Analysis of Copper in the In-Tank Precipitation Process Caustic Samples

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Savannah River Technology Center

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ANALYSIS OF COPPER IN THE IN-TANK PRECIPITATION PROCESS CAUSTIC SAMPLES (U)

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Summary

Inductively Coupled Plasma Emission Spectroscopy (ICPES) and Inductively Coupled Plasma Mass Spectrometry (ICPMS) procedures for measuring Cu in In-Tank Precipitation (ITP) caustic samples have been tested and implemented in the Analytical Development Section at the Savannah River Technology Center. Prior to introduction to the instruments, the samples must be acidified to a $\text{pH} \leq 2$ and diluted so that the total dissolved solids is less than 1% for ICPES and less than 0.1% for ICPMS. For the sample matrix listed in table 1, using 2% nitric acid as the diluent (routine practice) is not sufficient to acidify the sample for ICPES analysis and Cu precipitation is the probable cause of the inconsistent spike recoveries previously observed. By increasing to 5% nitric acid, an ICPES method detection limit (mdl) of 0.3 mg/liter and an accuracy of 10% at 1 mg/liter Cu can be achieved. In the ICPMS method, the sample matrix listed in table 1 gives a mdl of 0.4 mg/liter and Cu can be measured at 1 mg/liter with an accuracy of 30%.

Recommendations

- Samples should be acidified to a $\text{pH} \leq 2$ and diluted so that the total dissolved solids is less than 1% for ICPES and less than 0.1% for ICPMS. For the sample matrix listed in table 1, acidification and total dissolved solids reduction can be accomplished by a 10X dilution with 5% nitric acid for ICPES and a 100X dilution with 1% nitric acid for ICPMS.
- A spiked sample should be analyzed with each sample.
- A mdl for each batch of samples should be established using a synthetic salt blank diluted to the same concentration as estimated for the samples.

Introduction

The measurement of Cu in ITP samples by ICPES and ICPMS is difficult due to the complexity of the ITP sample matrix (See Table 1). Recoveries from samples, spiked with 1 mg/liter Cu and analyzed using the ADS routine ICP procedures, have varied from 35% to 70%. The customer requires a measurement method that can reliably measure Cu to at least 0.5 mg/liter and be accurate to within 30% at a concentration of 1.5 mg/liter.

Both ICPES and ICPMS require that the high salt sample be diluted to reduce the dissolved solids concentration and matrix effects (i.e. background noise and molecular ion interferences). Generally, copper is easily detected by ICP techniques. The element has two isotopes, ^{63}Cu and ^{65}Cu , with natural abundance of ~ 69% and ~ 31% respectively.

The instrument background spectrum, under ideal conditions, shows only a little noise at both masses. Defining instrument detection limit as 10 standard deviations of the blank response, at masses 63 and 65, ICPMS can measure Cu at 0.1 ug/liter. Under ideal conditions, the ICPES Cu instrument detection limit is 0.005 mg/liter at 324.754 nm.

Experimental

An ITP Tank 48 Batch 1 salt solution was obtained from IWT for testing the ICPES and ICPMS measurement methods. The composition of the Tank 48 solution is given in Table 1.

Table 1. Composition of Tank 48 Solution

Component	Concentration
Total Na +	3.5 M
Free OH	1.7 M
Nitrate	0.4 M
Nitrite	0.5 M
Carbonate	0.2 M
Aluminate	0.1 M
Chloride	0.013 M
Phosphate	0.008 M
Sulfate	0.003 M
Oxalate	0.005 M
Zn	7 mg/liter
Mo	10 mg/liter
Sn	3 mg/liter
Cr	55 mg/liter

ICPES

Calibration solutions were made by the appropriate volumetric dilution of a 1000 mg/liter Cu in 2% nitric acid standard from High Purity, Inc.. Dilutions were made using 5% nitric acid prepared using Seastar 16 molar nitric acid and 18 megaohm Millipore deionized water. Calibration standard concentrations used were 0.0, 1.0 and 10.0 mg/liter.

