

TENNESSEE BUREAU OF INVESTIGATION

Forensic Services Division

Microanalysis Standard Operating Procedures Manual

Quantitative Analysis of Aqueous Solutions



6.0 Quantitative Analysis of Aqueous Solutions for Heavy Metal Contaminants Using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

6.1 Scope - This method describes the examination for arsenic, cadmium, copper and lead in any aqueous and alcoholic solutions by ICP-MS.

6.2 Terms and Definitions –
Moonshine – Non-taxed alcoholic beverage produced, distributed or sold by a non-registered individual or group of individuals.

Aqueous – water based solution.

Alcoholic – Ethanol based solution.

6.3 References -

EAP Method 6020. “Inductively Coupled Plasma-Mass Spectrometer”. Revision September 1994

“Is contaminated unrecorded alcohol a health problem in the European Union? A review of existing and methodological outline for future studies”, Addiction, 106 (Suppl. 1), 20–30

EPA Drinking Water Standard Concerning Arsenic
<http://water.epa.gov/lawsregs/rulesregs/sdwa/arsenic/index.cfm>

EPA Drinking Water Standard Concerning Lead and Copper
http://water.epa.gov/lawsregs/rulesregs/sdwa/lcr/upload/LeadandCopperQuickReferenceGuide_2008.pdf

EPA Drinking Water Standard Concerning Cadmium
<http://water.epa.gov/drink/contaminants/basicinformation/cadmium.cfm>

World Health Organization Guidelines for Drinking Water Quality, 4th Edition
http://www.who.int/water_sanitation_health/publications/2011/9789241548151_ch08.pdf



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Council of the European Union Directive on the Quality of Water for Human Consumption

[http://eur-](http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:1998:330:0032:0054:EN:PDF)

[lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:1998:330:0032:0054:EN:PDF](http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:1998:330:0032:0054:EN:PDF)

6.4 Examination Procedures -

6.4.1 Evidence Types - Any aqueous or alcoholic evidence samples suspected of containing arsenic, cadmium, copper, or lead. Moonshine samples are submitted for the analysis of these heavy metals to distinguish them from legally produced liquor samples.

6.4.2 Reagents and Chemicals

6.4.2.1 Reagents and Chemicals

1. High Purity concentrated Nitric acid
2. High Purity water
3. ACS Grade Ethanol
4. Commercially prepared solutions of As, Cd, Cu, Pb, Ga, In, and Bi
5. Manufacture supplied tuning solution for ICP-MS

All chemicals, except Ethanol, used in this procedure must be high purity or trace metal free grade.

6.4.2.2 Reagent Preparation

1% Nitric acid solution

Add 200-500mL of ICP-MS grade water to dedicated 1000mL volumetric flask (non-glass). Analytically measure 10mL of high purity nitric acid into graduated cylinder (non-glass). Analytically transfer nitric acid to the dedicated volumetric. Make to volume with high purity water. Analytically transfer to dedicated storage container labeled with the date and initials. Document the solution in the reagent log.



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Internal Standard Solution

Analytically pipette 1000 uL of 1000 ppm Ga, In, and Bi standard solutions into a dedicated 100 mL volumetric flask (non-glass). Make to volume with 1% nitric acid. Analytically transfer to a dedicated storage container labeled with date and initials. Document the solution in the reagent log. This solution is stable for approximately six months. This solution will contain 10.0 ppm of Ga, In, and Bi.

P/A Stock Solution

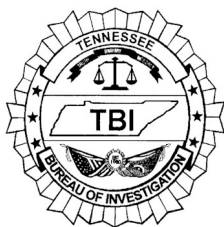
Analytically pipette 1000 uL of 1000 ppm As, Cd, Cu, and Pb standard solutions into a dedicated 100 mL volumetric flask (non-glass). Make to volume with 1% nitric acid. Analytically transfer to a dedicated storage container labeled with date and initials. Document the solution in the reagent log. This solution is stable for approximately six months. This solution will contain 10.0 ppm As, Cd, Cu, and Pb.

P/A Working Solution

Analytically pipette 1000 uL of P/A stock solution into dedicated 100 mL volumetric flask (non-glass). Make to volume with 1% nitric acid. Analytically transfer to a dedicated storage container labeled with date and initials. Document the solution in the reagent log. This solution is stable for approximately two months. This solution will contain 100 ppb As, Cd, Cu, Pb. Masses to be monitored are: ^{75}As , ^{63}Cu , ^{114}Cd , and ^{208}Pb .

Stock Standard Solution

1. Analytically pipette 400.0 uL of 1000 ppm As and Pb solutions into a dedicated 100 mL volumetric flask (non-glass). Analytically pipette 200.0 uL of 1000 ppm Cd solution into the same dedicated 100 mL volumetric flask (non-glass). Make to volume with 1% nitric acid. Analytically transfer to a dedicated storage container labeled with date and initials. Document the solution in the reagent log. This solution is stable for approximately six



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months. This solution will contain 4.0ppm As and Pb; and 2.0 ppm Cd.

2. Prepare an identical Stock Standard Solution using 1000 ppm As, Cd, and Pb from a second source. Properly label and document the solution as above.

50% Ethanol

Prepare equal parts ACS grade ethanol and high purity water in a polypropylene tube.

6.4.3 Procedural and Chemical Precautions – See section 6.0 of this manual for safety precautions.

6.4.4 Limitations

Concentration cut-offs are determined from a review of drinking water standards established by EPA, WHO, and EU for acceptable levels of As, Cd, Cu, and Pb. The following will be used as cut-offs for this procedure.

