Determination of Metals in Alcoholic Beverages by ICP-MS

Scope and Application

This method will be used for the determination of metals in alcoholic beverages such as wines, distilled spirits, and malt beverages using inductively coupled plasma mass spectrometry (ICP-MS). This method is applicable to samples containing 0-100% alcohol by volume.

At the time of this revision, chromium, cobalt, nickel, copper, arsenic, selenium, cadmium, antimony, cesium, thallium, lead, and uranium are included.

Samples with high levels of solids, such as crème liquors, should not be analyzed using this method. A special sample preparation scheme is needed for samples of this type.

Regulatory Tolerances

The tolerance levels of these elements are determined based on regulations enforced by the Environmental Protection Agency (EPA), United States Food and Drug Administration (USFDA) and Alcohol and Tobacco Tax and Trade Bureau (TTB).

Levels and Limitations

a. Instrument Levels and Limitations

Instrument Levels and Limitations			
	Linear Range	**Limit of Detection**	**Limit of Quantitation**
Cr_{52}	0.5 to 50 ppb	0.02 ppb	0.07 ppb
Co_{59}	0.5 to 50 ppb	0.01 ppb	0.04 ppb
Ni_{60}	1.0 to 50 ppb	0.28 ppb	0.94 ppb
Cu_{63}	1.0 to 50 ppb	0.19 ppb	0.64 ppb
Cu_{65}	1.0 to 50 ppb	0.18 ppb	0.59 ppb
As_{75}	0.5 to 50 ppb	0.01 ppb	0.05 ppb
Se_{82}	0.5 to 50 ppb	0.02 ppb	0.08 ppb
Cd_{111}	0.5 to 50 ppb	0.02 ppb	0.06 ppb
Sb_{121}	0.5 to 50 ppb	0.04 ppb	0.14 ppb
Cs_{133}	0.5 to 50 ppb	0.01 ppb	0.03 ppb
Tl_{205}	0.5 to 50 ppb	0.01 ppb	0.02 ppb
Pb_{207}	0.5 to 50 ppb	0.06 ppb	0.20 ppb
U_{238}	0.5 to 50 ppb	0.01 ppb	0.03 ppb

b. Method Levels and Limitations

Method Levels and Limitations *			
	Linear Range	**Limit of Detection**	**Limit of Quantitation**
Cr_{52}	10 to 1000 ppb	0.42 ppb	1.39 ppb
Co_{59}	10 to 1000 ppb	0.22 ppb	0.71 ppb
Ni_{60}	20 to 1000 ppb	2.85 ppb	9.41 ppb
Cu_{63}	20 to 1000 ppb	1.95 ppb	6.42 ppb
Cu_{65}	20 to 1000 ppb	1.79 ppb	5.89 ppb
As_{75}	10 to 1000 ppb	0.28 ppb	0.92 ppb
Se_{82}	10 to 1000 ppb	0.49 ppb	1.62 ppb
Cd_{111}	10 to 1000 ppb	0.36 ppb	1.19 ppb
Sb_{121}	10 to 1000 ppb	0.84 ppb	2.77 ppb
Cs_{133}	10 to 1000 ppb	0.17 ppb	0.58 ppb
Tl_{205}	10 to 1000 ppb	0.15 ppb	0.49 ppb
Pb_{207}	10 to 1000 ppb	1.19 ppb	3.91 ppb
U_{238}	10 to 1000 ppb	0.17 ppb	0.58 ppb
* Assuming a 1 to 20 dilution is performed			

Supplemental Documents

1. **Form:SSD:513:001** ICP-MS Daily Log (Formerly BAL:Form:513-1)
2. **Form:SSD:513:002** ICP-MS LCS Control Record (Formerly BAL:Form:513-3)
3. **Form:SSD:513:004** ICP-MS Standards Log Record (Formerly BAL:Form:302-4)
4. **WG:SSD:513:001** Reagents and Sample Preparation and Handling for SSD:TM:513 (Formerly SSD:WG:513)
5. **Form:ICPMS:004** ICP-MS Daily Maintenance Perkin Elmer Nexion (NLC_4_016) (Formerly NLC:Form:514)
6. **Form:ICPMS:005** Argon Dewar Installation (Formerly TL:Form:525-8)
7. **Form:ICPMS:006** ICP-MS Daily Performance Record (NLC_4_016) (Formerly TL:Form:525-10)
8. **Form:ICPMS:007** Cell Gas Installation (Formerly TL:Form:525-11)
9. **Form:ICPMS:008** ICP-MS Chiller Verification
10. **WG:SSD:1040:004** Procedure for Degassing Beer and Wine (Formerly SSD:WG:115)

