# ANALYSIS OF METALS USING THE THERMO ICAP INDUCTIVELY COUPLED PLASMA MASS SPECTROMETER (ICP-MS)

## TABLE OF CONTENTS

1. SCOPE AND APPLICATION 1
2. SUMMARY OF THE METHOD 3
3. INTERFERENCES 3
4. APPARATUS AND EQUIPMENT 4
5. STANDARDS AND CHEMICALS 6
6. SAMPLE COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE 9
7. SAMPLE PREPARATION PROCEDURE 10
8. SAMPLE ANALYSIS/QUANTITATION 10
9. DATA ARCHIVAL 15
10. QUALITY CONTROL 16
11. SAFETY/HAZARDOUS WASTE MANAGEMENT 17
12. TROUBLESHOOTING 17
13. MAINTENANCE 18
14. REFERENCES 19

## APPENDICES

A. Acquisition Parameters 21
B. Method Parameters 23
C. ICP-MS iCAP Q STD and KED Performance Report Limits 25
D. ICP-MS iCAP RQ STD and KED Performance Report Limits 26
E. Appendix of Significant Changes 26

## 1. SCOPE AND APPLICATION

1.1 This standard operating procedure (SOP) outlines the analysis of samples and sample digestates using Thermo iCAP (models Q and RQ) inductively coupled plasma mass spectrometry (ICP-MS).

1.2 The Florida Department of Environmental Protection Central Laboratory (DEP) analyzes for 21 elements using EPA method 200.8 (Revision 5.4) for test IDs W-ICPMS and W-ICPMS-F in aqueous and saline/estuarine matrices.


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| | Analyte | Method | NELAP approval | Matrices |
|---|---|---|---|---|
| 1 | Al | 200.8 Rev. 5.4 | Yes | aqueous, saline/estuarine |
| 2 | Sb | 200.8 Rev. 5.4 | Yes | aqueous, saline/estuarine |
| 3 | As | 200.8 Rev. 5.4 | Yes | aqueous, saline/estuarine |
| 4 | Ba | 200.8 Rev. 5.4 | Yes | aqueous, saline/estuarine |
| 5 | Be | 200.8 Rev. 5.4 | Yes | aqueous, saline/estuarine |
| 6 | B | 200.8 Rev. 5.4 | No | aqueous, saline/estuarine |
| 7 | Cd | 200.8 Rev. 5.4 | Yes | aqueous, saline/estuarine |
| 8 | Cr | 200.8 Rev. 5.4 | Yes | aqueous, saline/estuarine |
| 9 | Co | 200.8 Rev. 5.4 | Yes | aqueous, saline/estuarine |
| 10 | Cu | 200.8 Rev. 5.4 | Yes | aqueous, saline/estuarine |
| 11 | Gd | 200.8 Rev. 5.4 | No | aqueous, saline/estuarine |
| 12 | Pb | 200.8 Rev. 5.4 | Yes | aqueous, saline/estuarine |
| 13 | Mn | 200.8 Rev. 5.4 | Yes | aqueous, saline/estuarine |
| 14 | Mo | 200.8 Rev. 5.4 | Yes | aqueous, saline/estuarine |
| 15 | Ni | 200.8 Rev. 5.4 | Yes | aqueous, saline/estuarine |
| 16 | Se | 200.8 Rev. 5.4 | Yes | aqueous, saline/estuarine |
| 17 | Sr | 200.8 Rev. 5.4 | No | aqueous, saline/estuarine |
| 18 | Ag | 200.8 Rev. 5.4 | Yes | aqueous, saline/estuarine |
| 19 | Tl | 200.8 Rev. 5.4 | Yes | aqueous, saline/estuarine |
| 20 | Zn | 200.8 Rev. 5.4 | Yes | aqueous, saline/estuarine |
| 21 | U | 200.8 Rev. 5.4 | No | aqueous, saline/estuarine |

1.3 Samples are also analyzed using EPA method 6020A for 20 elements for tests W-ICPMS-R, S-ICPMS, T-ICPMS, TCLP-ICPMS, SPLP-ICPMS, and S-ICPMS-TO in aqueous, biological tissue, chemical waste, and solid matrices.

| | Analyte | Method | NELAP approval | Matrices |
|---|---|---|---|---|
| 1 | Al | 6020A | No | aqueous, biological tissue, chemical waste, solids |
| 2 | Sb | 6020A | Yes* | aqueous, biological tissue, chemical waste, solids |
| 3 | As | 6020A | Yes* | aqueous, biological tissue, chemical waste, solids |
| 4 | Ba | 6020A | Yes* | aqueous, biological tissue, chemical waste, solids |
| 5 | Be | 6020A | Yes* | aqueous, biological tissue, chemical waste, solids |
| 6 | B | 6020A | No | aqueous |
| 7 | Cd | 6020A | Yes* | aqueous, biological tissue, chemical waste, solids |
| 8 | Cr | 6020A | Yes* | aqueous, biological tissue, chemical waste, solids |
| 9 | Co | 6020A | Yes* | aqueous, biological tissue, chemical waste, solids |
| 10 | Cu | 6020A | Yes* | aqueous, biological tissue, chemical waste, solids |
| 11 | Gd | 6020A | No | aqueous |


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| | | | | |
|---|---|---|---|---|
| 12 | Pb | 6020A | Yes* | aqueous, biological tissue, chemical waste, solids |
| 13 | Mn | 6020A | Yes* | aqueous, biological tissue, chemical waste, solids |
| 14 | Mo | 6020A | Yes* | aqueous, biological tissue, chemical waste, solids |
| 15 | Ni | 6020A | Yes* | aqueous, biological tissue, chemical waste, solids |
| 16 | Se | 6020A | Yes* | aqueous, biological tissue, chemical waste, solids |
| 17 | Sr | 6020A | No | aqueous |
| 18 | Ag | 6020A | Yes* | aqueous, biological tissue, chemical waste, solids |
| 19 | Tl | 6020A | Yes* | aqueous, biological tissue, chemical waste, solids |
| 20 | Zn | 6020A | Yes* | aqueous, biological tissue, chemical waste, solids |
| 21 | U | 6020A | No | aqueous |

*Not NELAP approved for the biological tissue matrix.

## 2. SUMMARY OF THE METHOD

2.1 Aqueous samples and sample digestates are arranged on an autosampler. A peristaltic pump passes the liquid sample to the nebulizer. A sample aerosol is generated by the nebulizer. The nebulizer injects the sample aerosol into a Peltier cooled spray chamber which filters out larger aerosol droplets for improved signal stability and low oxide rates. The sample aerosol flows through the injector and into the torch where a radiofrequency plasma causes desolvation, atomization, and ionization. Ions generated in the plasma are transferred from atmospheric pressure to the vacuum region and introduced to the mass spectrometer as an ion beam. A series of lenses focus and accelerate the ion beam to the collision cell. The collision cell contains a quadrupole and is pressurized with a 93 % helium / 7 % hydrogen gas mixture gas for the iCAP Q and helium only for the iCAP RQ. Undesirable molecular ions are removed by kinetic energy discrimination. The ion beam is then introduced into the quadrupole mass analyzer, which filters out ions of specific mass to charge ratio, depending on the RF voltage and DC voltage applied to the quadrupole rods. The ions transmitted through the quadrupole are finally transferred to the dual mode secondary electron multiplier and detected.

