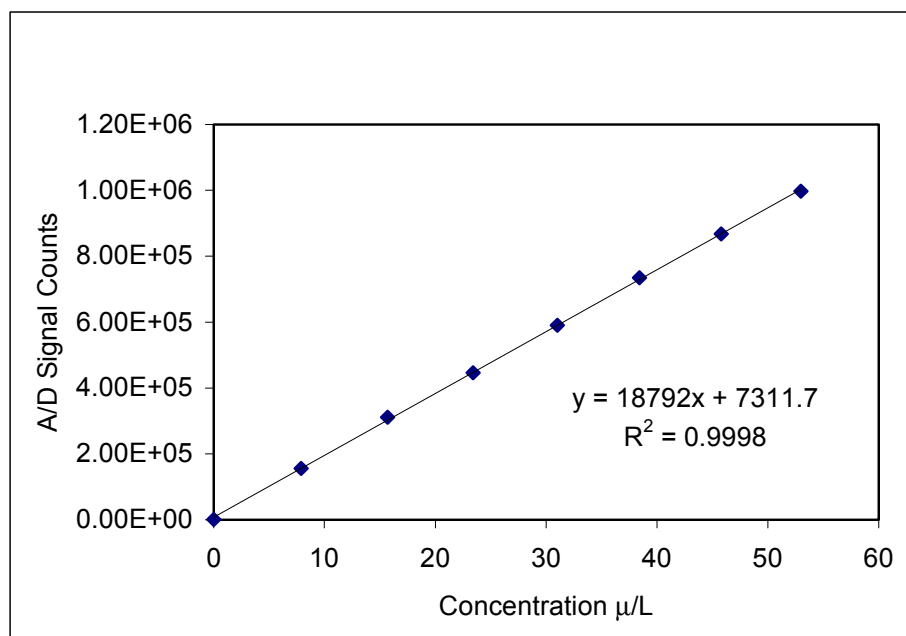


Figure 5. Response of the ATMA to Water Samples Spiked with 0-53 µg/l Arsenic(III).

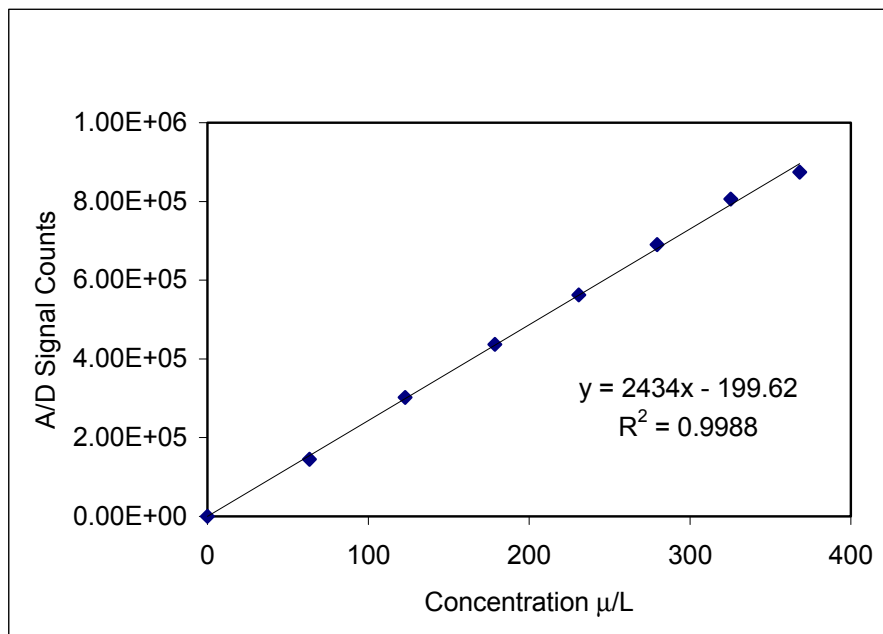


Figure 6. Response of the ATMA to Water Samples Spiked with 63-368 µg/l Arsenic(III).

Figure 7 shows the results for a single water sample spiked with arsenic(III) to 32 µg/l and measured 10 times. These results had a relative standard deviation of 9.2%. This was caused by a linear decrease in instrument sensitivity most likely due to degradation of the working electrode.

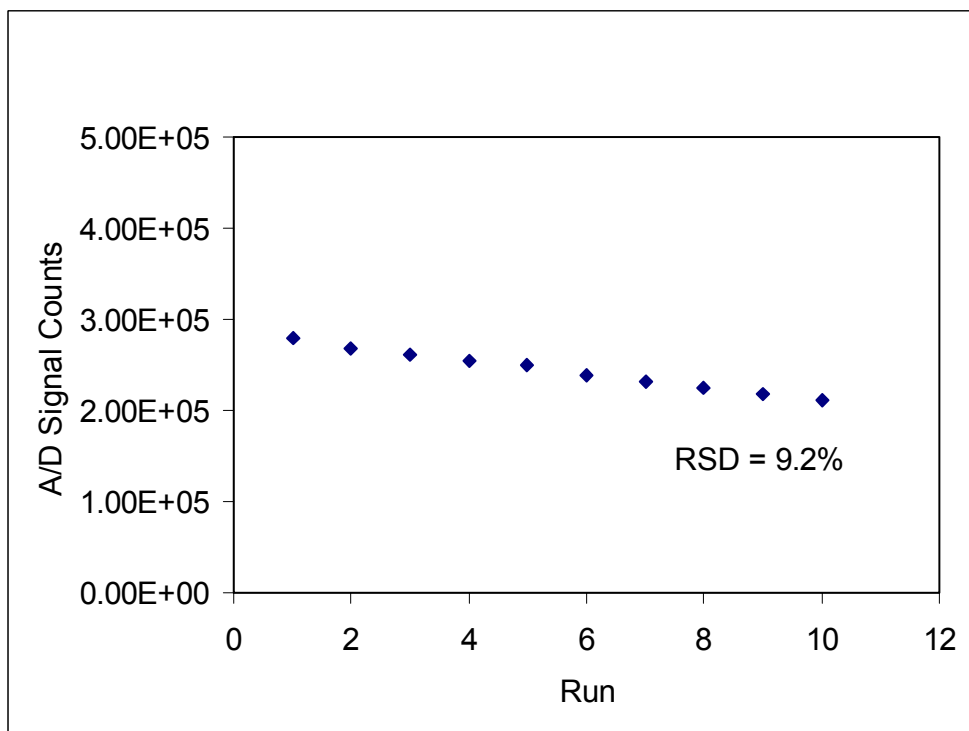


Figure 7. Response of the ATMA to a Single Water Sample Spiked with Arsenic(III) to 32 µg/l and Measured 10 Times.

Polishing the electrode restores its sensitivity. Using this data it is estimated that the electrode would require polishing after a 50% decrease in sensitivity or after approximately every 54 measurements.

4.1.2 Chromium

The original water sample was spiked with chromium(VI) to 16 µg/l and split three ways for each interfering metal tested. Aliquots Two and Three were spiked with the interfering ion to 625 µg/l and 1,490 µg/l respectively. The percent change in measured chromium levels between the spiked samples and the original 16 µg/l sample was recorded. In Table 4, it can be seen that, of the 15 metals tested, two, antimony(III) and iron(III), interfered with chromium measurements. Both occurred at the 1,490 µg/l level. It is recommended that test samples known to contain iron(II) or antimony(III) be analyzed using conventional methods to determine the levels of these interfering ions before using the ATMA for monitoring.

