West Virginia Department of Environmental Protection

Division of Water and Waste Management

Comparison of Analytical Techniques

for the Determination of Selenium (Se)

2010

 

 Atomic Absorption

 

 Inductively Coupled Argon Plasma (ICP) ICP Mass Spectrometer (ICP-MS)

WV Department of Environmental Protection

Division of Water and Waste Management

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Selenium analytical study conducted by WV DEP between April 2008 and June 2009.

**Introduction**

In recent years many more facilities with NPDES permits have received effluent limits and monitoring requirements for Selenium. Members of the regulated community have since voiced their concerns about the ability of the environmental laboratory community to produce accurate data at the levels required. Currently, the WQS for Se is 5 µg/L (47CSR2, Table 1). 5µg/L is very near the Method Detection Limit (MDL) for most analytical methods approved at 40CFR136. In an effort to determine whether laboratories reporting Se data to WV DEP could accurately detect Se concentrations in the range of 5 µg/L, this study was initiated.

West Virginia Department of Environmental Protection (WVDEP) personnel had received anecdotal evidence indicating a low bias for Se when Graphite Furnace Atomic Absorption (GFAA) was used for analysis. Personnel had also received anecdotal evidence indicating a high bias for Se when Inductively Coupled Plasma/Mass Spectroscopy (ICP/MS) was used for analysis. All samples collected for metals analysis for compliance purposes are sampled and preserved in accordance with 40CFR136 Table II. They are then digested (heated to between 85 – 95° C in the presence of mineral acids) according to the method to be used to detect the metal. 40CFR136 lists the following for the analysis of Selenium:

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| 60. Selenium—Total,4mg/L | Digestion4followed by: | EPA | SM 18th & 19th  | SM 20th | SM online | ASTM | USGS/AOAC/other |
|    | AA furnace |  | 3113 B |  | 3113 B–99 | D3859–98, 03 (B) | I–4668–9849 |
|    | STGFAA | 200.9, Rev. 2.2 (1994) |  |  |  |  |  |
|    | ICP/AES36 | 200.7, Rev. 4.4 (1994) | 3120 B | 3120 B | 3120 B–99 |  |  |
|    | ICP/MS | 200.8, Rev. 5.4 (1994) |  |  |  | D5673–03 | 993.143 |
|    | AA gaseous hydride |  | 3114 B |  | 3114 B-97 | D3859-98, 03(A)  | I-3667-85 |

The ICP/AES method is not sensitive enough to reach the WQS. The other approved methods can achieve the WQS with different challenges faced by each method.

The acceptable recovery and precision limits for each of the approved methods are:

Method Acceptable % Recovery Precision

SM 3113 B 85-115 ≤10% (variation)

EPA 200.9 70-1301 ≤20% (RPD)2

EPA 200.8 70-130 ≤20% (RPD)2

SM 3114 B 85-115 ≤20% (RPD)2

 1. 70-130% is the recovery limit, 85-115% is advisory limit. If recovery is outside 85-115% additional QC techniques should be employed.

 2. The method does not specify a precision limit. 20% RPD is the accepted limit for most analytical techniques when derived from matrix spike/matrix spike duplicate analyses.

The Quality Assurance Program (QAP) staff was approached by Ken Politan of WV DEP Division of Mining and Reclamation with the situation in January 2008. A review of Discharge Monitoring Reports (DMR) produced a population of laboratories routinely submitting Se data to WVDEP. A consensus was formed that this population should be assessed to determine whether a bias was present. The initial population of laboratories does not include all laboratories reporting data to WVDEP, only those routinely reporting Se on DMRs. Laboratories on the state contract were included in later phases of the study in order to assess their performance. The following laboratories participated in all or parts of this study:

|  |
| --- |
|  ACCULAB, INC |
|  P.O. Box 367 |
|  Mt. Gay, WV 25637

|  |
| --- |
| AEP – Dolin Chemical Laboratory |
| 4001 Bixby Road |
| Groveport, OH 43215 |

|  |
| --- |
| ANALABS, INCORPORATED |
| P.O. Box 1235 |
| Crab Orchard, WV 25827 |

|  |
| --- |
| APPALACHIAN LAB. INC. |
| P.O. Box 392 |
| Beckley, WV 25802 |

|  |
| --- |
| APPALACHIAN STATES ANALYTICAL, LLC |
| P.O. Box 520 |
| Shelbianna, KY 41562 |

