



Evaluation of the OVA5000 for Continuous Arsenic Monitoring at the Vineland Chemical Company Superfund Site

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Abstract

The management practices of the Vineland Chemical Company resulted in a large scale Arsenic contamination of the manufacturing plant area soils and groundwater. An OVA 5000, which uses Anodic Stripping Voltammetry (ASV), was installed to continuously monitor arsenic concentration in the effluent of the wastewater treatment plant during non-staffed hours. This will greatly assist the remediation process in that the effluent can be proactively controlled to minimize the chances of accidental release to the surrounding area. The operators will therefore be able to see that the effluent concentration is approaching a critical point and can begin corrective action with the plant control system before the personnel on call even arrive at the plant. This report details a study to determine how comparable the OVA 5000 was, to the onsite GFAA instrument and an independent offsite laboratory's ICP-MS instrument. The results showed that the GFAA and OVA 5000 compared to the independent laboratory's ICP-MS results with a correlation coefficient of 0.9853 and 0.9417 respectively. At concentrations of 10ppb the OVA had a better correlation with the reference method than the GFAA for this concentration range. This is particularly important given that the EPA has recently changed the discharge limits to 10ppb for arsenic. The combination of the continuous monitoring with the OVA 5000 and verification with the GFAA during staffed hours provides a confidence in plant operation that was not previously available. The OVA 5000 has now been purchased by Severson Environmental Services with the approval of the USACOE and will be involved in the clean up process over the next 30 years.

Site Background

Vineland Chemical Company caused a large scale arsenic contamination of a 54-acre site in Vineland, New Jersey by improper raw material storage and depositing waste herbicide material in untreated piles and lagoons over a period of 44 years. In 1994 the plant ceased activity and the site was put on the National Priorities List (NPL) of sites under the Superfund remediation program. The total extent of contamination has not fully been determined, but the runoff from the manufacturing site has contaminated an area river and lake, as well as a large area of groundwater. Arsenic from the site has been detected as far away as 36 miles downstream, near where the Maurice River empties into the Delaware Bay. The remediation process as a US EPA superfund site began in the 1990's. In late 2001, the United States Army Core of Engineers (USACOE – Site managers) and an engineering company contracted by Severson Environmental Services (plant operators) implemented the soil remediation

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portion of site remediation. The design of the plant was completed in December 2002. Severson constructed the plant in under a year to begin operation in October 2003 – the world's first full-scale application of this innovative technology for environmental remediation.

The treatment of the contaminated area consists of a soil fraction separation and washing process, in which approximately 200,000 cubic yards of sandy soil from the manufacturing site is excavated and treated. The three fractions consist of large bulk materials such as stones and vegetation debris, intermediate size particles that are treatable through the washing process, and a fraction of fine particles that are untreatable through the wash process. This portion of the remediation was estimated at 3 years for completion to an initial cleanup target of 20 parts per million (ppm). The contaminated soils and sediments in and around a nearby river and lake, related to run off from the site may also be added in the washing process depending on available funding.

The contaminated groundwater is pumped using an array of 13 extraction wells. The contaminated groundwater and wastewater from the soil washing process is treated through a chemical precipitation/sludge collection process. The sludge and untreatable fine particles containing high levels of Arsenic are transported to a chemical disposal facility in Ohio. The wastewater is then discharged to a local river when below the current discharge limit of 50 parts per billion (ppb). This was amended in 2006 to meet the new EPA discharge limit of 10ppb Arsenic in wastewater. The groundwater remediation operation is expected to last for 30 years, beginning in 2000.

The GFAA has been used to monitor the treatment efficiency in the plant by the analysis of the incoming wastewater from the soil washing process, along with the mixes of incoming ground water gathered by the well array. The GFAA has also been used to determine whether the plant is under its discharge limit during the hours of staffing. All of the treatment equipment in the plant is automated and the operating efficiency is monitored remotely by an operator when no one is present at the plant, both after the general work day, and on the weekends. The existing system, however, did not provide a value for arsenic in the wastewater, thus the operators relied on other measurements to monitor plant operation.



