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## Strategies for Trace Metal Analysis in Natural Water Samples

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The detection power of analytical methodologies based on atomic spectroscopic instrumentation has improved with a new generation of equipment and the advent of hyphenated techniques. Inductively coupled plasma mass spectrometry (ICPMS) is one technique finding widespread acceptance as a powerful analytical tool due to its high sensitivity, the ability to perform multielement analysis as well as isotope ratio determinations for isotope dilution analysis. Using ICPMS the direct determination of a considerable number of trace elements in fresh water is feasible, and if required, detection limits can be further decreased by the substitution of ultrasonic nebulization for the conventional pneumatic nebulization. However, the determination of many trace elements at "natural" levels found in seawater still require some form of sample preparation before introduction into the instrument due to interferences from concomitant elements and the high dissolved solid content.

In this laboratory concentration and/or separation schemes utilizing chelation/extraction, reductive precipitation, immobilized ligands and hydride generation have been successfully used off line to ICPMS and graphite furnace atomic absorption spectrometry (GFAAS). In this laboratory multielement extraction has been achieved using an ammonium pyrrolidine-N-carbodithioate-methyl isobutyl ketone (APDC-MIBK) extraction system(1). However, due to problems associated with manipulation of large sample volumes, high analytical blanks and incomplete recovery this technique was abandoned in favour of immobilized ligands. 8-Hydroxyquinoline immobilized on silica gel (I-8-HOQ) has been used for the preconcentration of Cd,Pb,Zn,Cu,Fe,Mn,Ni and Co from seawater prior to their determination by either GFAAS (2) or ICPMS (3). Following adjustment of the pH 8.0 the sample is passed through a 600 mg column of the resin at a flow rate of approximately 10 ml/min, the column is washed with high purity water and the chelated metals are eluted with an acid mixture of 10% HCl and 1% HNO<sub>3</sub>. Blanks are generally lower than solvent extraction techniques and enrichment factors of 50 can be easily be achieved.

Table 1  
Absolute Blank, ng

Element	APDC/MIBK	I-8-HOQ	Red. ppt.
Mn	<1	<1	4 ± 1
Fe	31 ± 4	75-100	--
Ni	<2	<3	<2
Cu	21 ± 5	<0.2	20 ± 12
Zn	62 ± 17	2 ± 1	8 ± 1
Cd	1 ± 1	<0.1	1.1 ± 0.3
Pb	7 ± 3	<0.8	1.7 ± 0.1

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Irreproducible Fe blanks are due to the high Fe content in the silica substrate and can be alleviated by using the resin only at low pH or immobilizing the oxine on a plastic substrate(4). For the determination of Cr, an alternate ligand, diphenylcarbazone immobilized on silica was also successful(5).

An alternate concentration technique based on reductive precipitation by sodium borohydride has been used for the determination of 16 trace elements in seawater(6). A mixed solution of iron and palladium is added to the sample (typically 900 ml), the pH adjusted to 9 and NaBH<sub>4</sub> is added which forms a black granular precipitate. After aging the precipitate for 24 hours, the solution is filtered and the precipitate dissolved in aqua regia. Blanks are generally larger than the 8-I-OH procedure, however, detection limits are suitable for the determination of many trace metals in nearshore and open ocean water samples. Additional benefits of this technique are complete recoveries of As, Sb, Se, which cannot be concentrated using the previously described procedures.

In conjunction with flow injection techniques many of these procedures have been implemented on-line, resulting in additional benefits such as economy of sample and reagents throughput and the ease of replicating precise chemical manipulations. Miniaturization of a 8-I-OH column for on-line determinations with GFAAS(7) and ICPMS(8) has successfully been applied to the determination of trace elements in a variety of natural water certified reference materials(CRM). Results are shown below for the analysis of a coastal seawater CRM, CASS-2, using a miniaturized 8-I-OH column with flow injection techniques and two different detection systems. Results are acceptable with the exception of Fe using ICPMS due to contamination and poor sensitivity since <sup>57</sup>Fe was used for quantitation.

Table 2  
Analytical Results for CASS-2

	GFAAS <sup>#</sup>	ICPMS <sup>*</sup>	Certified value
Mn	2.09 ± 0.10	2.22 ± 0.09	1.99 ± 0.15
Fe	1.15 ± 0.06	2.56 ± 0.06	1.20 ± 0.12
Ni	0.303 ± 0.011	0.305 ± 0.008	0.298 ± 0.036
Cu	0.664 ± 0.011	0.664 ± 0.004	0.675 ± 0.039
Zn	ND	2.22 ± 0.10	1.97 ± 0.12
Cd	0.017 ± 0.002	0.023 ± 0.003	0.019 ± 0.004
Pb	0.018 ± 0.005	0.021 ± 0.003	0.019 ± 0.006

# - reference 7.

\* - reference 8.