Equipment

1. **Perkin-Elmer NexION 2000 C ICP-MS** Inductively Coupled Plasma Mass Spectrometer or equivalent.
2. ESI SC4 DXCi Autosampler or equivalent

Instrument Conditions and Method Parameters

Note: Some of these values are approximations, some can change depending on the tuning of the instrument.Nebulizer	Concentric PFA-ST or Glass (Sea Spray DC nebulizer) with 0.4 mL/min uptake
Spray Chamber	Glass Cyclonic
Sampler, Skimmer Cone and Hyper Skimmer Cone	Nickel or Platinum (Hyper Skimmer is aluminum)
RF Power	1600 W
Plasma gas flow rate	15.0 L/min
Nebulizer gas flow rate	0.85-1.1 mL/min
Auxiliary gas flow rate	1.0 – 1.20 L/min
Sample uptake flow rate	0.4 mL/min
RPQ	0.25
Sweeps/reading	20
Readings/Replicate	1
Replicates	3
Dwell time	50 ms per AMU
Mode of analysis	Helium KED
Measurement Units	Counts per Second (CPS)

Signal Processing:

Detector	Dual
Process Spectral Peak	Average
QID	On
Isotope Ratio Mode	Off
Blank Subtraction	After Internal Standard
Process Signal Profile	Average
Baseline Readings	0
Apply Smoothing Factor	5

Interferences

1. Some metals, including arsenic, have strong Ar-Cl interferences that require correction compensation in the software.
2. Alcohol and other sources of carbon will interfere with metals analysis. Interference is minimized by preparation of standards in a similar carbon matrix. The addition of a small percentage of ethanol might be necessary to mitigate these carbon related interferences.
3. Some known interferences can be compensated using correction equations in the processing method.

Elements Monitored

Element	Mass	Mode
Cr	52	KED
Co	59	KED
Ni	60	KED
Cu	63 65	KED KED
As	75	KED
Se	82	KED
Cd	111	KED
Sb	121	KED
Cs	133	KED
Tl	205	KED
Pb	207	KED
U	238	KED

Internal Standards

The internal standard pairings at the time of this revision are:

Internal Standard	Elements grouped with this Internal Standard
Sc-45	Cr, Co, Ni, Cu (63, 65), As, Se
Y-89	Cd
In-115	Sb, Cs, Tl, Pb
Bi-209	U

Note: The internal standard pairings can be changed if necessary. Note any deviations.

Reagents and Sample Preparation and Handling

Please refer to WG:SSD:513:001 Reagents and Sample Preparation and Handling for SSD:TM:513.

Procedures

The instrument should be optimized as per vendor instructions and/or internal guidelines.

Example Sequence Tables

The Perkin-Elmer NexION 2000 C ICP-MS is paired with the ESI SC4 DXCi Autosampler: Standards rack positions 1-9 use 125 mL bottles; positions 101-121 on rack 1 and positions 201-221 on rack 2 use 50 mL conical tubes, positions 301-360 on rack 3 and positions 401-460 on rack 4 use 15 mL conical tubes.

Note: The autosampler setup can be modified to accommodate different sample racks if needed.

Example Sequence: The sequence can be modified accordingly depending on the number of samples to be analyzed or any other situation. Some parts of the sequence can only be viewed after clicking "build run list". This example sequence is a combination of the loaded sequence template and the "build run list".