Table 4. Chromium Interference Study of 15 Metals at 625 µg/l and 1,490 µg/l.

Chromium Interference (16 µg/l concentration)			
Interfering Ion	625 µg/l Interfering Ion Added	1,490 µg/l Interfering Ion Added	Interference
	% Decrease in Instrument Sensitivity	% Decrease in Instrument Sensitivity	>50% Decrease in Sensitivity
Aluminum(III)	15.4	17.9	No
Antimony(III)	41.5	62.3	Yes
Arsenic(III)	14.1	27.7	No
Bismuth(III)	4.0	39.1	No
Cadmium(II)	13.5	17.0	No
Copper(II)	25.2	3.5	No
Iron(III)	13.3	74.3	Yes
Lead(II)	18.1	16.5	No
Magnesium(II)	25.4	6.4	No
Manganese(II)	13.3	19.9	No
Mercury(II)	25.4	11.8	No
Nickel(II)	13.2	16.0	No
Selenium(IV)	13.1	17.8	No
Tin(IV)	20.9	20.2	No
Zinc(II)	8.6	28.1	No

As seen in Figures 8 and 9, the chromium response of the ATMA was linear with a $R^2 > 0.95$ for concentrations ranging from 0-65 µg/l. Beyond 65 µg/l, the electrode became saturated and rapidly lost linearity.

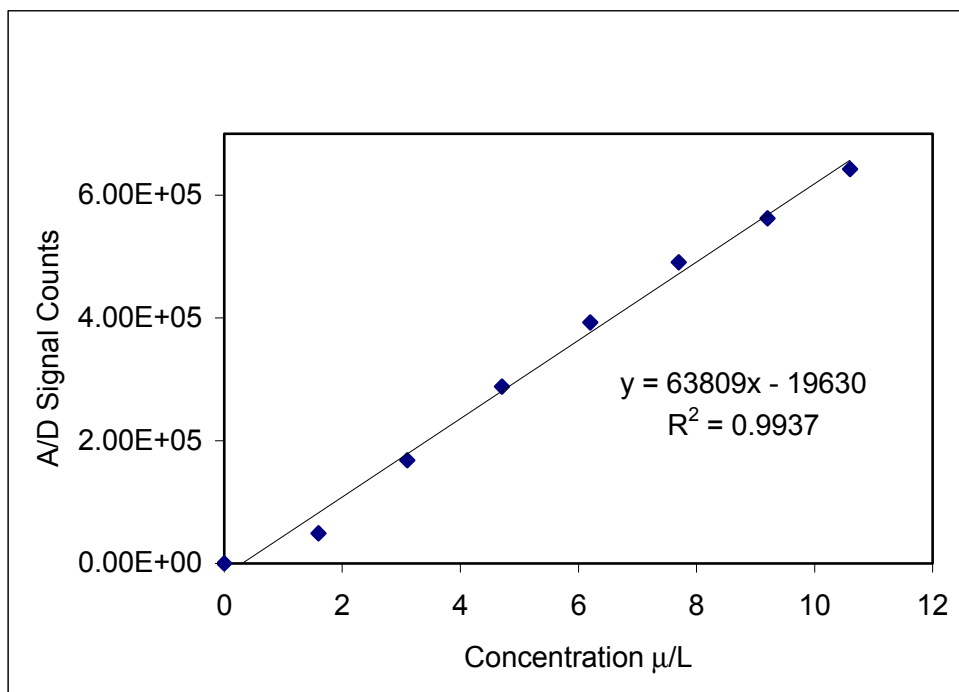


Figure 8. Response of the ATMA to Water Samples Spiked with 0-11 µg/l Chromium(VI).

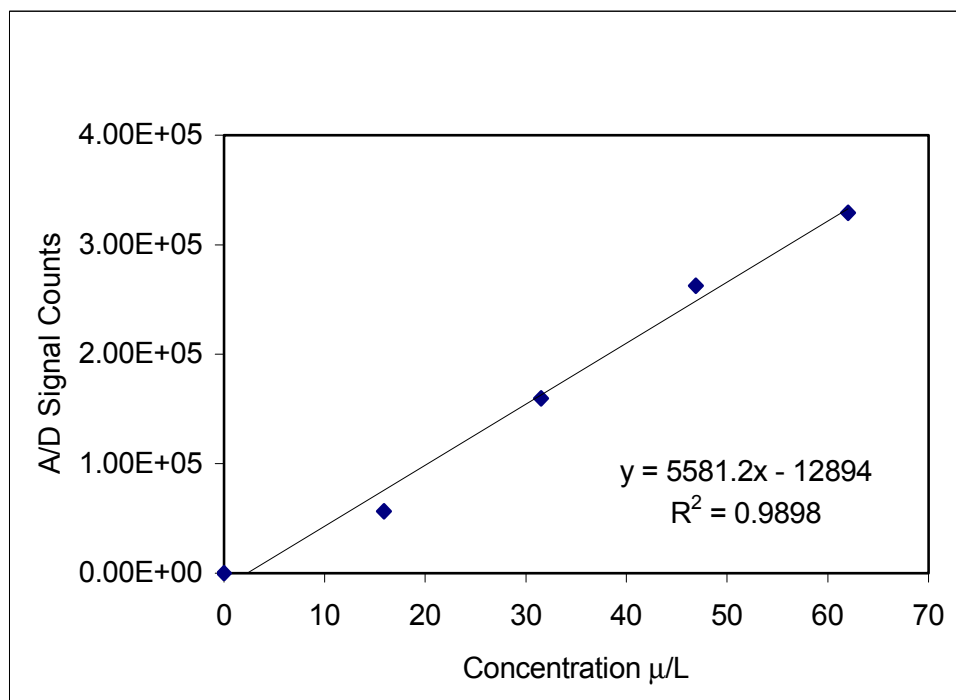


Figure 9. Response of the ATMA to Water Samples Spiked with 15-65 µg/l Chromium(VI).

Figure 10 shows the results for a single water sample spiked with chromium(VI) to 16 µg/l and measured 10 times. These results had a relative standard deviation of 3.1%. No decrease in sensitivity was observed during the runs.