Spikes were prepared by adding the appropriate volume of a 10 mg/liter Cu standard (prepared from the 1000 mg/liter Cu standard from High Purity) to the Tank 48 salt solution or to a 10X dilution of an ITP sample.

ICPES measurements were made using a Leeman PS1000 for non-radioactive samples and an ARL 3580 for radioactive samples. An ICPES measurement consists of three thirty

second integrations at 324.754 nm for each of the standards and samples. A sample uptake time of 75 seconds was used and a 4 minute rinse between samples was required.

Prior to measurement by ICPES, the solution needs to be acidified to a $\text{pH} \leq 2$. Using 2% nitric acid as the diluent (routine practice) is not sufficient to acidify the sample unless a 100X dilution is made. However, a method detection limit (mdl) of 0.3 mg/liter (5 sigma) was calculated from 10 determinations of the ITP Tank 48 salt solution. Whether the source of this increased mdl, as compared to an mdl from an acidic non-salt solution, is the result of matrix effects or Cu contamination of the salt solution is not known at this time. This mdl does preclude the use of a 100X dilution. Therefore, a 10X dilution is the most dilute solution that can be used and 5% nitric acid is required as the diluent to ensure that the solution is acidified to a $\text{pH} \leq 2$.

The Tank 48 matrix solution was spiked with 1 mg/liter Cu standard. From this spiked solution, five 1 milliliter aliquots were diluted with 9 milliliters of 5% nitric acid. These 5 dilutions were analyzed at least twice to demonstrate reproducibility. The results are summarized in Table 2.

Table 2. ICPES Results from a 1.0 mg/liter Cu Spiked ITP Salt Matrix.

	Dilution 1	Dilution 2	Dilution 3	Dilution 4	Dilution 5
	Cu (mg/liter)	Cu (mg/liter)	Cu (mg/liter)	Cu (mg/liter)	Cu (mg/liter)
	1.02	0.98	0.96	0.97	0.94
	0.94	0.97	1.04	1.01	0.99
	0.91	1.07	--	--	0.99
	0.90	0.99	--	--	1.00
	1.00	--	--	--	--
Average	0.95	1.00	1.00	0.99	0.98
Std. Dev.	0.05	0.05	0.05	0.03	0.03
% RSD	5	5	5	3	3

All spike recoveries are between 90 % and 110%. The data in Table 2 also shows the excellent reproducibility of the sample dilutions and instrument measurements.

Next, actual ITP research samples were analyzed and the results are summarized in Table 3. Samples 30007776, 30007777 and 300061327 were diluted 10X with 5% nitric acid. The ten remaining samples¹ had been acidified to a $\text{pH}=2$ by the customer prior to submission for analysis. Therefore, these samples were diluted with 2% nitric according to routine procedures. All spike recoveries are within 20%.

Table 3. ICPES Results of ITP Samples

LIMS #	Sample Unspiked Cu (mg/liter)	Spike Conc. (mg/liter)	Sample + Spike Cu (mg/liter)	% Recovery
30007776	-0.297	1.0	0.9517	95
30007777	0.679	--	--	--
300061327	0.023	1.0	1.005	98
300061327	0.023	0.2	0.221	99
300075187	0.0568	0.2	0.2380	91
300075188	0.3613	0.2	0.5377	88
300076152	0.0511	0.05	0.0918	81
300076153	0.2677	0.2	0.4410	87
300079985	0.0637	0.05	0.1103	93
300079988	0.2516	0.05	0.2959	89
300079989	0.0341	0.2	0.2222	94
300079990	0.0084	0.05	0.0562	96
300080384	0.1706	0.2	0.3651	97
300080385	0.0743	0.05	0.1158	83

** Not corrected for 10X dilution.

ICPMS

When Cu is present in a high sodium matrix (9.2 mg/liter or greater), the molecular ion, ArNa, begins to appear at mass 63. The Cu isotope ratio increases dramatically with increasing Na ion concentration, making the mass 63 response for Cu unusable. At the same time, a peak begins to appear at mass 62. Although it is not mentioned in the library of molecular ion interferences included in the instrument software, mass 62 corresponds to Na₂O. The relative intensities of both the mass 62 and mass 63 responses are equal and both increase at the same rate as the Na ion concentration increases.