 BIO-CHEM TESTING, INC P.O. Box 634 Teays, WV 25569

|  |
| --- |
| CENTRAL TESTING, INC. |
| P.O. Box 481 |
| Summersville, WV 26651 |

|  |
| --- |
| COMPLIANCE MONITORING LABORATORIES, INC. |
| 50 Caney Branch Road |
| Chapmanville, WV 25508 |

|  |
| --- |
| MINERAL LABORATORIES |
| P.O. Box 549 |
| Salyersville, KY 41465 |
| RELIANCE LABORATORIES P.O. Box 4657Bridgeport, WV 26330REI CONSULTANTS, INC. |
| P.O. Box 286 |
| Beaver, WV 25813 |
| SGS NORTH AMERICA, INC., |
| MINERAL SERVICES DIVISION-SOPHIA |
| P.O. Box 850 |
| Sophia, WV 25921 |

|  |
| --- |
| STANDARD LABORATORIES |
| 147 11th Avenue |
| South Charleston, WV 25303 |

|  |
| --- |
| STANDARD LABORATORIES, INC. |
| 8451 River King Drive |
| Freeburg, IL 62243 |

|  |
| --- |
| STANDARD LABORATORIES, INC  |
| N.E.S.T. DIVISION |
| Rt. 2 Box 88C |
| Belington, WV 26250 |

|  |
| --- |
| STURM ENVIRONMENTAL SERVICES |
| P.O. Box 650  |
| Bridgeport, WV 26330 |

|  |
| --- |
| TRA-DET, INC. |
| P.O. Box 2019 |
| Wheeling, WV 26003 |

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As the study progressed the number of labs was reduced due to the constraints of a “double-blind” evaluation study.

**Phase 1**

Phase I consisted of a single-blind Proficiency Test (PT) sample being provided to the laboratory for analysis. WV DEP solicited bids from Proficiency Test Providers approved by [American Association for Laboratory Accreditation](http://www.a2la.org). A list of the approved providers can be found at: <http://www.nelac-institute.org/PT.php>. The successful bidder was Environmental Resource Associates, Inc. (ERA).

 The Phase I PT sample was custom prepared as a concentrate to be prepared at the laboratory by dilution to 1 liter producing a solution with a concentration of 5 µg/L. ERA prepared the PT sample and shipped it to each lab with instructions on how to prepare the sample and supplemental instructions from WV DEP on how to analyze the sample and report the results.

A summary of the Phase I results is depicted below.

**Table 1**

|  |  |  |  |
| --- | --- | --- | --- |
| **Laboratory** | **Result** | **Units** | **Instrument** |
| Acculab, Inc. | 4.7 | µg/L | GFAA |
| AEP – Dolan Chemical Laboratory | 4.8 | µg/L | ICP-MS |
| Analabs, Inc. | 5.32 | µg/L | ICP-MS |
| Appalachian Lab, Inc. | 4.7 | µg/L | GFAA |
| Appalachian States Analytical, LLC | 5.10 | µg/L | GFAA |
| Central Testing, Inc. |   | µg/L |   |
| Compliance Monitoring Laboratories, Inc. | 5.95 | µg/L | GFAA |
| Mineral Laboratories |   | µg/L |   |
| REI Consultants, Inc. | 4.52 | µg/L | ICP-MS |
| 4.40 | µg/L | GFAA |
| SGS-NA, Mineral Services Division-Sophia | 4.7 | µg/L | GFAA |
| Standard Laboratories, Inc. | 5.02 | µg/L | GFAA |
| Standard Laboratories, Inc. | 5.4 | µg/L | ICP-MS |
| Standard Laboratories, Inc. NEST Division | 4.56 | µg/L | GFAA |
| Sturm Environmental Services | 4.37 | µg/L | GFAA |
| Tra-Det, Inc. | 3.90 | µg/L | GH-AA |
|  | Average | 4.82 |
|  | SD | 0.51 |
|  | RSD | 10.6% |

Personnel at Mineral Laboratories indicated they had received the sample, but that the sample was misplaced, consequently, no data was received from this lab. Central Testing, Inc. reported data after the close of the study time frame. The result was received from Central Testing, Inc. and reviewed. Central Testing, Inc. reported a value of 7.7 µg/L, which is 154% Recovery of the true value. This result was produced using GFAA. Since the data was received after the close and it would be considered an outlier, it is not included in the statistical review of the study data. (Central Testing, Inc. closed its lab in January 2009) Tra-Det, Inc. used the gaseous hydride/atomic absorption technique for determination of Se. The data from Phase I used for review is depicted in the table below.