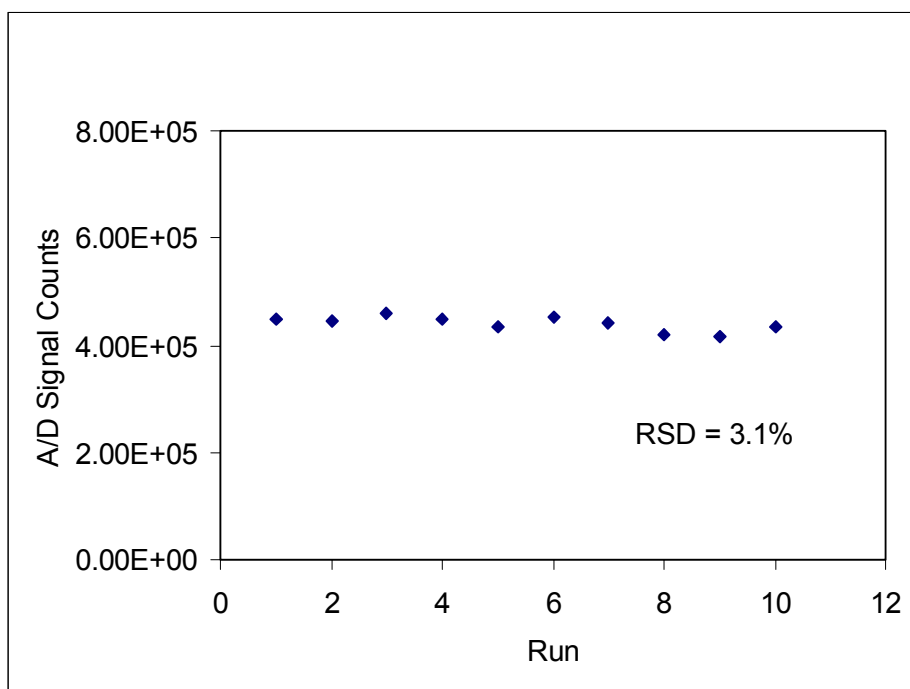


Figure 10. Response of the ATMA to a Single Water Sample Spiked with Chromium(VI) to 16 µg/l and Measured 10 Times.

4.1.3 Copper

The original water sample was spiked with copper(II) to 32 µg/l and split three ways for each interfering metal tested. Aliquots Two and Three were spiked with the interfering ion to 635 µg/l and 2,979 µg/l respectively. The percent change in measured copper levels between the spiked samples and the original 32 µg/l sample was recorded. In Table 5, it can be seen that, of the 15 metals tested, 9 interfered with copper measurements at the 635 µg/l level. At the 2,979 µg/l level there were 10 interferents. When measuring copper with the ATMA, the concentration of these interfering metal ions should be analyzed beforehand using conventional methods.

As seen in Figures 11 and 12, the copper response of the ATMA was linear with a $R^2 > 0.99$ for concentrations ranging up to 225 µg/l.

Copper measurements show excellent linearity. The relative standard deviation (Figure 13) from measuring a sample 10 times was less than 2%. No decrease in sensitivity was observed during these runs.

Table 5. Copper Interference Study of 15 Metals at 635 µg/l and 2,979 µg/l.

Copper Interference (32 µg/l concentration)			
Interfering Ion	635 µg/l Interfering Ion Added	2,979 µg/l Interfering Ion Added	Interference
	% Decrease in Instrument Sensitivity	% Decrease in Instrument Sensitivity	>50% Decrease in Sensitivity
Aluminum(III)	19.8	9.0	No
Antimony(III)	55.5	90.8	Yes
Arsenic(III)	78.0	88.2	Yes
Bismuth(III)	68.5	75.1	Yes
Cadmium(II)	20.0	13.7	No
Copper(II)			
Chromium(VI)	15.4	14.3	No
Iron(III)	12.7	13.0	No
Lead(II)	22.3	62.3	Yes
Magnesium(II)	56.7	54.3	Yes
Manganese(II)	55.0	53.9	Yes
Mercury(II)	98.8	89.6	Yes
Nickel(II)	63.0	54.8	Yes
Selenium(IV)	61.2	62.9	Yes
Tin(IV)	54.3	50.7	Yes
Zinc(II)	48.2	11.8	No

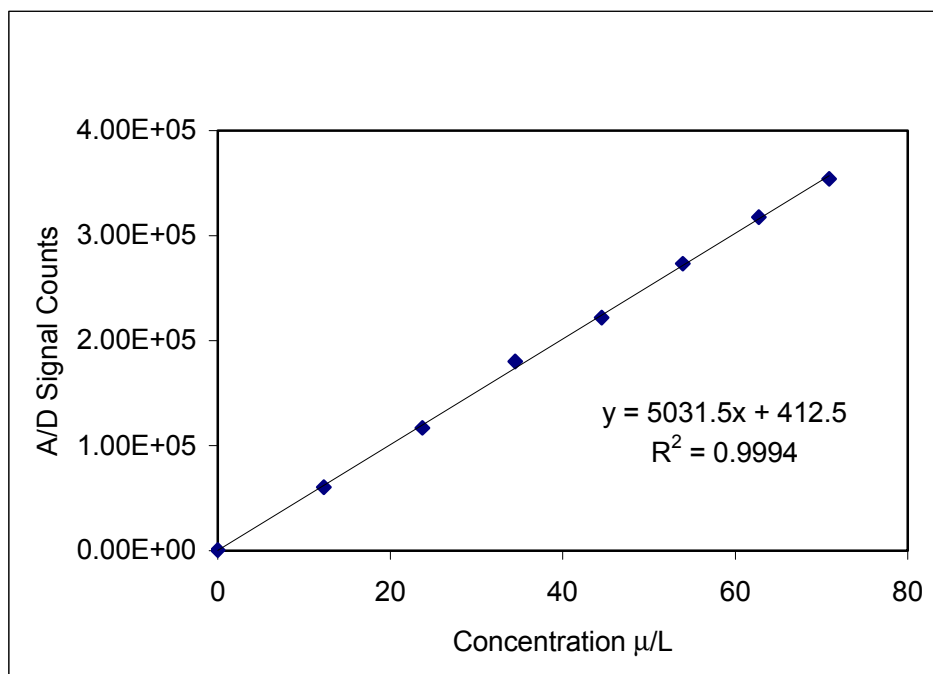


Figure 11. Response of the ATMA to Water Samples Spiked with 0-70 µg/l Copper(II).

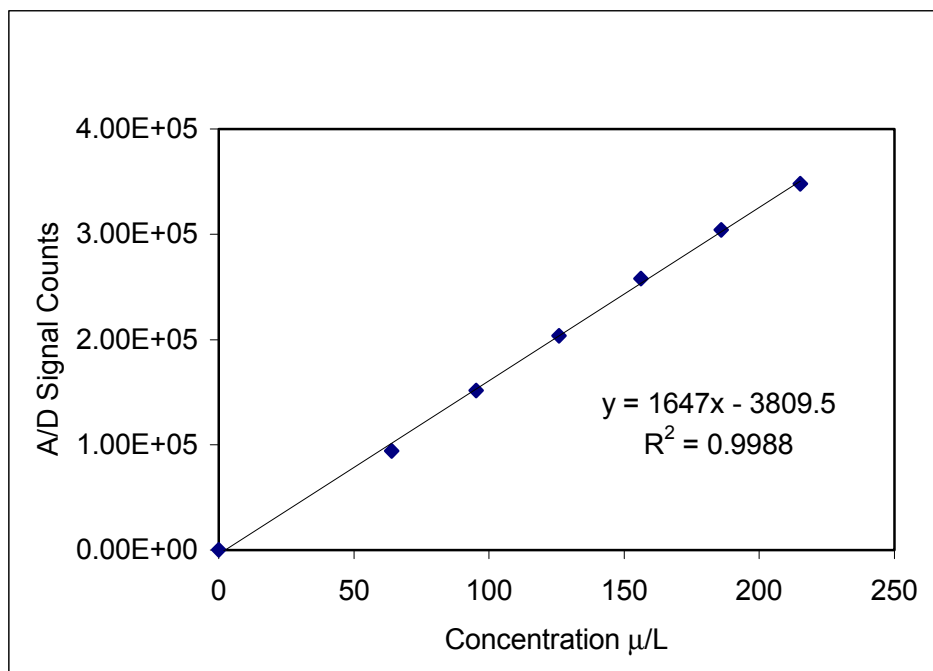


Figure 12. Response of the ATMA to Water Samples Spiked with 64-215 µg/l Copper(II).