ND - not determined

Reduced interferences resulting from the separation of the analyte from the matrix is a benefit of hydride generation. For the determination of hydride forming elements in natural water samples large sample volumes are required when using conventional atomization techniques such as a quartz tube for atomic absorption or an ICP for atomic emission or mass

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spectrometry detection . A technique utilizing the graphite furnace as both the hydride trapping medium and atomization cell has been successfully applied for the determination of As, Se and Sb in waters, biological tissues and sediments(9). Utilizing this in-situ preconcentration procedure, high sensitivity and a substantial increase in the detection power can be realized. Coupled with flow injection procedures, complete automation of this procedure permits simple, rapid and relatively interference free determination of As, Se and Sb in these types of environmental samples.

Significant advances in instrumentation and analytical procedures have resulted in the generation of reliable analytical data for the total concentration of a suite of elements at "natural" levels. However, improved techniques must continue to be developed for many elements for which reliable environmental information is not yet available. Additionally, the study of trace element speciation presents the analytical chemist with the challenge to provide innovative solutions to environmental questions.

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## Questions & Answers: Strategies for Trace Metal Analysis in Natural Water Samples

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Q. ERIC CRECELIUS (Battelle): You said you've just begun to do a little bit of work on silver in your standard reference materials. Do you have anything to report at this time?

A. No. I think all our new biological CRM's will be certified for silver. We are in the process of replacing existing CRM's. And our new sediments will also be certified for silver, I expect. We're also in the process of replacing some of those. As far as the natural waters go, we haven't made any real effort to do that yet, although we've looked at it but haven't spent the time. I would think that it wouldn't be too difficult to do silver in Spurs, our river water. But seawater is another factor, because we need alternate procedures if we want to do a certification. You can't just rely on one procedure. And that's somewhat difficult to come by. Maybe we'll get some ideas today.

Q. JIM KRAMER (McMaster Univ.): At these ppt levels, many of us have many problems defining what the blank problem is, and determining what the level is, and subtracting, and so on. Can you give us any insights on how you approach the blank problem?

A. That is our problem too. Because whenever you do one of these procedures, you generally take through ultrapure water as your blank. And when you get very low, you begin to wonder if you're measuring the metal concentration in your ultrapure water, and whether subtracting that blank is appropriate. All I can say is that we try and preconcentrate large enough so that the blank is not a major factor. And in some cases where it is, we try to do alternate techniques, again to try to overcome that. With the reductive precipitation, those blanks are fairly large, but at those concentrations that we use it at, for a specific sample, it's not a severe problem. It becomes a problem with elements like tin, where the blank is fairly large, and the analyte concentration is extremely low. We've never been able to determine tin in seawater, and we've tried numerous times. Antimony can even be a problem, because of blank problems. I can't really give you any hints as to what we do, other than use alternate techniques. That's what we try to do most of to overcome that.

Q. ANDERS ANDREN (Univ. of Wisconsin): In your bonded silica gel system, how sure are you that perhaps colloiddally associated materials won't pass through?

A. Well, we're dealing with filtered seawater all the time, filtered through 0.45 [microns]. In fact, our river water is filtered through 0.2 microns. What happens after the filter, we can't really be certain. I don't think we have a problem, although it's hard to say. If we digest the sample and analyze again, which we do for numerous elements, we can still get the same result. Whether or not that answers your question, I'm not sure. Because we don't deal with real samples, as I'm sure none of you do. We try and get our CRM's to be at the natural level as much as possible, but we want to make certain that that concentration in that sample is accurate.

Q. Sure. Well, the reason I ask is that, for example, when we deal with hydrophobic organic compounds, some of which are colloiddally associated, we know that if one uses resins, there is sometimes a problem with the colloiddally associated material not being adsorbed.

A. On the silica gel.

Q. Whatever the resin is. In our case, we use XAD-2 resin.

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- A. That might be some of the problems we're having with the XE-305.
- Q. Very briefly, in your crystal ball gazing, how do you consider polarographic techniques? We're especially interested in that to get more insight into total versus perhaps some idea about speciation.
- A. Well, there are a few people doing that kind of work around the world. And especially the voltammetry technique is very sensitive. Using various ligands like EDTA to complex copper and measuring its selectivity is becoming quite popular too. I really can't say. I think we'll see new advances in that area, especially with the adsorptive accumulation technique and the complexation. What happens to the sample when you add your complexing agent is another factor that I just can't answer, and it throws everything out of whack. But I really think that adsorptive accumulation is a very powerful technique, with the limit of detection you can obtain, because you can work on the sample directly; you don't have to do any preconcentration, or any kind of evaporation to alter the sample. So it's a great technique for working directly with the sample.