**Table 2**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Laboratory** |  | **Result** | **units** | **Date**  | **Method** | **% Rec.** |
| Appalachian Laboratories |  | 4.7 | µg/L | 4/25/2008 | GFAA | 94.0 |
| Appalachian States |  | 5.1 | µg/L | 4/30/2008 | GFAA | 102.0 |
| Standard Labs (NEST) |  | 4.56 | µg/L | 5/1/2008 | GFAA | 91.2 |
| REI Consultants |  | 4.4 | µg/L | 4/23/2008 | GFAA | 88.0 |
| Sturm Environmental |  | 4.37 | µg/L | 4/16/2008 | GFAA | 87.4 |
| Standard Labs (Charleston) |  | 5.02 | µg/L | 4/21/2008 | GFAA | 100.4 |
| Acculab |  | 4.7 | µg/L | 4/14/2008 | GFAA | 94.0 |
| Compliance Monitoring |  | 5.95 | µg/L | 4/22/2008 | GFAA | 119.0 |
| SGS |  | 4.7 | µg/L | 4/17/2008 | GFAA | 94.0 |
| REI Consultants |  | 4.52 | µg/L | 4/23/2008 | ICP-MS | 90.4 |
| American Elec. Power |  | 4.8 | µg/L | 5/12/2008 | ICP-MS | 96.0 |
| Analabs |  | 5.32 | µg/L | 4/26/2008 | ICP-MS | 106.4 |
| Tra-Det |  | 3.9 | µg/L | 4/29/2008 | GH-AA | 78 |
|  |  |  |  |  |  |  |
| Average, All data |  | 4.8 | µg/L |  |  | 95.4 |
| Average, GFAA |  | 4.8 | µg/L |  |  | 96.7 |
| Average, ICP/MS |  | 5.06 | µg/L |  |  | 97.6 |
| Average, Hydride |  | 3.9 | µg/L |  |  | 78 |

The following chart gives a visual depiction of the data for raw results from Phase I.

**Chart 1.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Graphite Furnace AA |   | ICP- Mass Spec |   | Gaseous Hydride-AA |   |

The following chart gives a visual depiction of the percent recovery data for raw results from Phase I.

**Chart 2.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Graphite Furnace AA |   | ICP- Mass Spec |   | Gaseous Hydride-AA |   |

As one can see from this data, there is not a significant bias associated with either analytical technique. In order to be considered a statistically relevant bias, one would need at least 20% difference between the recoveries reported. The data received in Phase I was surprisingly accurate considering the difficulty normally encountered during the analysis of samples for Se. However, one must bear in mind that these results were produced from a clean sample. Furthermore, the laboratory knew it was a test sample and the laboratory was asked to analyze for one element, Selenium.

**Phase II**

 After reviewing the data from Phase I of the study it was apparent that Phase II would have to be implemented. Phase II consisted of a double-blind PT study being supplied to the laboratory. In order for a double-blind study to be effective, the laboratory must not know that the sample is a PT sample. In order to accomplish this, an artificial sample was prepared by ERA. The sample contained Se at 5µg/L, and the following elements at approximate concentrations; iron (Fe) – 2000 µg/L, manganese (Mn) – 500 µg/L, aluminum (Al) – 1000 µg/L, calcium (Ca) – 15000 µg/L, and magnesium (Mg) – 7500 µg/L. This sample was prepared as a whole volume sample preserved with nitric acid (HNO3) just like a regular compliance sample. WVDEP personnel also collected a non-acidified sample for submission with the PT sample in order to further sell the labs on the premise that this was a regular sample submission. The values reported on the non-acidified sample were not assessed under this study protocol. The samples were packaged on ice and delivered to the laboratories by WVDEP personnel or by contract carrier (FEDEX). During Phase II of this study WVDEP was only able to assess those laboratories participating as WV vendors. In other words, only those laboratories under contract with WVDEP to analyze samples could be assessed under a double-blind situation. If WVDEP would have taken a sample to a laboratory that does not routinely analyze samples for WVDEP then the laboratory would have known that they were being assessed. The one exception was American Electric Power-Dolan. WVDEP did send a sample to them as a single-blind full volume sample in order to have a larger population of data for assessment by ICP/MS.