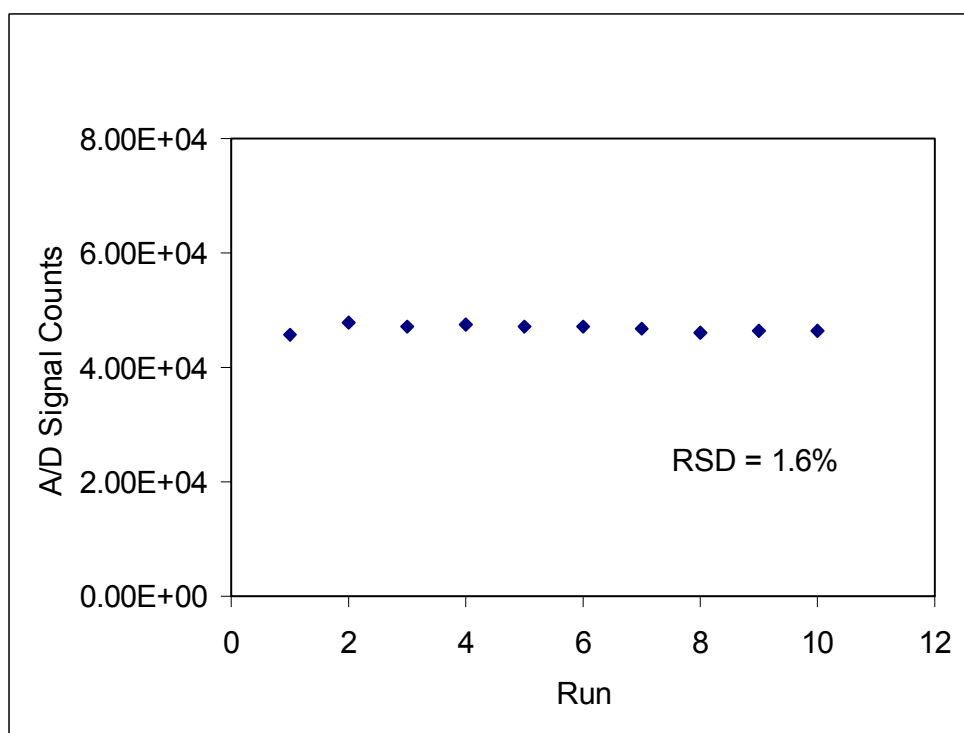


Figure 13. Response of the ATMA to a Single Water Sample Spiked with Copper(II) to 32 µg/l and Measured 10 Times.

4.1.4 Mercury

The original water sample was spiked with mercury(II) to 32 µg/l and split three ways for each interfering metal tested. Aliquots Two and Three were spiked with the interfering ion to 635 µg/l and 2,976 µg/l respectively. The percent change in measured mercury levels between the spiked samples and the original 32 µg/l sample was recorded. In Table 6, it can be seen that, of the 15 metals tested, two, bismuth(III) and selenium(IV), interfered with mercury measurements. Bismuth(III) was at the higher 2,976 µg/l level and selenium(IV) was at both levels tested. It would be recommended that test samples known to contain bismuth(III) or selenium(IV) be analyzed using conventional methods to determine the levels of these interfering ions before using the ATMA for monitoring.

As seen in Figure 14 and Figure 15, the response of the ATMA to mercury was linear ($R^2 > 0.99$) up to 400 µg/l and the linearity of multiple measurements (Figure 16) was 9.2%.

Table 6. Mercury Interference Study of 15 Metals at 635 µg/l and 2,976 µg/l.

Mercury Interference (32 µg/l concentration)			
Interfering Ion	635 µg/l Interfering Ion Added	2,976 µg/l Interfering Ion Added	Interference
	% Decrease in Instrument Sensitivity	% Decrease in Instrument Sensitivity	>50% Decrease in Sensitivity
Aluminum(III)	11.8	16.4	No
Antimony(III)	4.4	18.9	No
Arsenic(III)	16.0	17.0	No
Bismuth(III)	16.5	68.3	Yes
Cadmium(II)	13.1	4.2	No
Copper(II)	4.4	3.0	No
Chromium(VI)	3.5	22.5	No
Iron(III)	2.4	20.1	No
Lead(II)	0.1	13.0	No
Magnesium(II)	5.47	17.8	No
Manganese(II)	15.6	18.5	No
Nickel(II)	1.0	6.2	No
Selenium(IV)	92.8	100	Yes
Tin(IV)	3.9	8.7	No
Zinc(II)	2.4	9.9	No

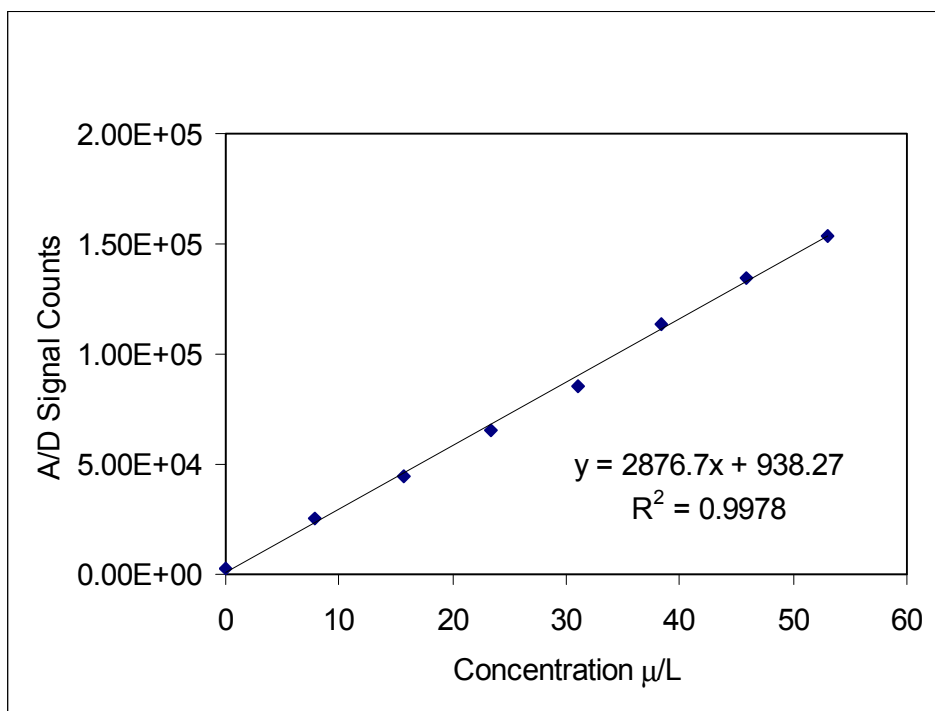


Figure 14. Response of the ATMA to Water Samples Spiked with 0-55 $\mu\text{g/l}$ Mercury(II).

