

## Selenium in Coal, Soils, Rocks, Plants, Coal Combustion By-Products and Sediments by the Perkin Elmer AAnalyst200<sup>1</sup>

### 1. Introduction

This method document describes how geologic and plant samples are digested using a multi-acid procedure in an open glass (coal and plant only) or Teflon™ vessel. Selenium (Se) is reduced to oxidation states, +3 and +4 in aqueous solution. Sodium borohydride is added to the solution resulting in rapid formation of hydrides as illustrated by:



The gaseous hydrides are stripped from the analytical stream and transported with inert gas to the atomizer (a heated quartz furnace at 900 degrees Celsius (°C)) of the atomic absorption spectrophotometer (AAnalyst200). Concentrations of Se are determined using calibration standards in aqueous solutions of similar matrix.

This method is similar to that cited in U.S. Geological Survey Open File Report 02-223-L.

When analyzing soils, sediments, rocks, or coal combustion by products, the acid mixture requires the addition of hydrofluoric acid to digest the silicates, thus a Teflon vessel and appropriate Personal Protective Equipment (PPE) is required for the digestion.

### 2. Interfaces with Other Methods

- EGL Method 26, Inorganic Sample Preparation.
- EGL Method 29, Calibration of Laboratory Scales and Balances.
- EGL Work Instruction 08, Preparation of samples of coals, plants, coal combustion by-products, soils, rocks, and sediments for selenium analysis.

### 3. Materials and Equipment

- AAnalyst200 and FIMS100 (automation system and injection)
- Personal Protection Equipment consisting of appropriately chemically resistant gloves, eye protection and outerwear.
- Standard Reference Materials (SRM) for coals (CLB-1, NIST 1635, Sarm20, NIST 1632d)
- SRM's for coal combustion by-products, soils, sediment and rocks (NIST 2709, NIST 2711)
- Acids: Nitric Acid, Sulfuric Acid, Hydrofluoric Acid, and Hydrochloric Acid (See EGL Work Instruction 8 for details)

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<sup>1</sup> Any use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

- Argon Gas
- Analytical Balance (4 place)

#### **4. Procedure**

This procedure provides concentrations of Se in coal, soil, sediments, coal byproducts, plants and rocks. The analysis proceeds by tuning the instrument for best stable response, calibrating the instrument with standards of known composition, and then analyzing the unknowns preferably in an automated routine to maximize reproducibility.

##### Operating Conditions

The instrument must be turned on and ‘warmed up’ for at least an hour prior to analysis in order for the Se lamp and Quartz cell to function optimally. Argon gas is currently used as the carrier gas for analysis.

##### Sample Analysis

Unknowns are analyzed only after a correct calibration curve has been established and verified for Se as defined by Section 5 of this method.

##### Operational Checks

Operational checks will be used to determine if the AAnalyst200 is operational and capable of providing acceptable data. Operational checks are performed by analyzing an SRM at least every 10 samples, and analyzing a duplicate of an unknown at the end of the run. Acceptable tolerances are within 3 sigma of the error specified for the SRMs. Duplicates of unknowns must be within 10% of the original value.

#### **5. Calibration and Quality Control Samples**

A suite of aqueous standards are prepared in order to construct a calibration curve that is typically non-linear (quadratic) with a correlation coefficient of 0.995 or greater. Then, at least one reagent blank and one SRM are analyzed as unknowns to verify the calibration is within an acceptable tolerance of 3-sigma of the known value of the SRM, or the calibration must be rejected and a new calibration curve must be completed. Records of the calibration curves and verification standard analyses are logged in a notebook, and stored on computer files.

#### **6. Limits, Precautions, and Interferences**

Upper and lower concentration limits are generally determined by the range of calibration standards used for Se. Unknowns with high concentrations of Se beyond the calibration range may be diluted so the sample may be analyzed and quantitatively recalculated. The lower reporting limit for the CERSC AAnalyst200 is 0.077 parts per million (ppm). The lower reporting limit is determined by the history of blank determinations. The lower reporting limit is updated on an annual basis.

#### Known Interferences

Certain transition and heavy metals (e.g. Cu, Fe, Ni, and Sn) compete with Se for available  $\text{NaBH}_4$ . Incomplete recoveries of Se may yield low analytical results if the concentration of these metals exceeds 500ppm.

If the concentration of Se is in excess of 1,000 ppm, Se will deplete the oxygen supply in the furnace that is needed to convert hydrides to ground state.

Incomplete digestion of organic material interferes with hydride formation.

Organometallic compounds may volatilize in organic compound rich matrices.

#### **7. Acceptance of Data**

The performance of activities in accordance with this procedure is considered acceptable by the satisfactory performance of the AAnalyst200 that can be determined by the calibration procedure described in Sections 4, 5, and 6. Se analyses that are determined under this procedure are quantitative. Acceptable tolerances are within 3 sigma of the established value for SRM's. The duplicate of an unknown must be  $\pm 10\%$  of the original value. Data is rejected if values for reference standards and duplicates fall outside of the specified margins.

#### **8. Data Handling and Transfer**

Data results are reported in ppm. Information obtained by this procedure is stored – 1. On the instrument's hard drive as 'raw data,' and 2. transferred from the instrument by the analyst to an Excel<sup>TM</sup> spreadsheet that includes the instrument, name of the analyst, element analyzed (Se), date of analysis, and concentration of Se. The spreadsheet is submitted to the Laboratory Information Management System (LIMS) and then reviewed and approved by the analyst.

#### **9. References**

References: U.S. Geological Survey Open File Report 02-223-L

#### **10. Attachments**

None.

#### **11. History of Changes**

R0: Initial issue