Chemical Separation of Metals using Reductive Precipitation

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Abstract

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 eleven years to improve performance. The method meets general USEPA 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. Isotope dilution is incorporated to demonstrate a relatively simple and inexpensive mechanism to enhance recovery of nickel. 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. Thus, the procedure is also applicable for extremely complex matrices occasionally encountered during environmental investigations.

Introduction

What is Reductive Precipitation?

A clean laboratory technique for preparing difficult sample matrices (aqueous and non-aqueous) for trace metals analysis prior to final determination by ICP-MS.

What's new?

- Various adaptations of the technique have been used for about 25 years, so the core procedure is not new.
- However, it's now included in EPA Method 1640 as an option for chemical separation.
- Since we originally adapted the technique for use with ICP/MS in 1993, improvements to the scope and performance of the method have been made at the Kelso Laboraotry (discussed in this report).
- In addition, the technique has been adopted for use in industrial applications (i.e. metals imports) to aid in identification of point of entry for heavy metals/metalloids.

Examples of Detection Limit Requirements (µg/L)

This table lists examples of typical requirements routinely seen by environmental laboratories.

Element	Target MDL for 103 Evaluation (Elutriates)	Lowest Ambient Water Quality Criterion	Target RL for Surface Water Ambient Monitoring Program (SWAMP)
As	1	0.018	0.3
Cd	0.5	0.37	0.01
Cr	0.5	-	0.1
Cu	2.5	2.5	0.01
Pb	2.5	0.54	0.01
Ni	0.2	8.2	0.02
Ag	1	0.32	0.02
Zn	1.5	32	0.1

Background

- The procedure is designed to circumvent physical & chemical interferences associated with hi-TDS samples.
- The procedure is well-suited for our facility (Class 100 hoods/benches; Class 1000 room) and our applications (wide range of aqueous samples, plus industrial applications).
- We adapted the procedure to ICP-MS (Christian-1993) from previous work done for ICP-AES and GFAAS (Sturgeon, et al - 1988 – GFAAS; Skogerboe, et al - 1985 – ICP/AES).
- The procedure, like others such as chelation/solvent extraction, chelating resins, and other coprecipitation techniques, allows for multi-element applications.
- Development needed to efficiently comply with evolving regulations (i.e. lower detection limit requirements).
- ACOE 103 Evaluation – Elutriates are seawater for marine studies.
- Lowest Ambient Water Quality Criterion – taken directly from a table in Method 1640.
- SWAMP - These limits are not particularly difficult in many aqueous samples, but are difficult or impossible in some hi-TDS samples using routine methodology.

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Theory Of Reductive Precipitation

- The procedure is based on the ability to precipitate the analytes of interest in the elemental state or as metal borides.
- Iron and Palladium carriers are added in the ionic state and converted to Iron Boride and elemental Palladium.
- The mechanism an element follows is dependent on its Reduction Potential vs. its propensity to form an insoluble metal boride.
- Borohydride is used as the reducing agent and as the source of boride

  $BH_4^- + 8\ OH^- \longrightarrow H_2BO_3^- + 5\ H_2O + 8\ e^- \quad E° = 1.24V$
- The mechanism for conversion to the elemental state is simple.

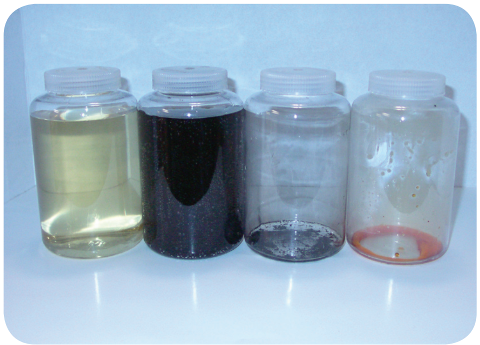
  $M^{n+} + ne^- \longrightarrow M(s)$

- The mechanism for precipitation as the boride is not simple due to the relatively complicated chemistry of metal boride formation.

  "Metal borides do not conform to ordinary concepts of valence in terms of stoichiometry or structure." Cotton/Wilkinson (1972)

Materials & Methods

- Operations Performed in Class 100 Laminar Flow Hoods (when exposed)
- Formulations and Operations Vary from EPA 1640



1. 1000 mL aliquot in polycarbonate bottle
2. 2 mg Pd and 2 mg Fe
3. pH between 8 and 9 (w/NH_4OH)
4. 5 mL 6% $NaBH_4$ (w/swirling)
5. Cap loosely ≥15 hr.
6. Centrifuge at 2000 rpm 30 min.
7. Decant supernatant
8. 0.4 mL HCl + 2.5 mL HNO_3
9. Warm in water bath
10. Transfer & dilute to volume w/DIW + IS

- Of note is the facility we have for performing the analysis with the appropriate care: a Class 1000 room with Class 100 benches are sufficient.
- Also of note are the variations from the EPA formulation that we use in our laboratory.
- The most significant change we have made in the past few years is the elimination of filtration.
- In addition, HCl is used in the dissolution mix because of its ability to solubilize transition elements via complex ion formation (Ag being the most notable).
- The drawback to HCl is the decreased sensitivity for Cr and As.