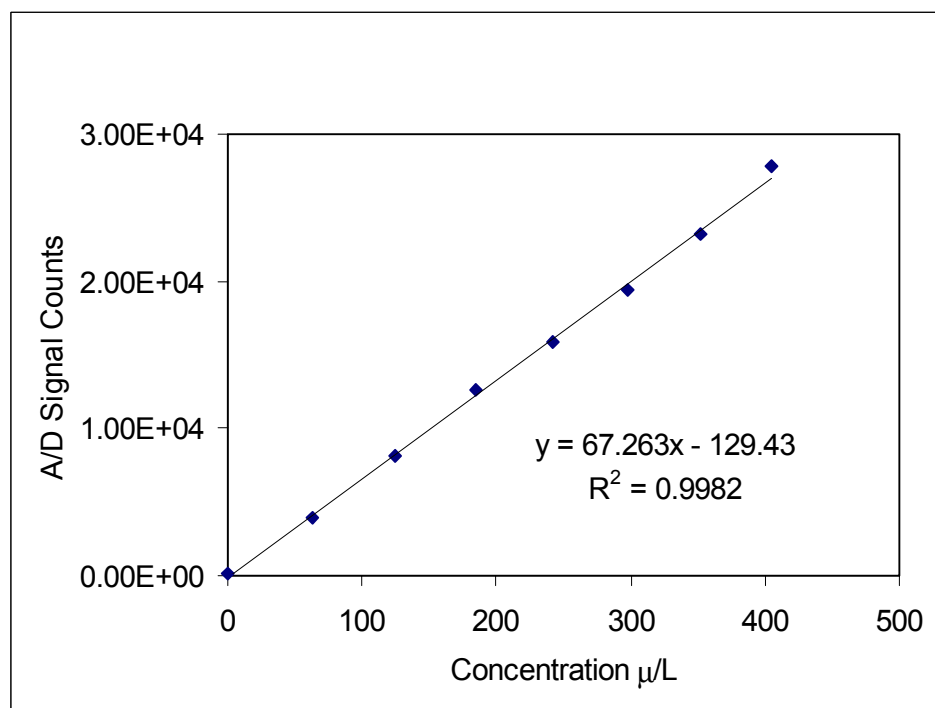


Figure 15. Response of the ATMA to Water Samples Spiked with 60-400 $\mu\text{g/l}$ Mercury(II).

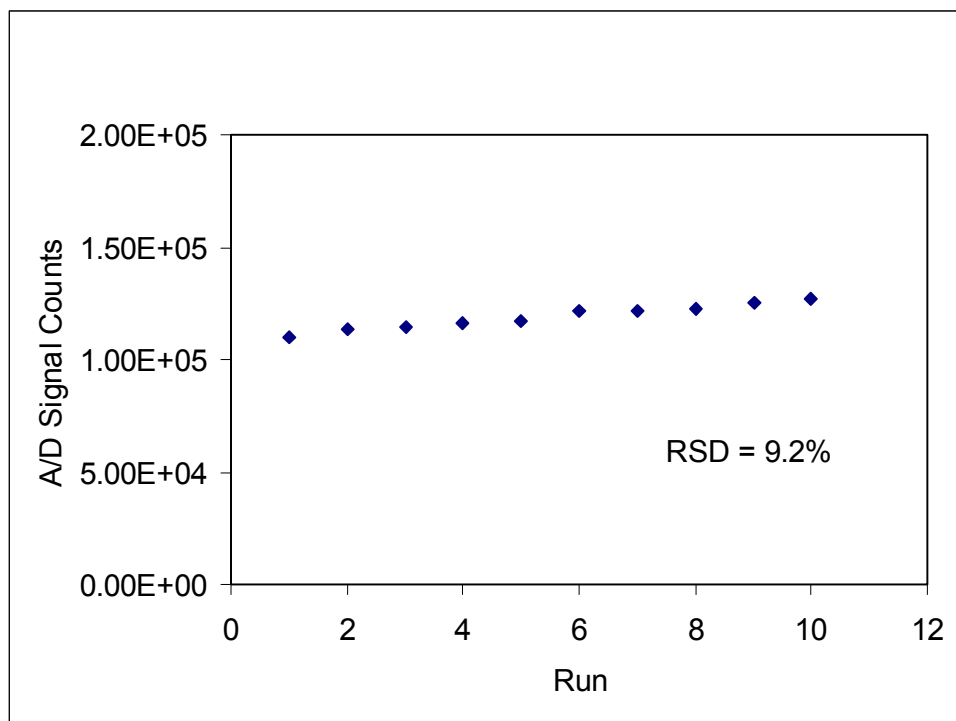


Figure 16. Response of the ATMA to a Single Water Sample Spiked with Mercury(II) to 32 $\mu\text{g/l}$ and Measured 10 Times.

4.1.5 Selenium

The original water sample was spiked with selenium(IV) to 32 $\mu\text{g/l}$ and split three ways for each interfering metal tested. Aliquots Two and Three were spiked with the interfering ion to 635 $\mu\text{g/l}$ and 2,979 $\mu\text{g/l}$ respectively. The percent change in measured selenium levels between the spiked samples and the original 32 $\mu\text{g/l}$ sample was recorded. From Table 7, it can be seen that seven of the tested ions interfered with the measurement of selenium. All these interferences occurred at the higher 2,979 $\mu\text{g/l}$ level. If the effluent is known to contain these high levels of metals represented, samples should be analyzed using conventional methods before using the ATMA.

As seen in Figure 17 and Figure 18, the response of the ATMA to selenium was linear ($R^2 > 0.99$) up to 400 $\mu\text{g/l}$ and the linearity of multiple measurements (Figure 19) was 4%.

Table 7. Selenium Interference Study of 15 Metals at 635 µg/l and 2,979 µg/l.

Selenium Interference (32 µg/l concentration)			
Interfering Ion	635 µg/l Interfering Ion Added	2,979 µg/l Interfering Ion Added	Interference
	% Decrease in Instrument Sensitivity	% Decrease in Instrument Sensitivity	>50% Decrease in Sensitivity
Aluminum(III)	10	54	Yes
Antimony(III)	31	88	Yes
Arsenic(III)	17	43	No
Bismuth(III)	14	75	Yes
Cadmium(II)	0.1	25	No
Copper(II)	3.6	59	Yes
Chromium(VI)	28	83	Yes
Iron(III)	10	50	Yes
Lead(II)	.3	28	No
Magnesium(II)	3.5	30	No
Manganese(II)	4.1	30	No
Mercury(II)	27	100	Yes
Nickel(II)	6.8	38	No
Tin(IV)	13	59	Yes
Zinc(II)	5.4	38	No