## 3. INTERFERENCES

3.1 The primary interferences in ICP-MS are molecular ions such as oxides, doubly charged ions, and isobaric interferences. The interference check solution, IC6020C, is used to assess the effects of a variety of molecular interferences. The acceptable recovery limit for trace metals in IC6020C is 85 – 115 %. The table below lists common interferences observed while analyzing environmental samples. Bold font indicates the isotope reported.

| Target Analyte | Common Interference | Monitor | Correction Based On |
|---|---|---|---|
| **$^{9}Be^{+}$** | | | |
| **$^{11}B^{+}$** | | | |
| **$^{27}Al^{+}$** | | | |


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| | | | |
|---|---|---|---|
| **$^{52}Cr^{+}$** | $^{40}Ar^{12}C^{+}$, $^{35}Cl^{16}O^{1}H^{+}$ | | |
| $^{53}Cr^{+}$ | $^{37}Cl^{16}O^{+}$ | | |
| **$^{55}Mn^{+}$** | | | |
| **$^{59}Co^{+}$** | | | |
| **$^{60}Ni^{+}$** | | | |
| $^{62}Ni^{+}$ | $^{46}Ti^{16}O^{+}$ | $^{47}Ti^{+}$, $^{48}Ti^{+}$ | |
| $^{63}Cu^{+}$ | $^{40}Ar^{23}Na^{+}$, $^{47}Ti^{16}O^{+}$ | | |
| **$^{65}Cu^{+}$** | $^{49}Ti^{16}O^{+}$ | $^{47}Ti^{+}$, $^{48}Ti^{+}$ | |
| **$^{66}Zn^{+}$** | $^{50}Ti^{16}O^{+}$ | $^{47}Ti^{+}$, $^{48}Ti^{+}$ | |
| $^{67}Zn^{+}$ | | | |
| $^{68}Zn^{+}$ | | | |
| **$^{75}As^{+}$** | $^{40}Ar^{35}Cl^{+}$ | $^{40}Ar^{37}Cl^{+}$ | |
| $^{77}Se^{+}$ | $^{40}Ar^{37}Cl^{+}$ | | |
| **$^{78}Se^{+}$** | $^{156}Gd^{2+}$, $^{40}Ar^{38}Ar^{+}$ | $^{83}Kr$, $^{156}Gd$ | $^{83}Kr$, $^{156}Gd$ |
| $^{82}Se^{+}$ | $^{82}Kr^{+}$ | | |
| **$^{88}Sr^{+}$** | | | |
| $^{92}Mo^{+}$ | | | |
| **$^{95}Mo^{+}$** | | | |
| $^{97}Mo^{+}$ | | | |
| $^{98}Mo^{+}$ | $^{98}Ru^{+}$ | | |
| $^{106}Cd^{+}$ | $^{90}Zr^{16}O^{+}$ | | |
| **$^{107}Ag^{+}$** | $^{91}Zr^{16}O^{+}$ | $^{90}Zr^{+}$, $^{91}Zr^{+}$, $^{94}Zr^{+}$ | |
| $^{108}Cd^{+}$ | $^{92}Zr^{16}O^{+}$, $^{92}Mo^{16}O^{+}$ | | |
| $^{109}Ag^{+}$ | | | |
| **$^{111}Cd^{+}$** | $^{95}Mo^{16}O^{+}$ | $^{95}Mo^{+}$ | |
| $^{114}Cd^{+}$ | $^{98}Mo^{16}O^{+}$ | | |
| **$^{121}Sb^{+}$** | | | |
| $^{123}Sb^{+}$ | | | |
| $^{135}Ba^{+}$ | | | |
| **$^{137}Ba^{+}$** | | | |
| $^{158}Gd^{+}$ | | | |
| $^{203}Tl^{+}$ | | | |
| **$^{205}Tl^{+}$** | | | |
| $^{206}Pb^{+}$ | | | |
| $^{207}Pb^{+}$ | | | |
| **$^{208}Pb^{+}$** | Abundance | $^{206}Pb^{+}$, $^{207}Pb^{+}$ | $^{206}Pb^{+}$, $^{207}Pb^{+}$ |
| **$^{238}U^{+}$** | | | |

3.2 To suppress polyatomic spectral interference, the Thermo iCAP Q/RQ employs a QCell (collision cell), along with a low mass cutoff and kinetic energy discrimination (KED).

## 4. APPARATUS AND EQUIPMENT

4.1 Inductively coupled plasma mass spectrometer

4.1.1 Thermo Scientific iCAP Q ICP-MS, serial number 03168R, purchased in 2014.


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4.1.2 Thermo Scientific iCAP RQ ICP-MS, serial number 00090, purchased in 2015.

4.2 Interface: Nickel/Copper Sample cone (part # 3600812), nickel skimmer cone (part # 1311870), and skimmer cone insert (part # 1318480).

4.3 Nebulizer: Perfluoroalkoxy (PFA), part # 1317090.

4.4 Spray chamber: Peltier-cooled quartz cyclonic spray chamber, part # 1317080.

4.5 Torch: Quartz, part # 1230790.

4.5.1 Injector: Quartz (2.5 mm I.D.), part # 1305600.

4.6 Collision Cell gas:

4.6.1 iCAP Q: A mixture of 7 % hydrogen and 93 % helium, purity > 99.996 %, delivered pressure 7 – 14.5 psi.

4.6.2 iCAP RQ: Helium, purity > 99.996 %, delivered pressure 7 – 14.5 psi.

4.7 Autosampler:

4.7.1 iCAP Q: CETAC model ASX-520.

4.7.2 iCAP RQ: Teledyne CETAC model ASX-560.

4.8 Peristaltic Pump tubing

4.8.1 Sample line: orange-green-orange, part # 1320040.

4.8.2 Internal standard line: black-black-black, part # 1320060.

4.8.3 Drain line: gray-gray-gray, part # 1320110.

4.9 Samples and standards are aspirated from 17 x 100 mm polypropylene round-bottom test tubes arranged in the autosampler. Rinse with deionized (DI) water and allow to dry prior to use. Use a Kimwipe to prevent dust from entering the tubes as they dry.