The following table depicts the data used for evaluation under Phase II (5 µg/L).

**Table 3.**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Laboratory** | **MDL** | **Result** | **units** | **Date**  | **Instrument** | **% Rec.** |
| Appalachian Laboratories |  | 2.36 | µg/L | 4/25/2008 | GFAA | 47.2 |
| Appalachian States |  | 5.3 | µg/L | 4/30/2008 | GFAA | 106.0 |
| Standard Labs (NEST) |  | 5.04 | µg/L | 5/1/2008 | GFAA | 100.8 |
| REI Consultants |  | 4.6 | µg/L | 4/23/2008 | GFAA | 92.0 |
| Sturm Environmental |  | 4.5 | µg/L | 4/16/2008 | GFAA | 90.0 |
| Standard Labs (Charleston) |  | 5 | µg/L | 4/21/2008 | GFAA | 100.0 |
| Acculab | <2 | 0 | µg/L | 4/14/2008 | GFAA | 0.0 |
| Compliance Monitoring |  | 4.42 | µg/L | 4/22/2008 | GFAA | 88.4 |
| SGS |  | 5 | µg/L | 4/17/2008 | GFAA | 100.0 |
| American Elec. Power |  | 4.4 | µg/L | 5/12/2008 | ICP-MS | 88.0 |
| Analabs | <0.359 | 0 | µg/L | 4/26/2008 | ICP-MS | 0.0 |
| Tra-Det |  | 4 | µg/L | 4/29/2008 | GH-AA | 80.0 |
|  |  |  |  |  |  |  |
| Average, All data |  | 3.7 | µg/L |  |  | 73.9 |
| Average, GFAA |  | 4.0 | µg/L |  |  | 80.5 |
| Average ICP/MS |  | 2.2 | µg/L |  |  | 44.0 |
| Average Hydride |  | 4 | µg/L |  |  | 80.0 |

As one can see the data was not as consistent when the laboratory was presented with a double-blind sample. However, the premise that GFAA produces a low bias and ICP/MS produces a high bias is clearly not supported by the data. Two labs reported Not Detected (ND) for this sample, one at a Method Detection Limit (MDL) of 2 µg/L (Acculab by GFAA) and one at 0.359 µg/L (Analabs by ICP/MS).

The following chart gives a visual depiction of the raw results from Phase II including the ND results.

**Chart 3.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Graphite Furnace AA |   | ICP- Mass Spec |   | Gaseous Hydride-AA |   |

The following chart gives a visual depiction of the percent recovery data for raw results from Phase II including the ND results.

**Chart 4.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Graphite Furnace AA |   | ICP- Mass Spec |   | Gaseous Hydride-AA |   |

For the purposes of this study, the following table of data was used to determine bias according to the scope of the study, which was to determine what if any bias is present in analytical results reported by GFAA or ICP/MS.

**Table 4.**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Lab** |  | **Result** | **units** | **Date**  | **Method** | **% Rec.** |
| Appalachian Laboratories |  | 2.36 | µg/L | 4/25/2008 | GFAA | 47.2 |
| Appalachian States |  | 5.3 | µg/L | 4/30/2008 | GFAA | 106.0 |
| Standard Labs (NEST) |  | 5.04 | µg/L | 5/1/2008 | GFAA | 100.8 |
| REI Consultants |  | 4.6 | µg/L | 4/23/2008 | GFAA | 92.0 |
| Sturm Environmental |  | 4.5 | µg/L | 4/16/2008 | GFAA | 90.0 |
| Standard Labs (Charleston) |  | 5 | µg/L | 4/21/2008 | GFAA | 100.0 |
| Compliance Monitoring |  | 4.42 | µg/L | 4/22/2008 | GFAA | 88.4 |
| SGS |  | 5 | µg/L | 4/17/2008 | GFAA | 100.0 |
| American Elec. Power |  | 4.4 | µg/L | 5/12/2008 | ICP-MS | 88.0 |
|  |  |  |  |  |  |  |
| Average, All data |  | 4.5 |  |  |  | 90.3 |
| Average, GFAA |  | 4.5 |  |  |  | 90.6 |
| Average ICP/MS |  | 4.4 |  |  |  | 88.0 |