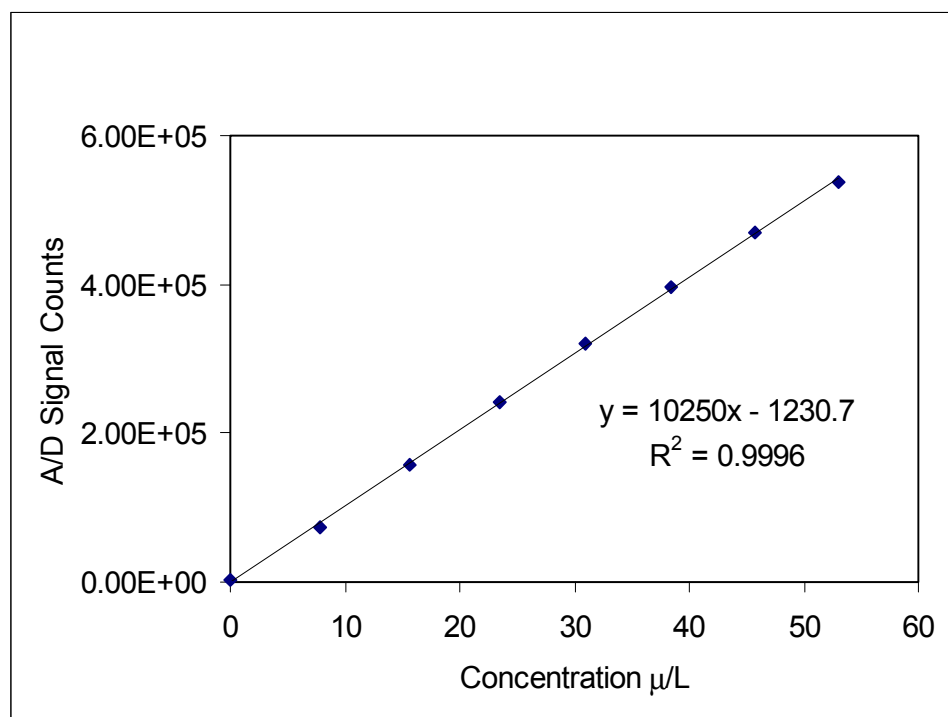


Figure 17. Response of the ATMA to Water Samples Spiked with 0-50 µg/l Selenium(IV).

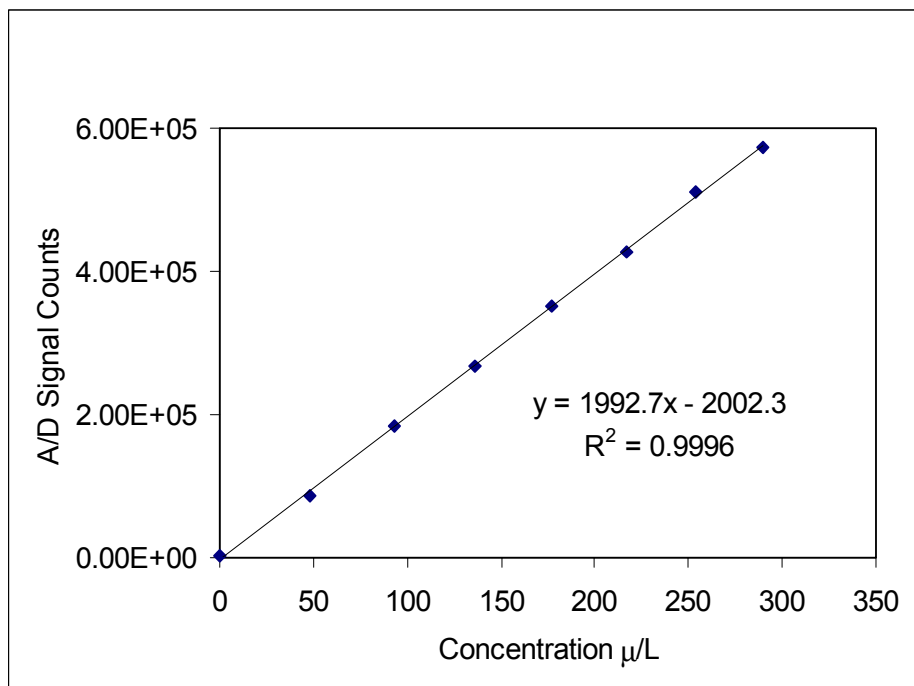


Figure 18. Response of the ATMA to Water Samples Spiked with 48-288 $\mu\text{g/l}$ Selenium(IV).

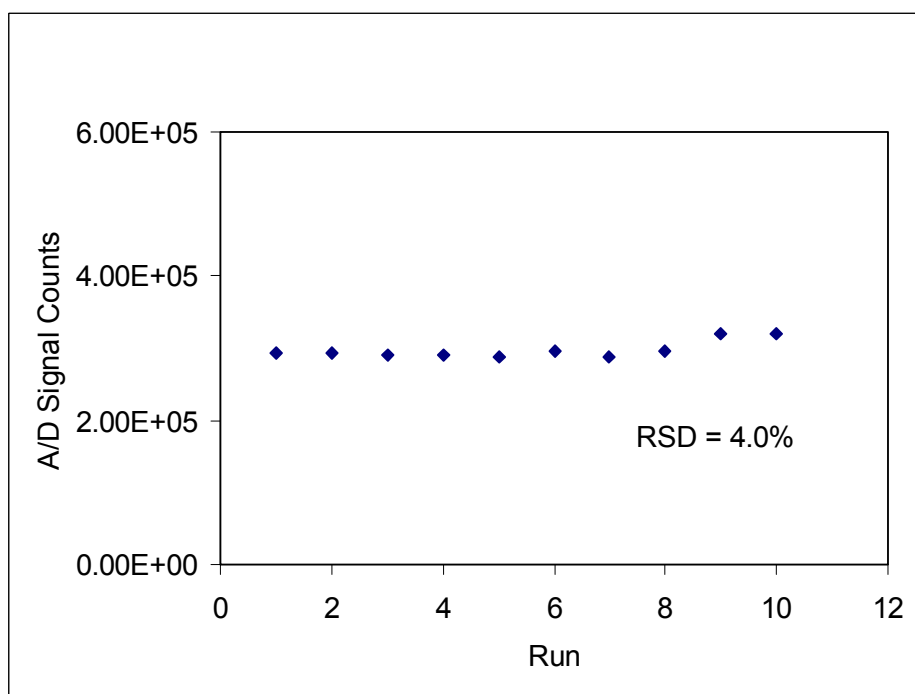


Figure 19. Response of the ATMA to a Single Water Sample Spiked with Selenium(IV) to 32 $\mu\text{g/l}$ and Measured 10 Times.

4.2 DATA ASSESSMENT

4.2.1 North Island NAS Wastewater Treatment Plant

The ATMA was setup at the North Island NAS Wastewater Treatment Plant. Upon arrival of a bulk shipment of plating bath waste, a sample was collected split and measured by the ATMA and by the standard laboratory methods as outlined in Table 8.

Two plating bath waste loads were tested on site. The original sample from the bulk delivery was tested at original strength and at 2X and 20X dilutions. The sample was retested after treatment with the Nalco Flocculent. The flocculent is used in the wastewater treatment plant to remove metals from plating bath waste loads. Concentrations are in µg/l.

Table 8. Metals Tested in Initial Plating Bath Sample.

Metal	Method	Min. Det. Limit (µg/l)
Mercury	EPA7470	0.2
Arsenic	EPA1632	53
Chromium	EPA200.7	7

Neither bulk sample tested contained any selenium. The ATMA and the laboratory tests confirmed that Selenium was not at detectable levels. This result was expected as none of the chemicals used in the plating baths contained Selenium.