4.10 Chiller: NESLAB ThermoFlex2500. During operation, 21 °C, 36 – 80 psi. Fill with distilled water.

4.11 Argon is supplied to the instrument from the laboratory's MicroBulk argon delivery system. The delivery pressure to the instrument should be 80 – 90 psi.

4.12 Class A volumetric flasks.

4.13 Pipettes

4.13.1 Class A volumetric glass pipettes.

4.13.2 100 µL Eppendorf.

4.13.3 100 – 1000 µL adjustable volume Eppendorf.

4.13.4 2 – 10 mL Finnpipette.

4.14 HF Scientific Inc. MicroTPW Portable Turbidimeter, S/N 201205062.


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## 5. STANDARDS AND CHEMICALS

**Note:** All purchased and prepared standards must be logged into the Laboratory Information Management System (LIMS) standard preparation tracker module. A label must be printed from the standard preparation tracker and the label must be placed on the bottle of standard.

All purchased chemicals (HCl, $HNO_3$, etc.) shall have the received date documented on the bottle.

Save all certificates of analysis for standards and standard reference materials as pdf files in the network location, \\FLDEP1\Lab\Lab5\Chemistry\InorganicPrep\Certificates of Analysis for Reagents and Standards\.

5.1 Trace Metal Grade Nitric Acid ($HNO_3$): The expiration date is provided by the manufacturer. Stored in the fume hood cabinet at room temperature.

5.2 Trace Metal Grade Hydrochloric Acid (HCl): The expiration date is provided by the manufacturer. Stored in the fume hood cabinet at room temperature.

5.3 Rinse Solution: 4 % $HNO_3$ / 3 % HCl. Between samples and while idle, the autosampler probe is parked in the rinse station of the autosampler. The rinse station is filled with the probe rinse solution with an on-board peristaltic pump. Dilute 80 mL of $HNO_3$ and 60 mL of HCl into a 2000 mL container with DI water. The solution expires according to the manufacturer's expiration date of the purchased concentrated acids.

5.4 Acid Rinse Solution: 2 % $HNO_3$ / 1 % HCl. Poured directly into autosampler tubes and analyzed after high concentration samples, between the continuous calibration verification standard (CCV) and the continuous calibration blank (CCB), and at the end of the analytical run. Dilute 20 mL of $HNO_3$ and 10 mL of HCl into a 1000 mL container with DI water. The solution expires according to the manufacturer's expiration date of the purchased concentrated acids.

5.5 Single Element Stock Standards: Purchased from vendors such as SPEX Certiprep, Inorganic Ventures, Exaxol, High Purity, Ricca, and ERA with concentrations of either 1000 mg/L or 10,000 mg/L. Two identical sets are purchased from two different companies. One set is used to prepare calibration standards and the other set is used to prepare the second source calibration verification standard. The expiration dates are assigned by the manufacturer.

5.6 Tune B Tuning Solution (1 µg/L): This solution is used for tuning the ICP-MS in STD and KED mode as well as for running performance reports. Purchased or prepared from single element stock standards. Dilute appropriate volumes of the single element stock standards to 1 L with 2 % $HNO_3$ / 0.5 % HCl to produce a solution with 1 µg/L Ba, Bi, Ce, Co, In, Li and U. This solution may be used passed the manufacturer's expiration date as long as the signal produced by the solution is stable.


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5.7 iCAP Q Setup solution: For performing the detector cross-calibration, detector voltage optimization, and mass calibrations. The setup solution can be purchased or prepared in the laboratory by diluting appropriate volumes of the single element stock standards to 1 L with 2 % $HNO_3$ to produce a solution with 3 µg/L of Bi, Ho, Rh, Tb, U, Ce, Cs, In, Ta, and Y; 4 µg/L Ba and Tl; 5 ug/L Sr, 6 µg/L Ag and Mn; 8 µg/L Co, Li, and Sc; 10 µg/L Al, Ga, and Mg; 15 µg/L Cu and Ni; 20 µg/L Zn; 35 µg/L Be. This solution can be used passed the manufacturer's expiration as long as the signal produced by the solution is stable.

5.8 Internal Standard: Dilute appropriate volumes of the single element stock standards to 2 L with 2 % $HNO_3$ to produce a solution with 10 µg/L $^6$Li, Rh, Bi, and Tb; 50 µg/L Sc; 100 µg/L Ga. This standard may be used passed the expiration date of the single element stock standards assigned by the manufacturer as long as a stable signal is produced during analysis. The detector response should be monitored each day and should not change significantly unless instrument maintenance is performed.

5.9 Calibration Standards

5.9.1 Calibration Blank (CCB, Rinse): Prepare by diluting 20 mL of $HNO_3$ and 10 mL of HCl to 1 L. The expiration date of the concentrated acids assigned by the manufacturer shall be used. The solution is also used as a continuous calibration blank every 10 samples. The solution can also be used as a rinse between samples.

5.9.2 ICAP STD 1, CPQLICAP: This standard is prepared at the concentration of the practical quantitation limit (PQL). Dilute appropriate volumes of the single element stock standards to 1 L with 2 % $HNO_3$ / 1 % HCl to produce a solution at the PQL level. The current instrument PQL concentrations can be found on the Laboratory's computer network, \\FLDEP1\DEAR\Labs\Lab5\Chemistry\Common\MDLs_Control_Limits\Metals_Mercury. The expiration date for this standard is the same as the single element stock standards from which it was made.

5.9.3 ICAP STD 2: Dilute appropriate volumes of the single element stock standards to 1 L with 2 % HNO / 1 % HCl to produce a solution with 2 µg/L Tl; 5 µg/L Ag; 10 µg/L Sb, As, Cd, Cr, Co, Cu, Mn, Ni, Se, Zn, Be, B, Pb, Mo, and U; 15 µg/L Ba; 50 µg/L Sr; 75 µg/L Al. The expiration date for this standard is the same as the single element stock standards from which it was made.

5.9.4 ICAP STD 3, ICAPCCV: Dilute appropriate volumes of the single element stock standards to 1 L with 2 % $HNO_3$ / 1 % HCl to produce a solution with 10 µg/L Tl; 25 µg/L Ag; 50 µg/L As, Cd, Cr, Co, Cu, Mn, Ni, Se, Zn, Sb, Be, B, Pb, Mo, and U; 75 µg/L Ba; 250 µg/L Sr; 375 µg/L Al. The expiration date for this standard is the same as the single element stock standards from which it was made.


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5.9.5 ICAP STD 4: Dilute appropriate volumes of the single element stock standards to 1 L with 2 % $HNO_3$ / 1 % HCl to produce a solution with 40 µg/L Tl; 200 µg/L Ag; 400 µg/L As, Cd, Cr, Co, Cu, Mn, Ni, Se, Zn, Sb, Be, B, Pb, Mo, and U; 600 µg/L Ba; 2000 µg/L Sr; 3000 µg/L Al. The expiration date for this standard is the same as the single element stock standards from which it was made.