With only one data point above the MDL available for assessment of ICP/MS data, no definite findings can be presented with respect to ICP/MS, however, one can still see that a high bias is not presented with this technique by the one laboratory reporting for this technique with a result above the MDL. On the contrary, one could conclude a low bias since one of the labs did not detect the Se in the sample. The median value reported by GFAA for Se was 4.5 µg/L, which is a 90.6 % recovery of the known concentration for the sample. When one considers the MDL for this element is in the 1 to 2 µg/L range, 4.5 µg/L is indistinguishable from 5.0 µg/L when analyzed by GFAA. In this phase of this study the result reported by ICP/MS was 4.4 µg/L, which is also indistinguishable from 5.0 µg/L due to the MDL.

**Phase III**

 After a review of the Phase II data, WV DEP staff discussed the need to further assess the laboratories with a double-blind sample that more closely represented some of the high specific conductance, alkaline mine discharges in the state. For Phase III two custom double-blind, full-volume samples were prepared by Wibby Environmental, Golden, CO. One sample was prepared at 20 µg/L and one sample was prepared at 5 µg/L. Both samples had the following constituents added in order to simulate a mine discharge: Iron (Fe) – 2000 µg/L, Manganese (Mn) – 500 µg/l, Aluminum (Al) – 1000 µg/L, Calcium (Ca) – 15000 µg/L, Magnesium (Mg) – 7500 µg/L, Chloride – 5000 µg/L, and Sulfate – 300 µg/L. (The sulfate concentration was supposed to be 300 mg/L) Wibby prepared preserved portions at both concentrations and unpreserved portions at both concentrations. The samples were tested by a referee laboratory to ensure the concentrations were accurate. The samples were delivered to the labs in the same manner as was accomplished during Phase II, again, only those labs that routinely analyze samples for WV DEP were assessed.

The following table depicts the data used for evaluation under Phase III for the 5 µg/L sample.

**Table 5.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Lab** | **MDL** | **Result** | **units** | **Method** | **% Rec.** |
| Appalachian Laboratories |  | 4.63 | µg/L | GFAA | 92.6 |
| Standard Labs (NEST) |  | 4.01 | µg/L | GFAA | 80.2 |
| REI Consultants |  | 6.4 | µg/L | GFAA | 128.0 |
| Acculab | <2 | 0 | µg/L | GFAA | 0.0 |
| Compliance Monitoring |  | 3.97 | µg/L | GFAA | 79.4 |
| Tra-Det |  | 5.8 | µg/L | GHAA | 116.0 |
| Tra-Det |  | 5.7 | µg/L | GHAA | 114.0 |
|  |  |  |  |  |  |
| Average, All data |  | 4.4 | µg/L |  | 82.7 |
| Average, GFAA |  | 3.8 | µg/L |  | 76.0 |
| Average Hydride |  | 5.75 | µg/L |  | 115.0 |
|  |  |  |  |  |  |
| Referee |  | 4.9 | µg/L | ICP-MS | 98.0 |

A review of the data revealed a problem with the results from Sturm Environmental. Daniel Arnold contacted Sturm Environmental and determined that the laboratory may have received two samples at the 20 µg/L level as both samples they analyzed gave similar results. Therefore, the data from Sturm Environmental was not included for the 5 µg/L evaluation. It was also clear that there was a problem with the samples submitted to Tra-Det. It appears that Sturm Environmental had two samples at 20 µg/L delivered to them and Tra-Det had two samples at 5 µg/L delivered to them. So, the 5 µg/L data has two data points from Tra-Det and the 20 µg/L data has two data points from Sturm Environmental.

The following chart gives a visual depiction of the raw results from Phase III 5 µg/L sample.

**Chart 5.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Graphite Furnace AA |   | ICP- Mass Spec |   | Gaseous Hydride-AA |   |

The following chart gives a visual depiction of the percent recovery data for raw results from Phase III 5 µg/L sample.

**Chart 6.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Graphite Furnace AA |   | ICP- Mass Spec |   | Gaseous Hydride-AA |   |

The following table depicts the data used for evaluation under Phase III for the 20 µg/L sample.