As seen in Table 9, the ATMA was unable to accurately measure the amount of trace metals in the treated or untreated plating bath waste samples. The ATMA was unable to obtain a concentration measurement for chromium due to the error of the standard addition measurements exceeding the instruments minimum linearity cutoff of $R^2=0.98$.

Table 9. Wastewater Treatment Samples from the North Island Treatment Plant.

North Island NAS Wastewater Treatment Plant Results									
		Hg		As		Cr ^{total}		Cr ⁶	
		Lab	TMA	Lab	TMA	Lab	TMA	Lab	TMA
September Run	Sample	1050	45	310	59	927	*	ND	*
	2X dilution	525	63	155	108	463	*	ND	*
	20X dilution	56	8	17	12.7	50	*	ND	*
	After Nalco Flocculent	58	13	42	ND	44	*	ND	*
October Run	Sample	766	106	240	22	926	*	ND	*
	2X dilution	383	62	120	95	463	*	ND	*
	20X dilution	41	13	13	5.8	50	*	ND	*
	After Nalco Flocculent	58	ND	42	ND	44	*	ND	*

The ATMA measurements of the treated samples were significantly below the laboratory measured concentrations. This is probably due to the tight binding of the remaining Nalco flocculent still in solution to all or most of the metal ions. This tight binding does not allow the ATMA to measure the ion concentration.

4.2.2 Puget Sound Naval Shipyard MRT Wastewater Treatment Plant

The ATMA was setup at the Puget Sound Naval Shipyard Wastewater Treatment Plant. The instrument measured the metal concentrations of the ESTCP-funded MRT demonstration. The MRT system uses macro-cyclic chelating ligands for removal, separation and recovery of metals. By taking advantage of the high affinity and selectivity of these ligands, MRT systems can be designed to target the toxic metals found in DoD industrial influents.

These specialized ligands are bonded to polymer supports and are very stable in the solid form. This allows the ligands to be used in a packed bed or membrane configuration at the high flow rates required by typical DoD IWTPs. This demonstration used the high volume acid/alkali influent waste stream at the PSNS IWTP. The ATMA was connected to Port 6 of the MRT system to monitor copper levels in real-time at 15 minute intervals. An initial analysis of the effluent at Port 6 is listed in Table 10. When breakthrough of the filtration process occurs, copper levels at the end of the treatment process (Port 6) rise above 40 µg/l, indicating that the filter system requires maintenance.

Table 10. Laboratory Analysis of the Effluent Stream at Port 6 of the MRT at the Start of the First Demonstration Run at PSNS.

PSNS/MRT Composite Sample Concentrations				
Metal	Anal. Method	Prep Method	Detection Limit (ppb)	Sample Conc. (ppb)
Antimony	EPA6010B	EPA3010A	5	6
Arsenic	EPA6010B	EPA3010A	5	ND
Barium	EPA6010B	EPA3010A	1	33
Beryllium	EPA6010B	EPA3010A	1	1
Cadmium	EPA6010B	EPA3010A	3	ND
Chromium	EPA6010B	EPA3010A	3	44
Cobalt	EPA6010B	EPA3010A	3	33
Lead	EPA6010B	EPA3010A	5	ND
Mercury	EPA6010B	EPA3010A	3	ND
Molybdenum	EPA6010B	EPA3010A	5	15
Nickel	EPA6010B	EPA3010A	4	6
Selenium	EPA6010B	EPA3010A	5	8
Silver	EPA6010B	EPA3010A	2	5
Thallium	EPA6010B	EPA3010A	5	20
Vanadium	EPA6010B	EPA3010A	3	ND
Zinc	EPA6010B	EPA3010A	10	3
Total Organic C	EPA415.1		3,000	11,000

The first demonstration run was used to compare the copper concentrations measured by the ATMA to grab samples measured in the laboratory using EPA Method 200.8. Measurement and sampling was done at Port 6 of the MRT. Grab samples were collected every 30 minutes. The MRT was run until the copper concentration reached 230 µg/l. The MRT process flow was started and run past breakthrough until copper concentrations at Port 6 exceed 200 µg/l. As seen in Figure 20, excellent linearity was achieved with a $R^2 = 0.99$. However, there was a slight offset of 15 µg/l throughout the measurement range. This is most likely due to the inability of the ATMA to measure the most tightly complexed copper ions.

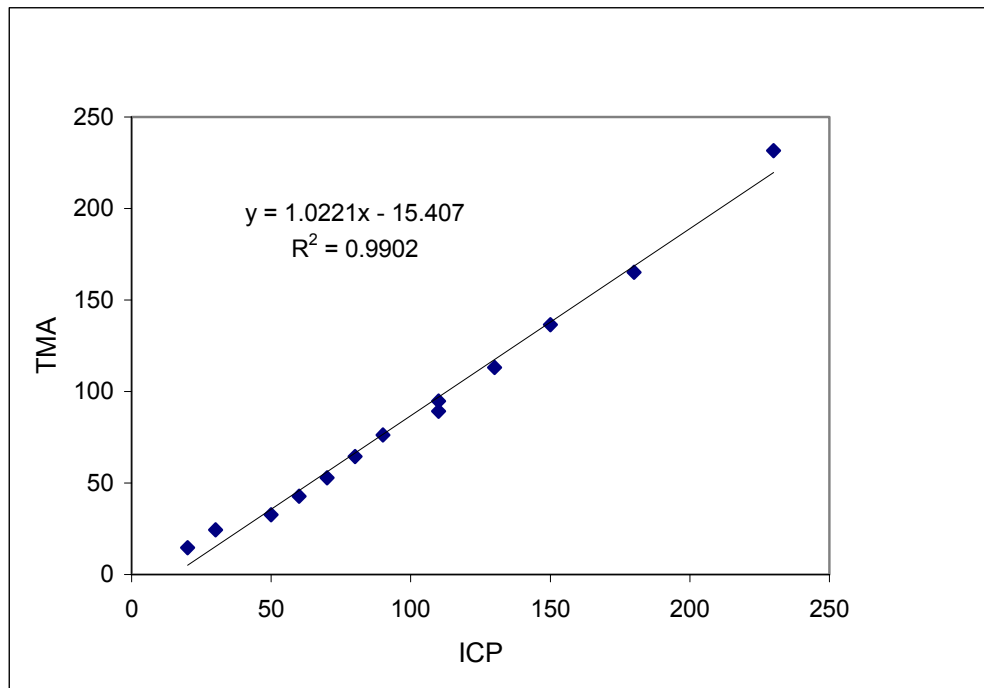


Figure 20. Comparison of the ATMA Copper Measurements with Grab Samples Measured Using an ICP-MS. (Measurements are in µg/l)

The second demonstration run was used to measure in real-time the actual performance of the MRT filter media. The ATMA was set to automatically measure Port 6 at 15 minute intervals and the ATMA output was calibrated to account for the 15 µg/l offset measured in the previous run. The MRT was initialized and run until the ATMA indicated breakthrough. In this demonstration run, the MRT was run just past breakthrough (40 µg/l). The ATMA was set to record measurements at 15-minute intervals. In this run the ATMA was calibrated to correct for the 15 µg/l offset measured in the initial run. The results of this run can be found in Figure 21. It can be seen in this figure that breakthrough occurred after processing 1,200 gallons of the waste stream.