5.10 ICAPMETC: This is the second source standard used to verify the calibration. This standard must be prepared with second source standards (single element stock standards different from the standards used to prepare the calibration standards). Dilute appropriate volumes of the single element stock standards to 1 L with 2 % $HNO_3$ / 1 % HCl to produce a solution with 10 µg/L of Tl; 100 µg/L Ag, As, Cd, Cr, Co, Cu, Mn, Ni, Se, Zn, Sb, Be, B, Pb, Mo, U, Ba, Sr, and Al. The expiration date for this standard is the same as the single element stock standards from which it was made.

5.11 CPQLICAP#: This is a calibration check standard at the PQL level. It is analyzed after every calibration. A suffix is added to the CPQLICAP abbreviation (e.g. 7, 8, etc.) to indicate the current PQL solution used. Dilute appropriate volumes of the single element stock standards to 1 L with 2 % $HNO_3$ / 1 % HCl to produce a solution at the PQL level. The current instrument PQL concentrations can be found on the Laboratory's computer network, \\FLDEP1\DEAR\Labs\Lab5\Chemistry\Common\MDLs_Control_Limits\Metals _Mercury. The expiration date for this standard is the same as the single element stock standards from which it was made.

5.12 DPQLICAP#: This is the PQL check standard for the digested water matrix. It is prepared at 50x the PQL concentration for digested water samples. A suffix is added to the DPQLICP abbreviation (e.g. 7, 8, etc.) to indicate the current PQL solution used. Dilute appropriate volumes of the single element stock standards to 1 L with 2 % $HNO_3$ / 1 % HCl to produce a solution at 50x the PQL level of digested water samples. The current digested water sample PQL concentrations can be found on the Laboratory's computer network, \\FLDEP1\DEAR\Labs\Lab5\Chemistry\Common\MDLs_Control_Limits\Metals _Mercury. The expiration date for this standard is the same as the single element stock standards from which it was made.

5.13 SDPQLICAP#: This is the PQL check standard for digested sediment, tissue, and waste samples. It is prepared at 250x the PQL concentration for digested sediment, tissue, and waste samples. A suffix is added to the SDPQLICAP abbreviation (e.g. 1, 2, etc.) to indicate the current PQL solution used. Dilute appropriate volumes of the single element stock standards to 1 L with 2 % $HNO_3$ / 1 % HCl to produce a solution at 250x the PQL level of digested sediment, tissue, and waste samples. The current digested sediment, tissue, and waste PQL concentrations can be found on the Laboratory's computer network, \\FLDEP1\DEAR\Labs\Lab5\Chemistry\Common\MDLs_Control_Limits\Metals


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_Mercury. The expiration date for this standard is the same as the single element stock standards from which it was made.

5.14 Interference Check Solution (IC6020C): This interference check solution is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of interference correction. Chloride in the solution provides a means to evaluate collision cell removal of chloride-related interferences such as $^{40}Ar^{35}Cl^{+}$ on $^{75}As^{+}$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to remove various molecular-ion isobaric interferences. The IC6020C solution must be analyzed as a calibration check prior to analyzing samples and every 12 hours during the analysis. This standard is typically prepared from two intermediate standards.

5.14.1 ICS Solution A: The interferences intermediate solution, which includes Mo and Ti at 20 mg/L; Al, Mg, P, K, and S at 1000 mg/L; C at 2000 mg/L; Fe and Na at 2500 mg/L; Ca at 3000 mg/L; and Cl at 21215 mg/L, can be purchased from SPEX Certiprep or High Purity (concentrations may vary). The interferences intermediate can also be prepared in the laboratory from single element stock standards and various concentrated acids. The expiration date is assigned by the manufacturer (if prepared, the expiration date of the single element stock standards/acids shall be used).

5.14.2 The trace elements in the IC6020C solution include As, Cd, Cr, Co, Cu, Ni, Se, Zn, and Ag at 20 µg/L and Mn at 100 µg/L. Prepare the intermediate solution by diluting appropriate volumes of the single element stock standards with 2 % $HNO_3$ / 1 % HCl to produce a solution with 50 mg/L of As, Cd, Cr, Co, Cu, Ni, Se, and Zn; 250 mg/L Mn. The expiration dates of the single element stock standards shall be used.

5.14.3 The two intermediates described in 5.14.1 and 5.14.2 are combined to prepare the IC6020C standard. Prepare the working standard by diluting appropriate volumes of the intermediate standards with 2 % $HNO_3$ / 1 % HCl to produce a solution with 2120 mg/L Cl; 300 mg/L Ca; 250 mg/L Na and Fe; 200 mg/L C; 100 mg/L Al, Mg, P, K, and S; 2 mg/L Mo and Ti; 100 µg/L Mn; 20 µg/L As, Cd, Cr, Co, Cu, Ni, Se, Ag, and Zn. Concentrations of interferences may vary by vendor.

## 6. SAMPLE COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

6.1 All samples are stored in the DEP Central Laboratory's Receiving Room. The sample pH for water matrices is checked upon arrival at the laboratory by receiving room staff to ensure the pH is less than 2. Samples consisting of water matrices are stored at room temperature and samples consisting of solid matrices


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are stored in one of the receiving room refrigerators as many of these samples also require organic analyses, which require refrigeration.

## 7. SAMPLE PREPARATION PROCEDURE

**Note:** Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples analyzed by direct analysis. The total recoverable sample digestion procedure, DEP SOP MT-024, is suitable for the determination of silver in aqueous solutions up to 100 µg/L. For samples with concentrations higher than 100 µg/L, the sample should be re-digested using a sample volume that will result in a silver concentration in the digestate of less than 100 µg/L.

Solid or waste samples prepared according to DEP SOP MT-060 that contain silver concentrations greater than 500 µg/L should be treated similarly.

7.1 Filtered water samples (Test ID: W-ICPMS-F): For undigested, filtered and acidified samples, which are checked out directly from the custody room, prepare matrix spikes and laboratory fortified blanks (LFBs) by pipetting 50 µL of the water spike HW6A and 50 µL of the water spike HW6B into a 10 mL centrifuge tube containing 10 mL of either sample (matrix spike) or the blank solution of 2 % $HNO_3$ / 1 % HCl (LFB). Mix thoroughly. Each batch of up to 20 samples must contain at least one matrix spike for every 10 samples (two different samples are spiked for batches that contain more than 10 samples) and one set of matrix spike duplicates. One LFB is required for each batch. A PQL check is also prepared for each batch of filtered water samples by pouring the instrument CPQLICP# solution into an analysis tube. See DEP SOP MT-061 for HW6A and HW6B preparation details.