A/S Location	Sample ID	Measurement Action	Method	Sample Type
101	Unspiked Wine (Conditioning)****	Run Diluted Sample	ssd tm 513_20x.mth	Sample
101	Unspiked Wine (Conditioning)****	Run Diluted Sample	ssd tm 513_20x.mth	Sample
101	Unspiked Wine (Conditioning)****	Run Diluted Sample	ssd tm 513_20x.mth	Sample
1	Method Blank	Run Diluted Sample	ssd tm 513_20x.mth	Sample
1	Method Blank	Run Blanks, Standards and diluted Samples	ssd tm 513_20x.mth	Sample
1	Calibration Blank		ssd tm 513_20x.mth	Blank
9100	0.5 ppb Calibration Standard #1		ssd tm 513_20x.mth	Standard
9050	1.0 ppb Calibration Standard #2		ssd tm 513_20x.mth	Standard
9010	5.0 ppb Calibration Standard #3		ssd tm 513_20x.mth	Standard
9002	25.0 ppb Calibration Standard #4		ssd tm 513_20x.mth	Standard
9	50.0 ppb Calibration Standard #5		ssd tm 513_20x.mth	Standard
1	Method Blank **	Run Diluted Sample	ssd tm 513_20x.mth	Sample
7010	5 ppb Std Check (2nd Source) **	Run Sample	ssd tm 513_20x.mth	Sample
1	Method Blank **	Run Diluted Sample	ssd tm 513_20x.mth	Sample
301	Unspiked LCS (unspiked Wine) *	Run Diluted Sample	ssd tm 513_20x.mth	Sample
1	Method Blank	Run Diluted Sample	ssd tm 513_20x.mth	Sample
302	LCS-1* (spiked LCS)	Run Diluted Sample	ssd tm 513_20x.mth	Sample
1	Method Blank	Run Diluted Sample	ssd tm 513_20x.mth	Sample
7010	5 ppb Standard (2nd Source Accuracy)	Run Sample	ssd tm 513_20x.mth	Sample
1	Method Blank	Run Diluted Sample	ssd tm 513_20x.mth	Sample
8010	5 ppb Standard (2nd Source Precision) ***	Run Sample	ssd tm 513_20x.mth	Sample
1	Method Blank	Run Diluted Sample	ssd tm 513_20x.mth	Sample
7010	5 ppb Standard (2nd Source) **	Run Sample	ssd tm 513_20x.mth	Sample
1	Method Blank	Run Diluted Sample	ssd tm 513_20x.mth	Sample
303	Sample	Run Diluted Sample	ssd tm 513_20x.mth	Sample
304	Sample	Run Diluted Sample	ssd tm 513_40x.mth	Sample
305	Sample	Run Diluted Sample	ssd tm 513_50x.mth	Sample
306	Sample	Run Diluted Sample	ssd tm 513_100x.mth	Sample
1	Method Blank	Run Diluted Sample	ssd tm 513_20x.mth	Sample
7010	5 ppb Std Check (2nd Source) **	Run Sample	ssd tm 513_20x.mth	Sample
1	Method Blank	Run Diluted Sample	ssd tm 513_20x.mth	Sample

* The unspiked LCS (unspiked Wine) will be placed before LCS 1 (spiked LCS). The spiked LCS does not have to be placed in any particular spot.

** Method Blank/2nd Source Check Standard can be placed in additional positions if necessary.

*** The 2nd source check for precision can be placed in any other position in the sequence.

**** The Unspiked wine (Conditioning) injections are placed at the beginning of the run (Recommended by ESI).

Quality Control

1. The sequence should start with 2-3 injections of wine to condition the system and cones. When a run is stopped and re-started, it is best to condition the system with a wine. These are also used to ensure all air bubbles have been removed from the pump tubing from the autosampler to the nebulizer. The method blank is the "blank" analyzed as a sample. The calibration curve begins with a calibration blank, which is subtracted from all samples and standards.
2. A linear calibration curve will be used. The correlation coefficients of the calibration curves should be 0.99 or above for all elements.
3. The 5 ppb second source standard is analyzed as a check for accuracy. It will be analyzed in duplicate as a check for precision. The values should fall within the accepted values of the control charts for the four monitored elements- Copper, Arsenic, Cesium and Lead.
4. The unspiked LCS (unspiked wine) and LCS (spiked LCS) will be analyzed, and the percent recovery will be checked and should be within 70 -130 % recovery for the four monitored elements Copper, Arsenic, Cesium and Lead.
5. Run the 2nd source check standard after the calibration is completed, at least once every 10 samples and at the end of the sequence. Values for this standard should be within ±30% of the expected value for all elements (between 3 and 7 ppb).
6. **Each occurrence of a failure for accuracy requires a CAR be initiated.** Refer to **SSD:QPD:2020** for additional instructions.
    a. If any of the four monitored elements in the 5 ppb second source standard for accuracy check fail, then:
        i. Re-run the sequence, if all the values pass the second time, report all the results from the 5 ppb second source standard and the sample data.
        ii. If any value(s) fail a second time, do not report any results and pause the sequence (if possible). Inspect the different components of the instrument to see if the cause of the failure can be identified. Prepare a new 50 ppb multi-element second source stock standard (or both if needed) and re-run the sequence if time allows and if enough argon is left in the tank.
        iii. If all the new values pass, then report all the results from the 5 ppb second source standard and the sample data. If any of the values fail, do not report any results. Verify the instrument before shutdown, if no obvious reason for the failure can be identified shut down the instrument and inspect the different components to see if the cause of the failure can be identified.
        iv. Tag out the instrument and contact the spectrometers instrument team if the cause of the failure cannot be identified.
        v. For precision failures the CAR can be logged in as an incident report (refer to SSD:QPD:3100).

