Online Total Arsenic and Selenium Combination Analyzer For Mine Wastewater Remediation Process Control

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Background

• Single metal application specific both arsenic (As) and selenium (Se) on independent analyzers, has been previously reported

• In some wastewater treatment situations (mining, metallurgical, etc.) species of As and Se may be present at high levels and should be monitored

• Due to the complexity of As/Se measurement methods and interferences between their signals; determination of both elements in a combination analyzer has historically been difficult
Mining Wastewater - Total Metal Analysis Challenges

• Highly complex and frequently changing composition of mine influent (high TDS, TSS, metals, etc.)

• Effect of wastewater treatment method used on the effluent sample matrix (bio-treatment, etc.)

• Extensive sample preparation is required to mineralize (dissolve) insoluble Se and As species and convert them and make them suitable for measurement

• Electrochemically active As and Se species produce interfering signals. Trace Se analysis is highly difficult in presence of arsenite.
Our Approach to As/Se Combination Analyzer

- New versatile sample preparation method allowing sequential sample treatment for As/Se methods
- Elimination of mutual interferences between elements
- Highly efficient and automated pretreatment method (100% analyte recovery in less than 15 min.)
Sample Preparation for Total As and Se Analysis

1 Mineralizing entire As and Se species

During this step, entire reduced selenium forms and colloidal arsenic compounds under highly oxidizing conditions turn into soluble selenate and arsenate respectively and mineralized.
2 Preparation for Total As Determination

Selective reduction of $\text{As}^{5+}$

$\xrightarrow{3 \text{min}}$  
As reducer  
$\rightarrow$  
$\text{As}^{3+}$

3 Preparation for Total Se Determination

Selective reduction of $\text{Se}^{6+}$

$\xrightarrow{10 \text{ min}}$  
Se reducer  
$\rightarrow$  
$\text{Se}^{4+}$
Se Determination using CSV- Measurement Principle

Step 1 - Accumulation

\[ 2\text{Cat} + \text{Se}^{4+} + 8e^- \rightarrow \text{CatSe} \]

Step 2 - Stripping

\[ \text{CatSe} + 2e^- \rightarrow 2\text{Cat} + \text{Se}^{2-} \]

Resulting Signal

![Graph showing potential vs. Ag/AgCl and current vs. Se concentration]
Quantification by MSA

Current (nA)

2\textsuperscript{nd} addition
1\textsuperscript{st} addition
sample

E vs. Ag/AgCl (mV) [50 mV/div]

Signal

Concentration of unknown

Signal of unknown
Determination of Se in Synthetic Samples

\[ y = 0.9636x - 0.1162 \]
\[ R^2 = 0.9921 \]
As Measurement Results - Correlation with ICP-MS

Total Arsenic Measurement Correlation:
SafeGuard (ASV) vs ICP-MS

\[ y = 1.0433x \]

\[ R^2 = 0.9963 \]
Se Correlation Results in Industrial Samples vs. ICP-MS

\[ y = 0.9628x + 29.393 \]

\[ R^2 = 0.9891 \]
Correlation Results - 0-250 µg/L Range

\[ y = 1.148x - 6.3906 \]

\[ R^2 = 0.971 \]
Raw Influent As Analyzer vs. Perkin Elmer SIMAA 6000

Arsenic Results (ppb)

As Analyzer

PE SIMAA 6000

1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31 33 35 37
Combined Filter Effluent As Analyzer vs. Perkin Elmer SIMAA 6000

The graph compares arsenic results (ppb) from January to November on a date range from 1 to 35. The graph includes two datasets: SafeGuard and PE SIMAA 6000. The results fluctuate throughout the period with SafeGuard generally showing lower arsenic levels compared to PE SIMAA 6000.
Accumulative Results of Total As Monitoring at Customer Site

Yellow – treated water
Blue  – check sample (10 or 0 ppb As)
Red   – failed or aborted measurement

As treatment system regeneration
Media breakthrough
Summary

• Total As/Se combination analyzer compatible with complex sample matrices has been developed
• Efficient and selective sample preparation methods for As and Se species have been determined and finalized
• Evaluation of new combination analyzer using real world mining samples and other industrial process samples is currently underway
• Universal electroanalytical method allowing integration of As and Se analytical methods using single probe is under development