7.2 Unfiltered, digested water samples: See DEP SOP MT-024 for preparation details.

**Note:** Where EPA Method 200.8 Rev. 5.4 is approved for the determination of metals in drinking water, samples may be analyzed directly without acid digestion if the samples have been properly preserved with acid and have turbidity of < 1 NTU at the time of analysis. This includes aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, copper, lead, manganese, nickel, selenium, thallium, and zinc.

7.3 Solid Samples (soils, sediments, and wastes): See DEP SOPs MT-060 for details of total recoverable metals preparation and DEP SOP MT-063 for details of total metals determination preparation. All samples and batch QC are diluted by a factor of 5.

7.4 TCLP and SPLP samples: See DEP SOP MT-068 for TCLP extractions and SPLP extractions. All samples and batch QC are diluted by a factor of 5.

## 8. SAMPLE ANALYSIS / QUANTITATION


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**Note:** Read the iCAP Q / RQ Operating Manual and the iCAP Q / RQ Software Manual to assist in the operation of the ICP-MS.

8.1 Instrument Startup: The following steps should be followed if the main power switch is off and the vacuum is vented.

8.1.1 Switch the main power switch to position 'On'.

8.1.2 Start the vacuum system in the Instrument Control window.

8.1.2.1 Click 'On' in the vacuum submenu.

8.1.2.2 Wait for the turbomolecular pump to reach at least a frequency of 800 Hz.

8.1.3 Check the vacuum. The vacuum pressure is correct when the vacuum LED is green.

8.1.4 If the vacuum was vented, the detector should not be calibrated regardless of whether it was changed or not.

8.2 Lighting the Plasma

8.2.1 Make sure the peristaltic pump tubing is not clogged and the collars are secured on the brackets.

8.2.2 Make sure the oil level in the forepump is at the appropriate level.

8.2.3 Make sure there is an adequate supply of the Rinse solution in the carboy.

8.2.4 Make sure the waste container is not full. The acidic waste can be poured down the sink drain while flushing with tap water.

8.2.5 Check the chiller to make sure the temperature is 21 °C ± 2 °C. Make sure the water level in the chiller is adequate. Refill with distilled water.

8.2.6 Check the argon pressure on the regulator on the wall behind the instrument. The pressure must be between 80 – 90 psi.

8.2.7 In the Instrument Control Window, click 'On' in the iCAP Q / RQ ribbon. The start-up procedure is triggered and the plasma is lit.

8.2.8 Allow 30 minutes for the temperature to equilibrate in the torch box.

8.3 Tuning the ICP-MS

8.3.1 Select the STD measurement mode from the drop-down box in the Measurement Mode ribbon tab. The settings last saved for this measurement mode are loaded into Instrument Control.

8.3.2 Place the sample probe and the internal standard probe into the Tune B solution.

8.3.3 In the Instrument Control window, select the iCAP Q / RQ tab. In the Wizard group, click 'Autotune' and then click 'Source Autotune'. Click next to initiate the autotune sequence.


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8.3.4 When finished, click 'Yes' to save the results. Select 'Open Report' to view the report.

8.3.5 Select the KED measurement mode from the drop-down box in the Measurement Mode ribbon tab. The settings last saved for this measurement mode are loaded into Instrument Control.

8.3.6 Make sure the sample and internal standard probes are in the Tune B solution.

8.3.7 In the Instrument Control window, select the iCAP Q / RQ tab. In the Wizard group, click 'Autotune' and then click '!CaliTune KEDS'. Click next to initiate the autotune sequence.

8.3.8 When finished, click 'Yes' to save the results. Select 'Open Report' to view the report.

## 8.4 Performance Report

**Note:** A passing performance report is required before calibrating the instrument and analyzing samples. To determine if the performance report passes, verify the sensitivity checks, the stability checks, and the mass calibration passes for all masses.

8.4.1 Select the STD measurement mode from the drop-down box in the Measurement Mode ribbon tab. The settings last saved for this measurement mode are loaded into Instrument Control.

8.4.2 Place the sample probe and the internal standard probe into the Tune B solution.

8.4.3 In the Instrument Control window, select the iCAP Q / RQ tab. In the wizard group, click 'Performance Report' and then click 'STD'. Click 'Run a Performance Report from the active Measurement mode', then click 'Next' to initiate the performance report sequence.

8.4.4 When the acquisition is completed, click 'Next', then select the check box 'Open Report' to view the results. Click 'Finish' to complete the performance report wizard.

8.4.5 Select the KED measurement mode from the drop-down box in the Measurement Mode ribbon tab. The settings last saved for this measurement mode are loaded into Instrument Control.

8.4.6 Make sure the sample and internal standard probes are in the Tune B solution.

8.4.7 In the Instrument Control window, select the iCAP Q / RQ tab. In the wizard group, click 'Performance Report' and then click 'KED'. Click 'Run a Performance Report from the active Measurement mode', then click 'Next' to initiate the performance report sequence.


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8.4.8 When the acquisition is completed, click 'Next', then select the check box 'Open Report' to view the results. Click 'Finish' to complete the performance report wizard.

8.5 Detector Setup

**Note:** The detector setup should only be performed when the instrument sensitivity is starting to decline. The procedure is performed on average once a month and typically, the automated procedure will increase the voltage applied to the pulse section of the detector so that it just lies on the plateau of the detector gain curve. The voltage of the analog section of the detector is normally also increased to ensure the cross calibration is accurate and maintained at a defined level.

8.5.1 To perform a detector setup and cross calibration with the Detector Setup Wizard, open the Instrument Control window.

8.5.2 Select the STD measurement mode from the drop-down box in the Measurement Mode ribbon tab. The settings last saved for this measurement mode are loaded into Instrument Control.

8.5.3 In the Instrument Control window, select the iCAP Q / RQ tab. In the wizard group, click 'Detector Setup'. Select 'Detector HV Setup and Cross Calibration'. Make sure the sample and internal standard probes are in the iCAP Q / RQ Setup solution and click next to initiate the sequence.

8.5.4 Click 'Finish' to save the detector voltages as well as the cross calibration factors and to exit the Detector Setup wizard.

8.6 Mass Calibration

**Note:** It is necessary to perform a mass calibration whenever the peak width determination specified in the performance report fails or the mass peaks are not aligned correctly. The mass calibration should be performed monthly. The software uses a mass calibration equation so that when a mass is selected for measurement, the control electronics can set the quadrupole to transmit that mass.

8.6.1 To perform a mass calibration with the wizard, open the Instrument Control window.

8.6.2 Select the STD measurement mode from the drop-down box in the Measurement Mode ribbon tab. The settings last saved for this measurement mode are loaded into Instrument Control.

8.6.3 In the Instrument Control window, select the iCAP Q / RQ tab. In the wizard group, click 'Mass Calibration'. The checkbox for 'Execute a Coarse Mass Calibration first' only needs to be checked if the mass calibration is expected to be significantly different, for example, due to new hardware, or if a mass calibration without this option has failed.