The OVA 5000 was chosen for the trial to try and resolve this problem in that, the instrument is automated and has the capacity to communicate the results of analysis to an external location. The premise being that if the trial was successful the OVA 5000 could be incorporated into the plant control system thus providing an arsenic concentration to the remote monitoring station, which is similar to the rest of the equipment in the treatment facility. To ensure the performance and reliability of the OVA 5000, a trial consisting of a 60 day period of continuous operation was initiated, with a comparison of the GFAA and OVA results with that of an offsite reference laboratory using an ICP-MS.

Instrumentation

Three fundamentally different analytical techniques were used for this evaluation. The first instrument, which the site already contained, was a Graphite Furnace Atomic Absorption (GFAA) instrument that is used to monitor the plant efficiency. This analytical technique utilizes the quantum mechanical principle of light frequency absorption / emission at a specific wavelength unique to the element being measured. The sample is placed on a graphite tube where it is heated to a high temperature, and it is then volatilized to an atomic vapour. A lamp which emits light at the frequency of the element of interest is set on one side of the furnace, and on the other side is a detector that measures the intensity of light received. The difference between the initial and final intensity of the light is used to quantify the amount of analyte present.

The second instrument was the OVA 5000 instrument which operates on an electrochemical principle known as Anodic Stripping Voltammetry (ASV). This technique utilizes the fact that ions in solution are charged particles that respond to electrical fields. The first step, being the deposition step, is achieved by applying a negative potential to a working electrode where the cationic (positively charged) form of the element is reduced to its ground state (no charge). In the second step, the solution is allowed to achieve quiescence (stability). The third and final step (stripping), the process of deposition is reversed, where a positive potential is applied to the working electrode and the ground state metal again becomes cationic and returns to solution. When the metal returns to solution, electrons are left behind and generate a current at a unique potential. The potential, at which this occurs, identifies the metal, and the amount of current generated quantifies it.

The third analytical technique Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) was used by the off - site reference laboratory, and was chosen due to its sensitivity. Initially, the forerunner to the ICPMS was used; Inductively Coupled Plasma Optical Emission Spectroscopy (ICPOES) but was found to not have the desired sensitivity that the other 2 techniques in the study possess, and was thus rejected. In ICP-MS, a strong radio frequency field is applied to an inert gas (Argon), where it produces plasma at an extremely high temperature. Plasma is a quasi matter state where the nuclei of atoms exist in a cloud of electrons. The sample is introduced into this plasma and itself becomes part of the quasi matter cloud. The cloud is then introduced into a mass spectrometer through a series of charged acceleration plates where the charges are focused and separated (positive and negative). The negative ion beam smashes into a positively charged plate and are thus eliminated from the ionic beam, while the focused positive ions (atomic nuclei) are directed through (in this case) a magnetic tunnel generated by 8 charged rods to the detector. The detector measures the mass to charge ratio of the ionic impact on the detector to identify and quantify the analyte.



Sampling and Reference Methods

The OVA 5000 has an external catch pot used to collect water from the filter unit. As the OVA was filling the acid treatment cell, the samples for the GFAA and ICP-MS were taken from the sample tap on the catch pot, trying to ensure that the 3 samples used for comparison were representative. The fixed laboratory using ICP-MS (SW846 6020 analysis) and total digestion method (SW846 3020A) was used as the reference point for the comparison. The sample preparation method SW846 3020A, titled: Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by GFAA Spectroscopy, Revision 1, July 1992 was the preparation method used. Though originally written for GFAA analysis, it has been found to be applicable to ICP-MS as well. The analytical method SW846 6020, titled: Inductively Coupled Plasma – Mass Spectrometry, Revision 0, September 1994 was the analytical method used by the reference laboratory. Both of these methods are available on-line at (<http://www.epa.gov/>) in the EPA publications.