b. For 5 ppb second source check:

i. Values for this standard should be within ±30% of the expected value (between 3 and 7 ppb for all elements).

ii. If any value is outside this range re-run the sequence with the samples from the corresponding bracket, if time allows. If all values pass continue the analysis. If any value is still outside the allowed range pause the sequence (if possible). Inspect the different components of the instrument to see if the cause of the failure can be identified. Prepare a new 50 ppb multi-element second source stock standard and re-run the sequence with the samples from the corresponding bracket. If all values are ok continue the analysis. If any value is still outside the allowed range shut down the instrument and inspect the different components to see if the cause of the failure can be identified.

Note: Any samples contained in a bracket with passing second source results can be reported.

iii. Tag out the instrument and contact the spectrometers instrument team if the cause of the failure cannot be identified.

7. It is recommended that the internal standard variation (ion counts) be 100% ± 30%. However, the results can be reported if the LCS recovery is within 70 – 130% and 2nd source standard checks are within ±30% of the expected value.

8. A method blank should be run at least every 10 samples to check for carryover.

9. The following items should be submitted with sample data.

a. Calibration curves and standards results.

b. 5 ppb second source standard checks, calibration blank and method blanks.

c. LCS and 5 ppb second source check data (accuracy and precision).

Sources of Measurement Uncertainty:

Pipetting
Cross-contamination

Calculations

$$LCS\ Recovery\ (\%) = \frac{Spiked\ LCS\ value\ (ppb) - Unspiked\ LCS\ value\ (ppb)\ x\ 100}{Added\ amount\ (ppb)}$$

Reporting Results

- Values should be reported to the nearest whole number (X ppb).
- If necessary, include a statement regarding how the methodological measurement uncertainty is determined. For example, "The methodological measurement uncertainty is calculated on the basis of 100 ppb spike recoveries of the LCS elements."

Safety Notes

Consult the SDS for any chemicals used that are unfamiliar. All chemicals should be considered hazardous and avoid direct physical contact.

Required Training, Certification, and Re-certification

1. In-house training by a certified chemist in the theory and operation of ICPMS, including software, maintenance, and troubleshooting.
2. Analyst has demonstrated competency after successfully obtaining 7 replicates of an unknown within the QC acceptance limits. (Prepare 7 spiked LCS samples and one unspiked LCS).
3. Chemists will be recertified periodically using proficiency test results and/or re-demonstration of competency.

Revision History

Rev. 1 – method converted from a "TMD" to a "TM". Changes in bold italics represent edits from the draft method to the final TM. (4/11/2013)

Rev. 2 – included samples with higher alcohol content. Separated out the reagent and sample preparation and handling into a separate working guideline. Added "Related Documents" section.

Rev. 3 – changes to linear range, LOD, LOQ for copper (63 and 65) and nickel; addition of statement to narrative for measurement uncertainty in Reporting Results.

Rev. 4 – changes to Instrument linear range for Copper (63 and 65) and Nickel; addition to Quality Control Section regarding reporting the LCS.

Rev. 5 – Linear Ranges for Nickel and Copper (63 and 65) updated; Sources of Uncertainty section added.

Rev. 6 – Equipment section updated to reflect new instrumentation; Mode changed to KED in the Elements Monitored table; and updates made to Quality Control section.

Rev. 7 – Add additional supplemental documents. Add new Perkin Elmer Nexion 2000 ICP-MS, remove old Nexion ICP-MS. Edit instrument conditions and parameters for both instruments. Edit example sequence table and quality control sections.

Rev. 8 – Add additional supplemental documents. Edit instrument conditions, parameters, and signal processing for both instruments. Add information about carbon related interference mitigation. Edit example sequence tables and added clarifications to Quality Control section. Added information for competency requirements.

Rev. 9 – Document reference ids changed to the new document id structure.

Rev. 10 – Removed retired document references. Last of the document reference IDs changed to the new document ID structure. Removed all references related to the Thermo Scientific iCap Q ICP-MS. Update nebulizer, spray chamber and sample uptake. In safety notes changed MSDS to SDS. Fixed autosampler rack positions. Added note that it can be modified if needed. Made corrections to sequence example. Updated quality control section to align with the use of control charts and the Perkin Elmer Nexion 2000 C ICP-MS. Deleted sequence template from the items to be submitted with sample data.