8.6.3.1 If 'Load Tune Settings' is checked, also select a tune setting from the drop-down list, otherwise, the tune settings currently loaded will be used.


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8.6.4 Make sure the sample and internal standard probes are in the iCAP Q / RQ Setup solution and click next to initiate the sequence.

8.6.5 When the wizard finishes the mass calibration, the result window opens automatically. Click 'Next' and then 'Finish' to save the new mass calibration.

8.7 Calibration and Sample Analysis

8.7.1 The Experiment Editor is the principal tool for preparing and running measurements. The Experimental Editor framework is the main Qtegra module and is used to design, start, and stop the measurements.

8.7.2 The Home Page opens on the Dashboard by default when the Experiment Editor is started. The Dashboard contains all functions offered by the Experiment Editor tool and gives access to all existing Templates and LabBooks.

8.7.3 On the Analysis page of the Experiment Editor, LabBooks are created and opened.

8.7.4 A LabBook that has not been scheduled includes the Method Parameters, the Sample List for the measurement, and Automatic Export settings. LabBooks created from a Template inherit the Method Parameters from the Template. The Sample List for the measurement is generated from the Sample Definition of the Template.

8.7.5 To create a new LabBook from a Template, open the Experiment Editor, then on the Home page, click the Analysis tab. Click the first radio button, 'Create a new LabBook from an existing Template', and select 'STD/KED DEP Template'. Then click 'Create LabBook'.

8.7.6 Type samples to be analyzed into the Sample List. The Sample List should start with a few rinses, followed by the calibration blank, calibration standards, calibration check standards, and then the samples to be analyzed. A CCV and CCB are analyzed every 10 samples. An example Sample List is shown below:

Rinse

Rinse

Calibration Blank

ICAP STD 1

ICAP STD 2

ICAP STD 3

ICAP STD 4

CCB

CPQLICAP

ICAPMETC



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IC6020C

Rinse

ICAPCCV

CCB

10 Samples from 1st batch

ICAPCCV

CCB

8.7.7 Once the Sample List has been typed in and the samples poured, initiate the experiment by clicking 'Run' in the menu of the LabBook. Make sure the internal standard probe is in the bottle of internal standard.

8.7.8 After each measurement cycle, the signal intensities and measured concentrations can be observed in the Experiment Editor.

8.8 Standby Mode: After the experiments are finished and the system was flushed with Rinse, the instrument is set to standby mode.

8.9 Complete System Shutdown: To completely shut down the system, in the Instrument Control Window, click 'Off' to turn the plasma off. Switch off the vacuum in the Vacuum submenu. Switch the main power switch to position Off.

## 9. DATA ARCHIVAL

9.1 A total of eight files are stored on the network for each analysis. All files are saved to the folder \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Metals\ICP-MS-iCAP or

\\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Metals\ICP-MS-iCAP-RQ.

9.1.1 Performance Report for STD mode. Exported from Qtegra and saved on the computer network as a .pdf file.

9.1.2 Performance Report for KED mode. Exported from Qtegra and saved on the computer network as a .pdf file.

9.1.3 Calibration Report. Exported from Qtegra and saved on the computer network as a .pdf file.

9.1.4 Mass uncorrected intensity as counts per second. Exported from Qtegra as a .csv file and saved again as a .pdf file after data review.

9.1.5 Cover Page for laboratory report. Created in Microsoft Excel and saved as a .xls file. Printed and included with each laboratory report.

9.1.6 Solutions Log. Created in Microsoft Excel and saved as a .xls file. Printed and included with each laboratory report.

9.1.7 Mass Corrected concentration data. Comma separated values file exported from Qtegra and converted into the LIMS QC Manager module.


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9.1.8 Intensity Report. Exported from Qtegra and saved as a .pdf.

9.2 To export the data of a currently opened LabBook, in the toolbar of the LabBook, click 'Export'. Select the exporter as 'CSV Export'. Check that the column separator is set to Custom with ',' selected and that the Decimal Symbol is set to Point. The checkboxes for 'Export sample lines as rows', 'Group exported blocks', and 'Export complete LabBook' are to be checked.

9.3 Select from the Schemes drop down the option of 'Concentration Export' that has Concentration average and Start Time selected. In the Excel Export Options, select a path and enter the file name. The path should be \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Metals\ICP-MS-iCAP or \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Metals\ICP-MS-iCAP-RQ.
For the ICP-MS iCAP Q, name the file with the format 'yyyymmdd-03168R' and export.
For the ICP-MS iCAP RQ, name the file with the format 'yyyymmdd-00090' and export.
Change the Schemes drop down option to 'Intensities' that has Intensity average, Intensity per Run, and Start Time selected. The path should be \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Metals\ICP-MS-iCAP or \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Metals\ICP-MS-iCAP RQ. For the ICP-MS iCAP Q, name the file with the format 'yyyymmdd-03168R Intensities'. For the ICP-MS iCAP RQ, name the file with the format 'yyyymmdd-00090 Intensities'.

## 10. QUALITY CONTROL

**Note:** The calibration range for each analyte is demonstrated to be within the linear operating range of the instrument at the beginning of each and every analytical run. The instrument is calibrated with 4 standards of varying concentration and a blank and the calibration is forced through the blank.

The correlation coefficient for the first order linear plot of the calibration curve must be 0.998 or greater. The validity of the curve is then further tested with a solution (ICAPMETC) prepared from standards purchased from a vendor that is different from the one used to prepare the calibration standards. The ICAPMETC standard verifies the calibration curve, serving as the initial calibration verification and instrument performance. The analytes present in the second source standard, ICAPMETC, are the same as those the instrument was calibrated for and at a concentration of 100 µg/L (Tl 10 µg/L). If the determined concentration for any analyte in the ICAPMETC standard is less than 90 % or greater than 110 % of the stated value then the data for that analyte are considered invalid and cannot be used, unless appropriately qualified. Data are not reported for samples with concentrations of analytes outside of the established calibration range without qualification. The calibration range may be extended by dilution.

10.1 The procedure for data review is summarized in DEP SOP MT-058, which also lists the acceptance criteria for standard reference materials, matrix spikes,


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internal standards, and precision data. Contingencies for out-of-control QC data are listed in DEP SOP LB-027 as well as DEP SOP MT-058.

10.2 A minimum of three replicate integrations are required for data acquisition. The average of the integrations must be used for instrument calibration and data reporting.

10.3 Interference Check Solution (IC6020C): The acceptable recovery limits are 85 – 115 %. If the analyte recoveries in the initial IC6020C analyzed after calibration and prior to samples are outside of the acceptable recovery limits, no data may be reported without appropriate qualifications, except for when the IC6020C recovery is > 115 %, non-detect sample results may be reported. If the analyte recoveries in the continuing IC6020C (analyzed every 12 hours) are outside of the acceptable limits, the instrument software has the ability to automatically re-analyze the IC6020C. If the analyte recoveries are within the acceptable limits after immediate re-analysis, samples analyzed prior and after the continuing IC6020C may be reported.