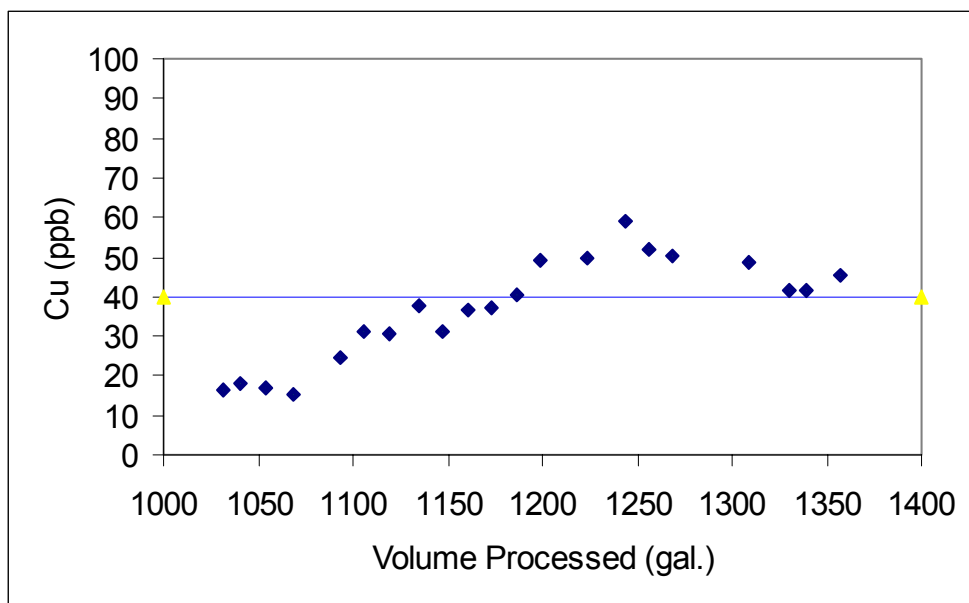


Figure 21. Measurement of Copper at Port 6 of the MRT.

4.3 TECHNOLOGY COMPARISON

There is no technology comparable to the ATMA capable of measuring metal ions in solution at $\mu\text{g/l}$ levels in real-time. When cost is factored in, there is no comparable technology, real-time or batch, capable of this level of sensitivity.

Technologies comparable to the ATMA are the ICP-MS and the GF-AA instruments. Both these complex and large instruments are considered the standard against which all other technologies are compared. As seen in the previous section, the performance of the ATMA can be equal to standard batch methods as demonstrated in the Puget Sound Naval Shipyard MRT demonstration or fall short as shown in the North Island NAS Wastewater Treatment Plant demonstration.

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5.0 COST ASSESSMENT

5.1 COST PERFORMANCE

Table 11 is an estimate of the costs incurred over an expected 10 year life span of the instrument assuming a processing rate of 100 samples per month. The labor rate was fixed at \$50 per hour resulting in a total life cycle cost of \$207K.

Table 11. Cost Performance for the Metals Analyzer over a 10 Year Life Span.

Cost Performance					
Cost by Category					
Start-up		Annual Operation & Maintenance		Demobilization	
Activity	\$K	Activity	\$K	Activity	\$K
Capital Equipment	25.0	Labor	150.0	Disposal (just throw it away)	0.0
		Consumables & Supplies	18.0		
		Effluent Disposal	12.0		
		Training required to operate equipment	2.0		
Total	25.0	Total	182.0	Total	0.0

5.2 COST COMPARISONS TO CONVENTIONAL AND OTHER TECHNOLOGIES

Costs are best compared with current practice for determining metal ion concentrations at the IWTPs (Table 12). In the current practice, typically samples are collected and preserved, the samples are then packed in ice and shipped over-night to a trace metal laboratory. The approximate payback period for the \$25,000 capital investment for the ATMA is six months.

Table 12. Cost Breakdown per Sample between Traditional Laboratory GF-AA Analysis and On-Site PSA Analysis.

Cost Breakdown Per Sample			
GF-AA		PSA	
Activity	Cost	Activity	Cost
Sample Collection (\$50/hr)		Sample Collection (\$50/hr)	
- 5 min collection	4.17	- 5 min collection time	4.17
- 10 min preservation, labeling packing	8.34	- 10 min operator time	8.34
- shipping	1.86		
Sample Analysis (contract w/laboratory)	50.00	Consumables	
		- Reagents	1.25
		- Electrodes	0.25
		Capital Cost of Instrument	0.63
		- \$25K/40,000 samples	
		Haz/Mat Disposal (3ml)	1.00
Total	64.37	Total	15.64

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6.0 IMPLEMENTATION ISSUES

6.1 COST OBSERVATIONS

Cost for the laboratory analysis can vary from \$20 to \$75 per sample depending on the laboratory and the volume of samples. Even at the lower \$20 per sample, PSA compares very favorably at less than half the cost of conventional methods. Typically, the turnaround time for conventional methods is 2-4 weeks versus 15 minutes with PSA. At the two laboratories surveyed, the cost of sample analysis was the same for GF-AA or ICP-MS. PSA allows immediate resampling if results warrant it. Using traditional methods, resampling time could take over a month.

6.2 PERFORMANCE OBSERVATIONS

These two demonstrations point out the critical need to know the boundaries of the matrix test effluent before using the ATMA. Interferents can have a dramatic affect on the accuracy of the instrument. The ATMA should be used with caution on unpredictable or unknown effluents.

6.3 APPROACH TO REGULATORY COMPLIANCE AND ACCEPTANCE

Currently regulators require wastewater treatment plants to monitor their process via scheduled grab samples. These samples are measured using EPA accepted methods. The frequency of the samples is typically determined in the treatment plant's National Pollutant Discharge Elimination System permit. This demonstration examined the usefulness of the ATMA for continuously monitoring the "end of process" in wastewater treatment. The ATMA ensured that this permitted sampling process met regulatory discharge requirements. In these demonstrations the ATMA was not intended to replace EPA methods or permit required sampling and, as such, regulatory acceptance was not sought.

6.4 END-USER ISSUES

Metal contamination has been identified at more than 900 military sites. Typical military activities associated with heavy metal contamination include plating operations, motor pool activities, metal finishing and cooling water treatment. These discharges are typically treated at military IWTPs on base. Real-time sensors to monitor treated effluent flows will allow operators to rapidly correct for failures in the treatment process before costly exceedences occur.

6.5 LESSONS LEARNED

The most difficult problem encountered was technology transfer to the commercial sector. Commercial production of this type of instrumentation is critical to its successful transition and widespread use. Commercial partners often have conflicting goals when compared to those of the technology originator. For example, in this project, the initial CRADA partner began manufacturing the instrument with a list price of \$30,000. The ATMA cost \$10,000 in parts and labor to produce using engineers and technicians to hand-build the instrument. The high selling price led to the eventual demise of the product and of the commercial division manufacturing the product. After the commercial division was eliminated, the parent company refused to relinquish the technology rights, making it impossible to transfer them to another company until recently.

The main lesson learned is to be very careful in selecting a commercial partner. Make sure they have the financial and technical capability to launch a new product and that they have a proven track record in the field.

7.0 REFERENCES

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APPENDIX A

POINTS OF CONTACT

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