Sampling consisted of 4 effluent and 1 spiked effluent samples per week, for a total of 8 weeks. The spiked effluent samples were used to check the response time of the OVA to an extreme change in the concentration of Arsenic. This was designed to simulate a disruption in plant operation or malfunction of equipment. The results were evaluated in a number of ways to determine if the analytical techniques gave comparable results.

Results

During the trial one of the criteria was that over the 60 day period the instrument would operate with no failures. The initial set up of the sample delivery system that provided the effluent sample to the OVA 5000 did require modification. The delivery line quickly clogged with sediment blocking sample delivery. A slight configuration modification consisting of moving the filter pump and shortening of the sample delivery line, along with a rigorous cleaning procedure eliminated this problem. The OVA 5000 completed the 60 days with no equipment failures.

The results for the 3 instruments for all samples are shown in Figure 1. In general the desire was that all 3 analytical techniques would be within 5ppb of each other for an absolute difference of <5ppb. A default recovery limit on the spiked samples set at 75–125% was used to evaluate spike recovery for the OVA 5000 and the onsite GFAA. This comparison is based on the ICP-MS result for the spiked effluent sample and the background effluent result, to determine the numeric spike value. Duplicate samples analyzed for the OVA 5000 and the GFAA instruments were not carried out on both instruments for all of the spiked samples, and were thus left from the data group for the purposes of this comparison.

The correlation of the OVA 5000 and the GFAA instruments with the ICP-MS in the offsite fixed laboratory can be seen in Figure 2. The correlation coefficient (R^2 in Figure 2) can be thought of as a percentage correlation, with a maximum of 1.00 (100% correlation). The GFAA and OVA 5000 instruments displayed an $R^2=0.9853$ (98.53%) and $R^2=0.9417$ (94.17%) correlation with the ICP-MS respectively. This is inclusive of a rather suspect data point for the OVA 5000. It was found that one of the tubes in the Acid / UV treatment system was pulled from the solution surface during maintenance, and was the most likely cause of the low result on the OVA spike (sample number 7, Figure 1). The initial criterion of a 5 ppb absolute difference from



the reference value was not met by either the GFAA or the OVA. The GFAA had 4 values (10%) outside that limit, while the OVA had 6 values (15%) outside that limit: one of which is the point 7. The most significant instances occurred in the final week of the trial and a direct cause of the disparity between all 3 instruments has not been identified.

Most of the methods for the determination of metals in environmental samples have a default spike recovery limit of 75–125% represented by the dashed lines in Figure 3. Both the OVA and GFAA had one instance of recovery outside those limits (14.3% for each instrument); though it should be noted the value for the OVA that was outside the limit is the suspect data point 7. Another aspect of both the spike sample recoveries and the slope of the linear regression lines indicate is the bias exhibited by each instrument when compared with the ICP-MS. The GFAA has a positive bias based on the slope of the regression line (coefficient of the x variable) being above 1, at 1.1378, and the average percent recovery on spiked samples is >100%. The OVA experienced the opposite bias, in that the slope was 0.7842 and the spike recovery on average was <100%. Since the reference laboratory used the ICP-MS as the analytical method this comparison is based on that instrument, thus the 1:1 line would be the ICP-MS plotted against itself. The previously mentioned bias is based against that reference point, so the GFAA slope being greater than 1 indicates that its bias is high, which means it generally reads higher than the reference method for higher concentration samples, and low for low level concentration samples. This is verified by the percent recovery for Arsenic on the spiked samples, in that the average percent recovery for the data is greater than 100%. The OVA exhibits the opposite bias having a slope of less than the 1:1 line, indicating that at high concentrations it would generally read lower than the reference method, and higher than the reference method at low level concentrations. Again, verified by the average percent recovery for the spiked samples being less than 100%.



When examining the regression lines together, the intersection point for the 2 regression lines is calculated at 7.5ppb. This is calculated by setting the two equations equal to each other and solving for x (concentration of Arsenic by ICP-MS). This turns out to be right under the new limit (10 ppb) for arsenic discharge in wastewater that the plant is now operating under. The operators can therefore be confident that in the concentration range of most importance, both the GFAA and OVA are comparable - and are still under the discharge limit.