## 11. SAFETY / HAZARDOUS WASTE MANAGEMENT

11.1 Review the Health and Safety Plan located on the Laboratory's intranet.

11.2 Use caution with strong irritants such as acids and bases. Avoid breathing the fumes of these irritants by using them in a hood when possible and keeping the face away from open containers of these. Avoid contact of these irritants with skin and clothing by appropriate use of gloves, apron, facemask, safety glasses, hood shield, etc.

11.3 Store any waste that cannot be disposed of down the sink drain (see Laboratory Health and Safety Plan) in the appropriate plastic waste container properly labeled with hazardous waste labels. These wastes include used vacuum pump oil and aqueous solutions known to contain metals at concentrations that exceed the sewer discharge limits. Empty full containers of waste into the waste barrels located in the waste storage room on the loading dock. The limits for discharging metals to the City of Tallahassee sewer system are: As < 132 µg/L, Cd < 79 µg/L, Cr < 2898 µg/L, Cu < 852 µg/L, Pb < 540 µg/L, Mo < 105 µg/L, Ni < 1428 µg/L, Se < 353 µg/L, Ag 3190 µg/L, Zn < 2730 µg/L.

## 12. TROUBLESHOOTING

**Note:** See chapter 7 of the iCAP Q / RQ Operating Manual for additional details.

12.1 If a problem occurs, first examine the recent history of use of the instrument. Consider the simple causes first (for example, sample introduction failure is more likely than quadrupole failure). The most useful tool for probing analytical problems is the performance report.

12.2 Problem: Plasma does not ignite / plasma goes out unexpectedly. Make sure all components of sample introduction are installed correctly. Ensure gas flow parameters are correct by comparing to the last successful analysis.


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12.3 Problem: Sensitivity problems / no signal. Make sure all components of sample introduction are installed correctly. Make sure all cables between instrument and computer are securely connected. Make sure the peristaltic pump is delivering sample.

12.4 Problem: Signal drifts with time. The usual cause of signal drift is gradual deposition of undissociated sample matrix on the sample and skimmer cones. Make sure cones are conditioned (see iCAP Q Operating Manual, p. 8-19 and iCAP-RQ Operating Manual, p. 8-17 for cone conditioning procedure). Make sure the sample flow rate is consistent and continuous and is being drained appropriately from the spray chamber. Make sure the chiller and room temperature are stable.

12.5 Problem: Poor signal stability. Examine sample introduction system and make sure all components are installed correctly.

## 13. MAINTENANCE

**Note:** The maintenance procedures do not require removing the instrument housing. Always wear clean, talc-free, and lint-free gloves when handling components of the iCAP ICP-MS. Always place components on clean, lint-free surfaces.

13.1 Peristaltic pump tubing: Check daily for clogging or damage. Replace if necessary.

13.2 Nebulizer: Clean when necessary. Replace when necessary. See iCAP Q Operating Manual, page 8-13, for the nebulizer cleaning procedure. See iCAP RQ Operating Manual, page 8-12, for the nebulizer cleaning procedure.

13.3 Spray Chamber: Clean when necessary. Replace when necessary. See iCAP Q Operating Manual, page 8-15, for the spray chamber cleaning procedure. See iCAP RQ Operating Manual, page 8-14, for the spray chamber cleaning procedure.

13.4 Injector: Clean when necessary. Replace when necessary. See iCAP Q Operating Manual, page 8-16, for the injector cleaning procedure. See iCAP RQ Operating Manual, page 8-15, for the injector cleaning procedure.

13.5 Torch: Clean when necessary. Replace when necessary. See iCAP Q/RQ Operating Manual, page 8-16, for the torch cleaning procedure.

13.6 Cones: Clean the cones when build-up of matrix has visibly reduced the orifice size, sensitivity of the instrument is below performance specifications, a detector set-up is not increasing the sensitivity, and cleaning the extraction lens did not increase sensitivity. Replace when necessary. See iCAP Q Operating Manual, page 8-22 & 8-23, for the cone cleaning procedure. See iCAP Q/RQ Operating Manual, page 8-20, for the cone cleaning procedure.

13.7 Extraction Lens: Clean the extraction lens when the sensitivity of the instrument is below specification and a detector set-up is not increasing the sensitivity.


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13.8 Detector: The detector has reached the end of its life when it cannot be calibrated anymore. See page 8-29 of the iCAP Q Operating Manual for replacement procedure. See page 8-27 of the iCAP RQ Operating Manual for replacement procedure.

13.9 Gas supply: Leak check the gas lines annually. See page 8-9 of the iCAP Q/RQ Operating Manual for the leak check procedure.

13.10 Air filter: The instrument air filter is located on the left side, bottom. Check and clean monthly.

13.11 Vacuum pump: See the Leybold Vacuum Operating Instructions for further detail.

- Check oil level daily. While the pump is in operation, the oil level should be close to the MAX mark.
- Check gas ballast valve monthly.
- Replace exhaust filter annually.
- Check anti-suck back valve annually.
- Clean fan cover annually.
- Replace PFPE (perfluoropolyether) oil annually.

13.12 Chiller: See the Thermo Scientific ThermoFlex SID Recirculating Chiller Installation, Operation, and Basic Service Manual.

- Replace fluid bag filter as needed.
- Condenser filter: Check weekly and clean at least once per month.
- Clean reservoir as needed.

## 14. REFERENCES

14.1 Thermo Fisher Scientific iCAP

14.1.1 Q Operating Manual, Revision C – 1288090.

14.1.2 RQ Operating Manual, Revision B – BRE0003606.

14.2 Thermo Fisher Scientific iCAP

14.2.1 Q Software Manual, Revision B – 1288010.

14.2.2 RQ Software Manual, Revision B – BRE0005922.

14.3 EPA Methods 200.8 Revision 5.4 and 6020A.

14.4 DEP SOP LB-027, Standard Operating Procedure for Reporting Qualified Data and Correcting Quality Control Problems.

14.5 DEP SOP MT-007, Procedure for Cleaning Metals Labware.

14.6 DEP SOP MT-024, Preparation of Water Samples for Metals Analysis by ICP-AES and ICP-MS.

14.7 DEP SOP MT-058, Procedure for Metals Data Review and Authorization.


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14.8 DEP SOP MT-060, Hot Block Digestion of Soil, Sediment, Waste, and Tissue Sample for Total Recoverable Metals.