Results & Discussion

Comparison of Formulations

- Since our laboratory has been performing this procedure for about 10 years, we felt the need to compare our SOP with recently published EPA version of the method.
- We had already evaluated the effect of filtration versus centrifuging for isolation of the precipitate, we only wanted to evaluate two other variables – Digestion solution and the use of APDC, a common chelating agent.
- The EPA procedure lists HNO_3/H_2O_2 as the digestion mix and also suggests that APDC be added prior to the borohydride.
- We also evaluated the use of a larger concentration factor.
- The values in boldface represent the best recoveries.
- Although all four formulations showed reasonably good results, the values derived from the HNO_3/HCl without APDC yielded the best overall results.

Evaluation of Digestion Solutions – All Trials

Recovery Comparison - All Seawater Trials

This table shows the mean recoveries for each of the four formulations tested (n=7)

Element	Avg. % Rec. HNO_3/HCl	Avg. % Rec. HNO_3/H_2O_2	Avg. % Rec. HNO_3/HCl w/APDC	Avg. % Rec. HNO_3/H_2O_2 w/APDC
As	**101*** ±3	83 ±4	36 ±5	90 ±4
Be	89 ±6	81 ±10	82 ±4	92* ±2
Cd	**96*** ±2	93 ±2	93 ±3	92 ±2
Cr	**98*** ±6	93 ±2	102* ±8	93 ±1
Co	87 ±1	77 ±4	91* ±3	86 ±2
Cu	88 ±3	79 ±3	95* ±3	84 ±3
Pb	**91*** ±2	84 ±1	88 ±3	86 ±1
Ni	84 ±2	75 ±4	94* ±4	83 ±3
Ag	**90*** ±4	85 ±2	83 ±3	79 ±6
Tl	**91*** ±3	86 ±2	89 ±4	88 ±2
Zn	**94*** ±3	86 ±3	93 ±5	86 ±2

MDL Results for Standard Kelso Lab SOP
Method Detection Limit (MDL) for 10x Concentration

Initial Volume = 1000 mL Final Volume = 100 mL
Formulation = HNO_3/HCl (w/o APDC)

Analyte	Spike Level (µg/L)	Mean Conc. (µg/L)	Average % Rec.	Calc. MDL (µg/L)
As	0.2	0.20	100	0.16
Be	0.02	0.023	115	0.0029
Cd	0.05	0.046	92	0.0068
Cr	0.5	0.80	160	0.18
Co	0.02	0.017	85	0.0049
Cu	0.1	0.11	110	0.014
Pb	0.02	0.024	120	0.011
Ni	0.2	0.21	105	0.035
Ag	0.02	0.026	130	0.0080
Tl	0.02	0.019	95	0.0035
Zn	0.5	0.57	114	0.15

- The procedure incorporates a 10x concentration. So, 1000 mL of sample is concentrated to 100 mL.
- As and Cr are biased high due to high background signal from chloride-containing isobaric interferences.
- Zn is high due to general background contamination.
- Pb, Cd, Co, and Cu suffer to some degree from background contamination (limitations of facility).

Evaluation of Larger Concentration
Method Detection Limit (MDL) for 50x Concentration

Initial Volume = 1000 mL Final Volume = 20 mL
Formulation = HNO_3/H_2O_2 (w/APDC)

Analyte	Spike Level (µg/L)	Mean Conc. (µg/L)	Average % Rec.	Calc. MDL (µg/L)
As	0.1	.070	70	**0.031 (5)**
Be	0.002	.0012	60	**0.0010 (3)**
Cd	0.005	.0092	184	**0.0075 (0)**
Cr	0.1	.073	73	**0.033 (5)**
Co	0.002	.0046	230	**0.0016 (3)**
Cu	0.02	.031	155	**0.019 (0)**
Pb	0.02	.023	115	**0.014 (0)**
Ni	0.02	.030	150	**0.019 (2)**
Ag	0.005	.00073	15	**0.0016 (5)**
Tl	0.02	.0049	25	**0.022 (-7)**
Zn	0.1	0.14	140	**0.039 (4)**

- These are results from using a larger concentration factor of 50x. (1000 mL was concentrated to 20 mL).
- The formulation had to be altered because the HCl would have been too high in the final solution to obtain usable results for Cr and As.
- However, the tradeoff was unusable results for Ag and Tl.
- In addition, laboratory contamination prevented improvement to Cd, Cu, and Pb.
- The value in parenthesis in the far right column is the improvement factor.