With the changes in the discharge limit to 10ppb, it is of interest to see the performance of the GFAA and OVA compared to the ICP-MS below that level. For this comparison the ICP-MS value for the effluent was used to select the results that were below 10ppb, thus if the ICP-MS result was 10ppb or less (regardless of the other 2 instrument readings) they were included. Figure 4 is a correlation for both the GFAA and the OVA in comparison to the ICP-MS. The GFAA exhibited no apparent bias, since the correlation slope was very close to 1, and the correlation for this data group was 0.6772 (67.72%). The OVA still experienced a negative bias by the slope regression value of 0.6442, but had a correlation coefficient of 0.7113 (71.13%). From this, it appears that the OVA had a better correlation with the reference method than the GFAA for this concentration range. The combination of the continuous monitoring with the OVA 5000 and verification with the GFAA during staffed hours provides a confidence in plant operation that was not previously available.

Conclusions

An OVA 5000 monitor was installed to monitor arsenic concentrations in the effluent of the wastewater treatment plant, which treats a combination of wastewater from a soil washing process and contaminated groundwater, at the Vineland Chemical Company EPA Superfund site in New Jersey. During a trial period of 60 days the OVA 5000 was compared to the on-site GFAA and an off-site independent laboratory ICP-MS results. The results showed that the GFAA and the OVA 5000 compared with the ICP-MS results by 98.53% and 94.17% correlation respectively.

The GFAA and OVA 5000 both had to analyze simulated high level samples during the course of the trial. Both instruments exhibited one value outside the accepted 75-125% spike recovery limit, though the only value outside this limit for the OVA is suspect. The GFAA recorded a high bias of 1.1378 and the OVA 5000 recorded a low bias of 0.7842, when examining the linear regression equations using the ICP-MS results as the reference point. When the results of the GFAA and the OVA were compared at low levels, less than 10ppb, it was found that the OVA had a correlation co-efficient closer to the ICP-MS results than the GFAA.

Another part of the trial required the OVA 5000 to operate continuously for 60 days with no failures. At the end of the 60 day period no system failures had occurred meaning that the OVA had passed this criteria. Following this rigorous testing the instrument was deemed acceptable to be used at an EPA superfund site, was subsequently purchased and will be involved in the clean-up for the next 30 years.

The OVA 5000 being connected to the plant control system will allow the operators to monitor plant performance remotely with the existing parameters, as well as a quantified arsenic concentration in the effluent 24 hours a day 7 days a week. This will greatly assist the remediation process in that the effluent can be proactively controlled to minimize the chances of accidental release to the surrounding area. The operators will be able to see that the effluent concentration is approaching a critical

point and can begin corrective action with the plant control system before the personnel on call even arrive at the plant. The recent changes to arsenic discharge regulations by the EPA to protect public health, and the limited resources available to remediate contaminated areas on the superfund list, shows that the addition of the OVA 5000, linked to a plant control system provides a rapid round-the-clock response to arsenic levels in the effluent. This combination of continuous rapid response to arsenic levels, coupled with the remote automated monitoring, greatly reduces the chances of accidental arsenic release from the plant, which provides greater confidence and increased protection to both public and environmental health. The remediation process at this site is expected to last for the next 30 years.