- As – present when concentration is above 10 ppb,
- Cd – present when concentration is above 5 ppb,
- Cu – present when concentration is above 2000 ppb,
- Pb – present when concentration is above 15 ppb.

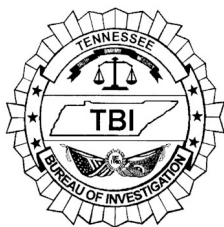
Some legally produced whiskeys may contain copper above the cut-off concentration.

6.4.5 Procedure -

A blank shall be analyzed before each sample. The blank shall be prepared as outlined for S1 under Analytical Standards. These blanks will be considered the negative controls.

Analytical Standards

Label four polypropylene tubes as: S1, S2, S3, and S4. Prepare analytical standards as outlined below:



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<u>Std</u>	<u>ISTD</u>	<u>50% Ethanol</u>	<u>As, Cd, & Pb Std</u>	<u>1000 ppm Cu Std</u>	<u>1% Nitric Acid</u>
S1	50 uL	1000 uL	0.0 uL	0.0 uL	8950 uL
S2	50 uL	1000 uL	50.0 uL	10.0 uL	8890 uL
S3	50 uL	1000 uL	100.0 uL	20.0 uL	8830 uL
S4	50 uL	1000 uL	250.0 uL	50.0 uL	8650 uL

Pipet the above volumes into the pre-labeled tubes, tightly cap, and vortex.

If the samples are known to contain significantly less than 50% ethanol, the 50% ethanol solution will be changed to a percentage that approximates the amount of ethanol in the samples.

Amounts are listed below for each standard in micrograms per liter (ppb) as prepared above:

	<u>S1</u>	<u>S2</u>	<u>S3</u>	<u>S4</u>
As & Pb	0.0 ppb	20.0 ppb	40.0 ppb	100.0 ppb
Cd	0.0 ppb	10.0 ppb	20.0 ppb	50.0 ppb
Cu	0.0 ppb	1000.0 ppb	2000.0 ppb	5000.0 ppb
ISTD	50.0 ppb	50.0 ppb	50.0 ppb	50.0 ppb

Calibration Verification

Label a polypropylene tube as CV. Pipette the following into the tube:

50 uL ISTD
1000 uL 50% Ethanol
100 uL Second Source Stock Standard Solution
20.0 uL Second Source 1000 ppm Cu Standard
8830 uL 1% Nitric Acid

Tightly cap and vortex the tube. If the samples are known to contain significantly less than 50% ethanol, the 50% ethanol solution will be changed to a percentage that approximates the amount of ethanol in the samples.

This solution will contain 40.0 ppb of As and Pb, 20.0 ppb of Cd, 2000.0 ppb of Cu and 50.0 ppb of ISTD. It will be used as a calibration verification sample and considered the positive control. Reported values must be +/- 20% of expected values. This sample will be analyzed at the beginning and end of the run,



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Sample Preparation

Prepare samples by pipeting the following into a properly labeled polypropylene tube:

- 50 uL ISTD solution
- 1000 uL of sample liquid
- 8950 uL of 1% nitric acid.

Cap tightly and vortex. Use a dilution factor of 10 in the sequence table.

In samples involving high dissolved solids, it will be necessary to dilute the sample more than described above by adjusting the amount of sample and the amount of 1% nitric acid. Document the dilution in case notes and matrix match the standards so that the amount of alcohol in the sample equals the amount in the standards. Note the dilution factor for use in the sequence table below.

Some samples may require an acid digestion prior to analysis. Pipette 1000 uL of sample into a polypropylene tube and add 1000 uL of concentrated nitric acid. Allow mixture to stand overnight. Add 8.0 mL of water. Vortex the sample. Prepare analysis samples by pipeting the following into a properly labeled polypropylene tube:

- 50 uL ISTD solution
- 1000 uL of digested liquid sample
- 8950 uL of water.

Cap tightly and vortex. Use a dilution factor of 100 in the sequence table.

Analysis

Place each pre-labeled plastic tube into the autosample tray. Arrange them so that the calibration verification and each sample are preceded by a blank.

Create a sequence table for all the blanks, samples and the calibration standard solutions. For each sample, enter the appropriate dilution factor for the sample, usually 10.

Prepare a calibration table using the above concentration data for the standard solutions.



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The method used to analyze the samples is Mshine.m. The critical parameters for this analysis are as follows:

Element masses monitored

63, 69, 75, 77, 114, 115, 206-208, 209

Tune file used – he.u

Interference equations used

$(75)^*1 - (77)*0.55$

$(208)^*1 + (206)^*1 + (207)^*1$

Run the sequence. Instrumental data is reported in ppb. Use the cutoff concentrations to determine if the element is absent or present.

6.5 Instruments and Equipment

1. Inductively Coupled Plasma Mass Spectrometer
2. Vortex
3. 10-100uL pipette and polypropylene pipette tips
4. 100-1000uL pipette and polypropylene pipette tips
5. 500uL pipette and polypropylene pipette tips
6. 0.5-5mL pipette and polypropylene pipette tips
7. 2-10uL pipette and polypropylene pipette tips
8. 15mL polypropylene tubes

6.6 Measurement Traceability

Certified element standards are traceable to NIST standards. Pipettes are calibrated yearly to NIST standards.

6.7 Reference Materials -

ICP-MS grade certified standards of As, Bi, Cd, Cu, In, Ga, Pb

6.8 Reports -

The following are possible results concluded from the examination:

Analysis of this exhibit revealed the presence of (list elements present).

Analysis of this exhibit did not reveal the presence of (list elements absent).

If copper is present, include the following note:

It should be noted that some legally produced alcoholic beverages may contain copper.