Ultra-trace Metals Determinations using Reductive Precipitation and ICP-MS

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Columbia Analytical Services' (CAS) Kelso laboratory has continued the development of analytical techniques for pre-concentration and chemical separation of trace metals in saline aqueous samples using reductive precipitation followed by inductively coupled plasma-mass spectroscopy (ICP-MS). This technique replaces conventional techniques for the analysis of trace metals in complex aqueous matrices such as sea water where matrix problems prevent the ability to achieve desired low levels of detection. Detection limits for various metals of interest using these techniques are displayed in the table below. Details of this procedure were presented at the recent National Environmental Monitoring Conference (NEMC) held July 21-24 in Arlington, Virginia. The full abstract follows:

A procedure for analyzing a relatively wide range of trace metals in samples containing elevated levels of dissolved solids is discussed. The procedure incorporates a chemical separation to remove interfering matrix components so final analysis can be performed using inductively coupled plasma-mass spectroscopy (ICP-MS). The separation utilizes reduction of certain target analytes to the elemental state and precipitation of others as the boride, depending on reduction potentials and/or boride solubility. The precipitation is facilitated using elemental palladium plus iron boride as carriers. Once separated from the seawater matrix, the precipitate is dissolved and analyzed using ICP-MS. A number of modifications to the procedure have been made over the past ten years to improve performance. The method meets general U.S.E.P.A. performance criteria. A general outline of the procedure is included in the most recent version of EPA Method 1640. However, variations are presented that allow a wider range of elements to be tested. Additional modification eliminates filtration and filter manipulation, which is a source of significant potential contamination. Considerations are given to the introduction of excessive chloride via the acid mixture used for dissolution of the precipitate. Thus, arsenic and chromium are validated as part of the multi-element suite of target analytes. Recovery data for low level determinations is reported and demonstrates elements suitable for this procedure, as well as elements that do not conform to the reaction mechanism(s). Detection limits are presented that show this technique is a viable approach for many elements when a procedure is needed to measure trace metal concentrations at or near ambient levels in various sample types, including open-ocean seawater. The procedure has also been adapted to the analysis of industrial chemicals such as concentrated sodium hydroxide used by municipal drinking water suppliers for pH adjustment. For additional information or to request a complete version of this document, contact Jeff Christian at jchristian@kelso.caslab.com or (360) 501-3316.

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Routine Seawater Detection Limits
Method Detection Limit (MDL) for Study Results

Initial Volume = 1000 mL
Final Volume = 100 mL
Formulation = HNO3/HCl (w/o APDC)

Analyte:	Spike Level (ug/L)	Mean Conc.(ug/L)	Average % Rec.	Calculated MDL (ug/L)
Arsenic	0.2	0.20	100	0.16
Beryllium	0.02	0.023	115	0.0029
Cadmium	0.05	0.046	92	0.0068
Chromium	0.5	0.80	160	0.18
Cobalt	0.02	0.017	85	0.0049
Copper	0.1	0.11	110	0.014
Lead	0.02	0.024	120	0.011
Nickel	0.2	0.21	105	0.035
Silver	0.02	0.026	130	0.0080
Thallium	0.02	0.019	95	0.0035
Zinc	0.5	0.57	114	0.15