The Cu isotope at mass 65 is not significantly bothered by a molecular ion interference with a 100X dilution of the Tank 48 solution. The detection limit, as calculated from the average response of the Tank 48 salt solution, is 4 ug/liter as compared to the detection limit of 0.1 ug/liter at mass 63 calculated from the standard blank (no salt matrix). As with ICPES, whether the salt solution response is the result of matrix effects or from Cu contamination of the salt solution has not been determined at this time.

Another effect of the high salt concentration is the suppression of the instrument response. This is demonstrated by monitoring the response of the 50 ug/liter Indium

internal standard at mass 115. In 920 mg/liter salt solutions, the response suppression is about 25% of its value in the non salt containing standards.

Five aliquots of the unspiked and Cu spiked salt solution were prepared by adding 0.1 milliliter of the tank 48 salt solution plus 0.05 milliliter of a 10 ug/liter In/Sc/Bi internal standard solution to 9.85 milliliters of a dilute nitric acid solution. The internal standard concentration in the dilution was 50 ug/liter. The nitric acid diluent was prepared by adding 25 milliliters of 16 M ultra high purity nitric acid to 4 liters of 18 megaohm Millipore deionized water. In all 10 sample preparations, the solution pH ≤ 1 .

Mass spectrometer concentration calibration solutions were prepared by appropriate volumetric dilution of a 10 ug/liter High Purity, Inc. mixed element concentration standard (ICPMS-CS) that contained Cu. The calibration concentrations were blank, 0.1 ug/liter, 0.5 ug/liter, 1 ug/liter, 5 ug/liter, 10 ug/liter, 50 ug/liter, and 100 ug/liter. Each concentration standard and blank also contained 50 ug/liter of the Sc/In/Bi internal standard.

The Fisons PQ1 ICPMS was used for analysis. Four one minute scans from mass 43 to mass 249 were made on each sample and standard. A ninety second sample/standard uptake was selected. At the end of the four data acquisitions, the sample delivery system was washed for 90 seconds. A one minute wash is necessary to return the mass 65 response to background levels.

The standard/sample run sequence had the standards in increasing concentration order followed by alternating the unspiked and spiked samples. After the last spiked sample, a 10 minute wash was required to eliminate 99% of the ArNa response at mass 62. Then the standards were run again.

Table 4. ICPMS Results from a 10 ug/liter Cu Spiked ITP Salt Matrix

Dilution #	Sample Unspiked Cu ($\mu\text{g/liter}$)	Sample + Spike Cu ($\mu\text{g/liter}$)	Cu Recovery ($\mu\text{g/liter}$)	% Recovery
1	2.9	15.8	12.9	129
2	4.1	15.4	11.3	113
3	3.5	15.2	11.7	117
4	4.1	16.7	12.6	126
5	3.6	16.2	12.6	126
Average	3.6	15.9	12.2	122
Std. Dev.	0.5	0.6	0.7	6.6
% RSD	13.2	3.7	5.4	5.4

Conclusions

Copper can be measured in ITP caustic solutions by ICPEs and ICPMS. Prior to introduction to the instruments, the samples must be acidified to a $\text{pH} \leq 2$ and diluted so that the total dissolved solids is less than 1.0% for ICPEs and less than 0.1% for ICPMS. Spiked samples should be run as verification that there is no loss of Cu. A different sample matrix from the one listed in table 1 will require the determination of a new mdl.

References

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