**Table 6.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Lab |  | Result | units | Method | % Rec. |
| Appalachian Laboratories |  | 19 | µg/L | GFAA | 95.0 |
| Standard Labs (NEST) |  | 13.38 | µg/L | GFAA | 66.9 |
| REI Consultants |  | 23.7 | µg/L | GFAA | 118.5 |
| Sturm Environmental |  | 19.7 | µg/L | GFAA | 98.5 |
| Sturm Environmental |  | 19.4 | µg/L | GFAA | 98.5 |
| Acculab |  | 2.26 | µg/L | GFAA | 11.3 |
| Compliance Monitoring |  | 15.8 | µg/L | GFAA | 79.0 |
|  |  |  |  |  |  |
| Average, All data |  | 16.2 | µg/L |  | 80.9 |
| Average, GFAA |  | 16.2 | µg/L |  | 80.9 |
|  |  |  |  |  |  |
| Referee |  | 20 | µg/L | ICP/MS | 100.0 |

The following chart gives a visual depiction of the raw results from Phase III 20 µg/L sample.

**Chart 7.**

|  |  |  |  |
| --- | --- | --- | --- |
| Graphite Furnace AA |   | ICP- Mass Spec |   |

The following chart gives a visual depiction of the percent recovery data for raw results from Phase III 20 µg/L sample.

**Chart 8.**

|  |  |  |  |
| --- | --- | --- | --- |
| Graphite Furnace AA |   | ICP- Mass Spec |   |

A review of the Phase III data indicated problems with the analysis of Selenium and a decision was made to go forward with Phase IV.

**Phase IV**

After a review of the Phase III data, WV DEP staff discussed the need to further assess the laboratories with a double-blind sample with a higher concentration of sulfate in the sample. For Phase IV two custom double-blind, full-volume samples were prepared by Wibby Environmental, Golden, CO. One sample was prepared at 20 µg/L and one sample was prepared at 5 µg/L. Both samples had the following constituents added in order to simulate a high specific conductance, alkaline mine discharge: Iron (Fe) – 2000 µg/L, Manganese (Mn) – 500 µg/l, Aluminum (Al) – 1000 µg/L, Magnesium (Mg) – 7500 µg/L, Chloride – 5000 µg/L, and Sulfate – 600 mg/L. Calcium was present at approximately 180 mg/L because the source of the sulfate was CaSO4. Wibby prepared preserved portions at both concentrations and unpreserved portions at both concentrations. The samples were tested by a referee laboratory to ensure the concentrations were accurate. The samples were delivered to the labs in the same manner as was accomplished during Phase II and III.

The following table depicts the data used for evaluation under Phase IV for the 5 µg/L sample.

**Table 7.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Lab** |  | Result | units | Instrument | % Rec. |
| REI Consultants |  | 4.2 | µg/L | GFAA | 84.0 |
| BioChem |  | 5.8 | µg/L | GFAA | 116.0 |
| Sturm Environmental |  | 3.9 | µg/L | GFAA | 78.0 |
| Acculab |  | 3.85 | µg/L | GFAA | 77.0 |
| Standard Labs (NEST) |  | 4.01 | µg/L | GFAA | 80.2 |
| REI Consultants | <1 | 0 | µg/L | ICP/MS | 0.0 |
| Reliance - Bridgeport | <1 | 0 | µg/L | ICP/MS | 0.0 |
| Analabs |  | 3.79 | µg/L | ICP/MS | 75.8 |
| Tradet |  | 5.7 | µg/L | GHAA | 114.0 |
| REI Consultants |  | 4.8 | µg/L | GHAF | 96.0 |
|  |  |  |  |  |  |
| Referee |  | 5.2 | µg/L | ICP/MS | 104.0 |
|  |  |  |  |  |  |
| Average, All data |  | 3.6 | µg/L |  | 72.1 |
| Average, GFAA |  | 4.4 | µg/L |  | 87.0 |
| Average ICP/MS |  | 1.3 | µg/L |  | 25.3 |
| Average Hydride |  | 5.25 | µg/L |  | 105.0 |

The following chart gives a visual depiction of the raw results from Phase IV 5 µg/L sample.

**Chart 9.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Graphite Furnace AA |   | ICP- Mass Spec |   | Gaseous Hydride-AA or AF |   |

The following chart gives a visual depiction of the percent recovery data for raw results from Phase IV 5 µg/L sample.