Comparison of OPR Limits with EPA Method 1640

OPR Limits (% of True)			
Element	**Columbia Analytical**	**EPA Method 1640 (Table 2)**	**EPA Method 1640 (Table 3)**
As	58-116	-	58-110
Be	61-103	-	-
Cd	83-106	73-123	64-105
Cr	75-114	-	-
Co	81-109	-	-
Cu	80-108	63-159	77-109
Pb	82-111	52-144	62-129
Ni	81-109	71-130	26-147
Ag	73-110	-	30-151
Tl	80-105	-	-
Zn	79-123	-	75-95

- OPR comparisons between the EPA published values and the Columbia Analytical values.
- The 1640 limits are taken from two separate tables published in the method (specifics of analytical procedure are not listed in the EPA document).
- Inspection of the results shows our formulation compares very well and also shows more elements validated by a single technique.

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Isotope Dilution for Enhancing Method Performance

- Enhancement of method performance by using isotope dilution was tested..
- Ni is an element that often yields unpredictable recoveries. It generally acts okay in clean seawater, but does not always recover well in estuarine waters and some groundwaters.
- Since Ni has an isotope suitable for this technique, a limited number of tests were performed to get an idea of whether we could improve performance.
- The standard Columbia Analytical formulation was used.
- 4 µg of ^{61}Ni was added to all samples that were carried through the procedure.

Other Applications – Metals Imports Example of Analytical Scheme for 50% NaOH

Element	Initial Sample Mass (g)	Final Volume (mL)	Manufacturer's Specification (mg/kg)	Reporting Limit w/Red. Ppt. (mg/kg)
As	10	100	0.10	0.005
Pb	10	100	1.0	0.001
Ni	10	100	1.0	0.004
Cu	10	100	0.50	0.004

- The results suggest the procedure is an excellent means to normalizing Ni performance.
- The internal standard recoveries were in the 45-60% range.
- The matrix spike recoveries were very close to 100%.

Isotope Dilution Results for Ni in Saline Water

	Nickel (µg/L)	^{61}Ni Internal Standard Response*	Matrix Spike Recovery
Method Blank - R1	0.07J	64.6%	-
Method Blank - R2	0.06J	61.9%	-
Unspiked Saline Water - R1	0.55	53.0%	-
Unspiked Saline Water - R2	0.55	48.3%	-
Unspiked Saline Water - R3	0.54	50.1%	-
Spiked Saline Water - R1	2.55	51.7%	100%
Spiked Saline Water - R2	2.58	47.1%	102%
Spiked Saline Water - R3	2.60	47.6%	102%

***IS response as a percentage of ICAL blank.**

- When adapted accordingly, the procedure serves as an excellent tool for evaluating metals imports to various industrial processes.
- We have used the technique to measure trace elements in concentrated caustic solutions, concentrated acids, salts (e.g. Na2SO$_4$, NaClO$_3$, etc.) used in industrial processes, and various complex inorganic solutions representing various process streams within an industrial setting.
- The data in the table represent an analysis of 50% NaOH, which is used for pH adjustment in a municipal drinking water supply system.
- To easily meet the specifications, a 10 g sample mass was diluted to 100 mL, neutralized, then carried though the procedure.
- Note the "Manufacturer's Specifications" could be met by alternative procedures. However, this technique gets all target elements and yields RLs well below the requirements.

Conclusions

- The Reductive Precipitation technique is an effective and efficient means for dealing with hi-TDS matrices.
- A good facility is required, but not a Class 1 clean room.
- The formulation Columbia Analytical has developed over the past 10 years yields valid results.
- In addition, the formulation increases the scope of the method.
- The procedure meets or exceeds the EPA method performance criteria.
- Isotope dilution is a viable approach for Ni and also adds no extra cost other than the initial purchase of the enriched standard.
- The procedure is adaptable to "non-environmental" samples (although metals imports studies often are conducted for environmental purposes) .

References

1. U.S. Environmental Protection Agency. Office of Solid Waste. Test Methods for Evaluating Solid Waste-Physical/Chemical Methods. SW-846 3rd Edition. Washington, D.C. Update III, December 1996.

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