Figure 1

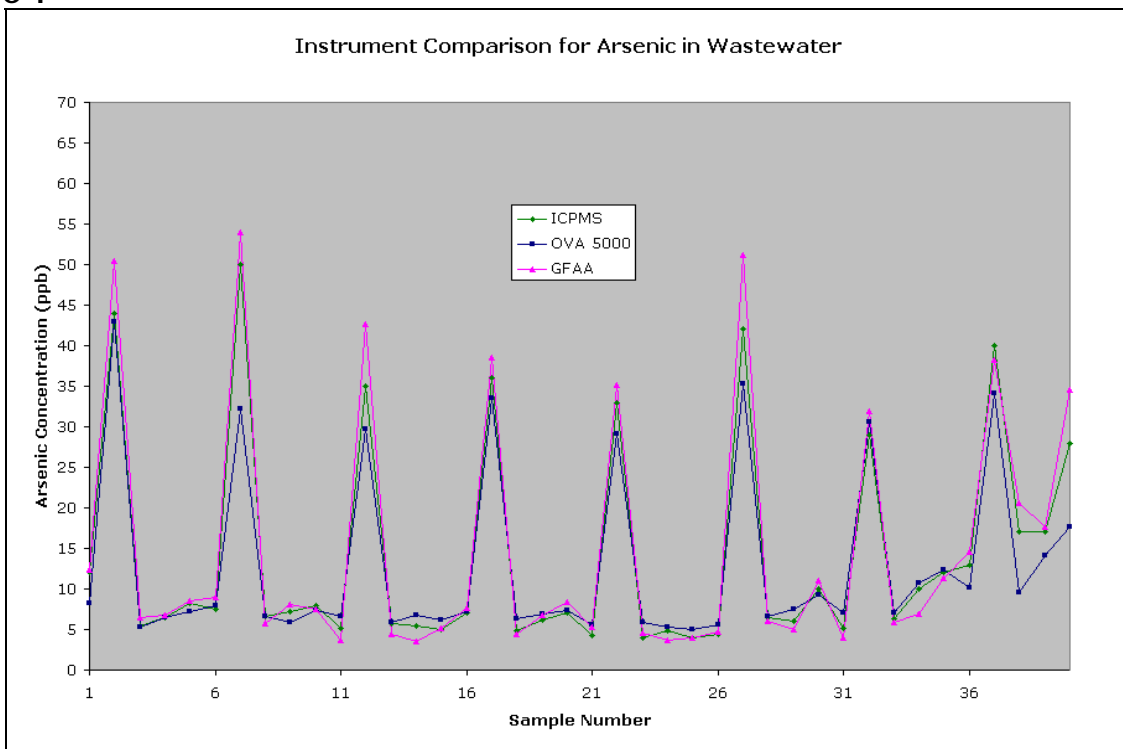


Figure 2

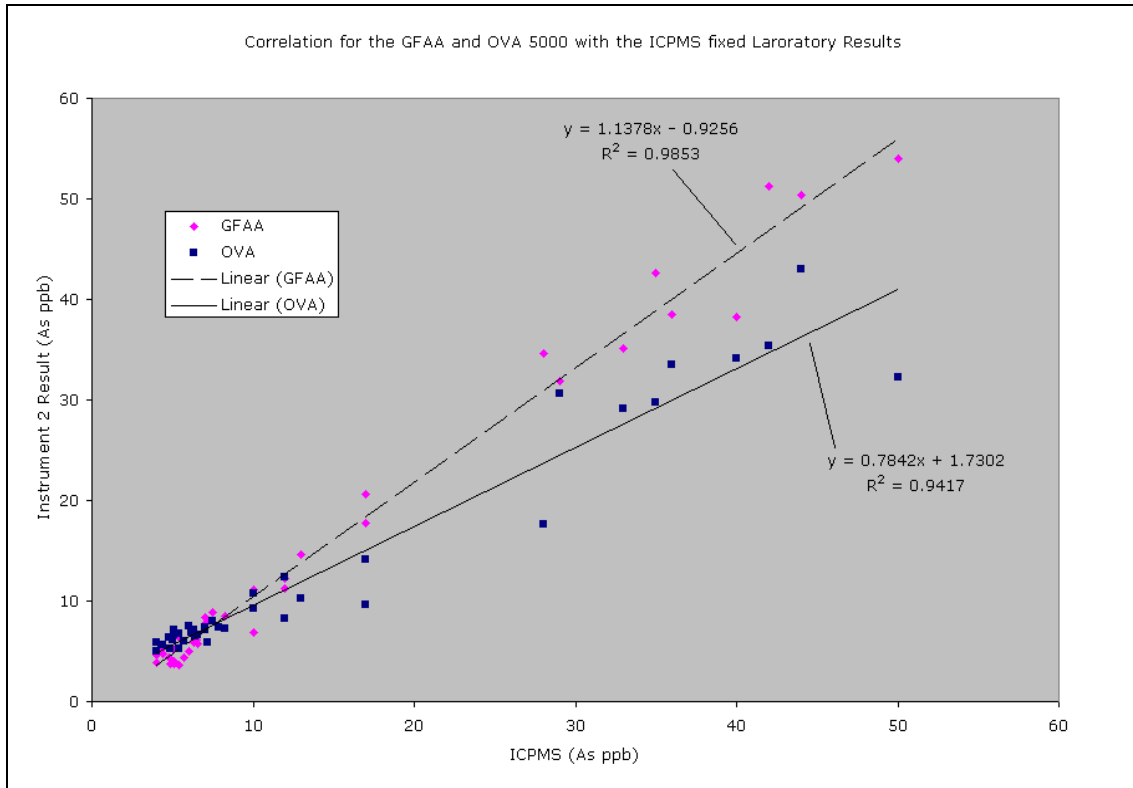