**Chart 10.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Graphite Furnace AA |   | ICP- Mass Spec |   | Gaseous Hydride-AA or AF |   |

The Phase IV samples were similar to the Phase III samples except for the concentrations of Calcium and sulfate ions. In this situation GFAA did give a bias low recovery, however, the average recovery was well with the method recovery limits of 70-130%. ICP/MS, on the other hand shows difficultly in detecting the Selenium in this matrix. REI Consultants, Inc. was sent a single-blind whole volume sample to analyze by ICP/MS and gaseous hydride with atomic fluorescence detection.

The following table depicts the data used for evaluation under Phase IV for the 20 µg/L sample.

**Table 8.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Lab** |  | Result | units | Method | % Rec. |
| REI Consultants |  | 15 | µg/L | 200.9 | 75.0 |
| BioChem |  | 21.8 | µg/L | 200.9 | 109.0 |
| Sturm Environmental |  | 17.7 | µg/L | 200.9 | 88.5 |
| Acculab |  | 6.5 | µg/L | 3113B | 32.5 |
| Standard Labs (NEST) |  | 9.88 | µg/L | 200.9 | 49.4 |
| REI Consultants |  | 17.2 | µg/L | 200.8 | 86.0 |
| Reliance - Bridgeport | <1 | 0 | µg/L | 200.8 | 0.0 |
| Analabs |  | 14.7 | µg/L | 200.8 | 73.5 |
| REI Consultants |  | 17.8 | µg/L | 3114M | 89.0 |
| Tradet |  | 19.2 | µg/L | 3114 | 96.0 |
|  |  |  |  |  |  |
| Referee |  | 20 |  | 6020 | 100.0 |
|  |  |  |  |  |  |
| Average, All data |  | 14.0 | µg/L |  | 69.9 |
| Average, GFAA |  | 14.2 | µg/L |  | 70.9 |
| Average ICP/MS |  | 10.6 | µg/L |  | 53.2 |
| Average Hydride |  | 18.5 | µg/L |  | 92.5 |

The following chart gives a visual depiction of the raw results from Phase IV 20 µg/L sample.

**Chart 11.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Graphite Furnace AA |   | ICP- Mass Spec |   | Gaseous Hydride-AA or AF |   |

The following chart gives a visual depiction of the percent recovery data for raw results from Phase IV 20 µg/L sample.

**Chart 12.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Graphite Furnace AA |   | ICP- Mass Spec |   | Gaseous Hydride-AA or AF |   |

A review of the 20 µg/L data shows, as did the 5 µg/L data, that when the concentration of the sulfate ion increases, so does the difficultly in accurately quantifying Selenium in the sample.

**Conclusion**

In the absence of interfering contaminants, any of the approved methods are satisfactory for analyzing Selenium. However, in the presence of common mine-related interferences, GFAA and ICP/MS show difficultly in accurately quantifying Selenium. ICP/MS appears to have difficultly even detecting Selenium in more contaminated samples, without using extraordinary techniques to examine each sample. The gaseous hydride technique seems to generate the best data when used in a routine manner, regardless of whether the AA (Atomic Absorption) or AF (Atomic Fluorescence) detection technology is used, although this observation is based on a small sample set as only two laboratories assessed used this technique.

If one is to generate acceptable data by GFAA in the presence of difficult matrices, some additional practices will have to be employed. Method of Standard Additions (MSA) should give much better results than a single analysis in an analytical sequence. At a minimum, a matrix spike will need to be analyzed with each sample and assessment of the matrix spike recovery used to determine if additional measures need to be taken to assure quality data.

If one is to generate acceptable data by ICP/MS in the presence of difficult matrices, some additional practices will have to be employed. The analyst will have to review the raw data for each sample in detail. Matrix spikes, dilutions, or MSA may need to be analyzed in order to qualify the data.

For GFAA and ICP/MS mine related samples present inherent problems with detection and quantification of Selenium. In order to generate accurate data, laboratories will have to increase the number of Quality Control samples analyzed by these techniques. This will increase the cost per analysis for Selenium.

Based on this study and other sources, recommendations for ensuring better quality selenium data when working with mining samples or samples with elevated levels of constituents will be forthcoming from the WV DEP, DWWM Laboratory Certification Program.

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