Figure 3

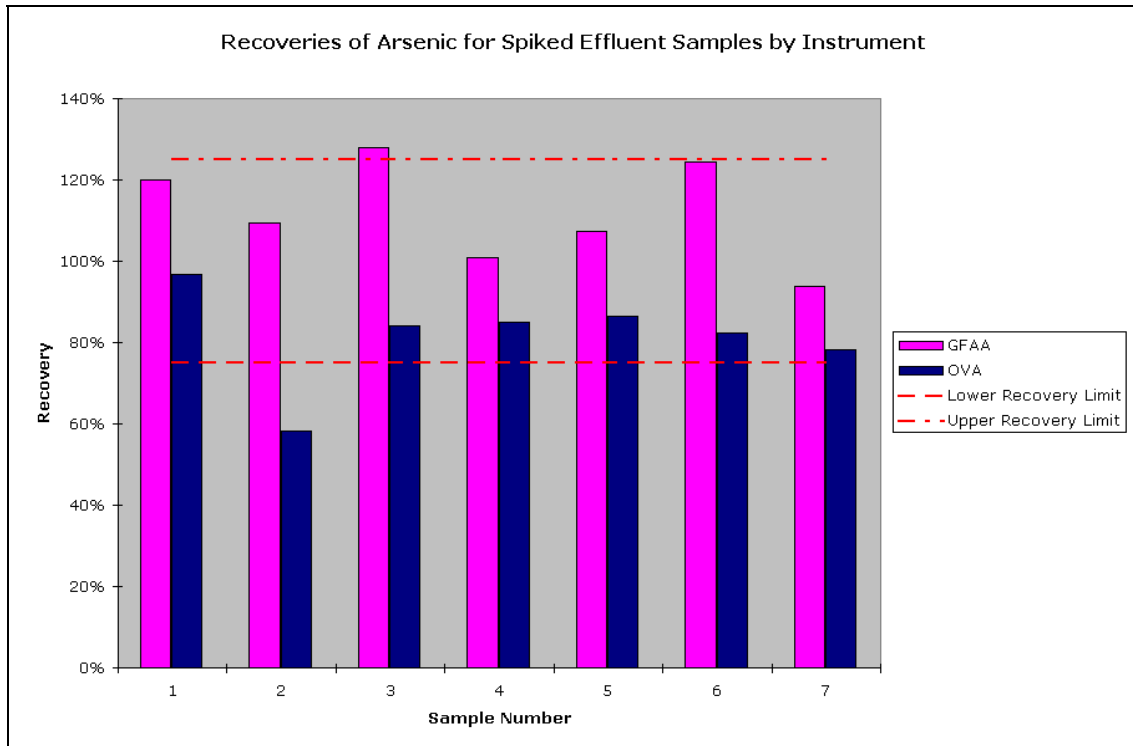


Figure 4