14.9 DEP SOP MT-061, Analysis of Selected Metals by Dual View Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

14.10 DEP SOP MT-063, Microwave Assisted Hydrofluoric Acid Digestion of Solid Matrices for Total Metals Determination (Adapted from EPA Method 3052 for the Milestone Ethos EZ microwave system).

14.11 DEP SOP MT-068, Toxicity Characteristic Leaching Procedure (EPA Method 1311) and the Synthetic Precipitation Leaching Procedure (EPA Method 1312).

14.12 DEP SOP MT-069, Metals Standard and Reagent Preparation Procedure.

14.13 Laboratory Quality Manual, DEP.

14.14 Laboratory Health and Safety Manual.


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# APPENDIX A. ACQUISITION PARAMETERS

| Identifier | Dwell time (s) | Channels | Spacing (u) | Measurement mode | Resolution |
|---|---|---|---|---|---|
| 6Li (STD) | 0.1 | 1 | 0.1 | STD | Normal |
| 9Be (STD) | 0.1 | 1 | 0.1 | STD | Normal |
| 11B (KED) | 0.2 | 1 | 0.1 | KED | Normal |
| 27Al (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 45Sc (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 45Sc (STD) | 0.1 | 1 | 0.1 | STD | Normal |
| 47Ti (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 51V (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 52Cr (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 53Cr (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 54Fe (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 55Mn (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 59Co (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 60Ni (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 62Ni (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 63Cu (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 65Cu (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 66Zn (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 67Zn (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 68Zn (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 71Ga (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 75As (KED) | 0.2 | 1 | 0.1 | KED | Normal |
| 77Se (KED) | 0.2 | 1 | 0.1 | KED | Normal |
| 78Se (KED) | 0.2 | 1 | 0.1 | KED | Normal |
| 82Se (KED) | 0.2 | 1 | 0.1 | KED | Normal |
| 83Kr (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 88Sr (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 91Zr (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 92Mo (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 94Zr (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 95Mo (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 97Mo (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 98Mo (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 99Ru (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 103Rh (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 105Pd (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 106Cd (KED) | 0.05 | 1 | 0.1 | KED | Normal |


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| | | | | | |
|---|---|---|---|---|---|
| 107Ag (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 108Cd (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 109Ag (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 111Cd (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 114Cd (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 118Sn (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 121Sb (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 123Sb (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 135Ba (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 137Ba (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 159Tb (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 203Tl (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 205Tl (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 206Pb (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 207Pb (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 208Pb (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 209Bi (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 232Th (KED) | 0.05 | 1 | 0.1 | KED | Normal |
| 238U (KED) | 0.05 | 1 | 0.1 | KED | Normal |


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## APPENDIX B. METHOD PARAMETERS

| Analyte | Measurement Mode | Quantify | Internal Standard | Fit Type | Weighting | Forcing | Use for SemiQuant |
|---|---|---|---|---|---|---|---|
| 6Li | STD | No | Use as Internal Standard | Linear | None | Blank | Yes |
| 9Be | STD | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 11B | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 27Al | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 45Sc | STD | No | Use as Internal Standard | Linear | None | Blank | Yes |
| 45Sc | KED | No | Use as Internal Standard | Linear | None | Blank | Yes |
| 47Ti | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 51V | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 52Cr | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 53Cr | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 54Fe | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 55Mn | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 59Co | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 60Ni | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 62Ni | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 63Cu | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 65Cu | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 66Zn | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 67Zn | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 68Zn | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 71Ga | KED | No | Use as Internal Standard | Linear | None | Blank | Yes |
| 75As | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 77Se | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 78Se | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 82Se | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 83Kr | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 88Sr | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 91Zr | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 92Mo | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 94Zr | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 95Mo | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 97Mo | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 98Mo | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 99Ru | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |


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| Analyte | Measurement Mode | Quantify | Internal Standard | Fit Type | Weighting | Forcing | Use for SemiQuant |
|---|---|---|---|---|---|---|---|
| 103Rh | KED | No | Use as Internal Standard | Linear | None | Blank | Yes |
| 105Pd | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 106Cd | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 107Ag | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 108Cd | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 109Ag | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 111Cd | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 114Cd | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 118Sn | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 121Sb | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 123Sb | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 135Ba | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 137Ba | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 159Tb | KED | No | Use as Internal Standard | Linear | None | Blank | Yes |
| 203Tl | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 205Tl | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 206Pb | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 207Pb | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 208Pb | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 209Bi | KED | No | Use as Internal Standard | Linear | None | Blank | Yes |
| 232Th | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |
| 238U | KED | Yes | Use Interpolation | Linear | None | Blank | Yes |


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## APPENDIX C. ICPMS iCAP Q PERFORMANCE REPORT LIMITS

### STANDARD MODE (STD) PERFORMANCE REPORT LIMITS

| | |
|---|---|
| $^{7}Li$ | > 50,000 cps |
| $^{59}Co$ | > 100,000 cps |
| $^{115}In$ | > 220,000 cps |
| $^{238}U$ | > 300,000 cps |
| $^{137}Ba^{++}$ / $^{137}Ba$ | < 3 % |
| $^{140}Ce^{16}O$ / $^{140}Ce$ | < 2 % |
| Bkg 4.5 | < 1 cps |
| Bkg 220.7 | < 2 cps |

Mass Calibration Verification:

$^{7}Li$: minimum peak width: 0.65 amu; maximum peak width: 0.85 amu

$^{59}Co$: minimum peak width: 0.65 amu; maximum peak width: 0.85 amu

$^{115}In$: minimum peak width: 0.65 amu; maximum peak width: 0.85 amu

$^{238}U$: minimum peak width: 0.65 amu; maximum peak width: 0.85 amu

### KINETIC ENERGY DISCRIMINATION (KED) PERFORMANCE REPORT LIMITS

| | |
|---|---|
| $^{59}Co$ | > 30,000 cps |
| $^{115}In$ | > 30,000 cps |
| $^{238}U$ | > 80,000 cps |
| $^{140}Ce^{16}O$ / $^{140}Ce$ | < 1 % |
| Bkg 4.5 | < 0.5 cps |
| Bkg 220.7 | < 2 cps |

Mass Calibration Verification:

$^{59}Co$: minimum peak width: 0.65 amu; maximum peak width: 0.85 amu

$^{115}In$: minimum peak width: 0.65 amu; maximum peak width: 0.85 amu

$^{238}U$: minimum peak width: 0.65 amu; maximum peak width: 0.85 amu


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## APPENDIX D. ICPMS iCAP RQ PERFORMANCE REPORT LIMITS

### STANDARD MODE (STD) PERFORMANCE REPORT LIMITS

| | |
|---|---|
| $^{7}Li$ | > 55,000 cps |
| $^{59}Co$ | > 100,000 cps |
| $^{115}In$ | > 240,000 cps |
| $^{238}U$ | > 330,000 cps |
| $^{137}Ba^{++}$ / $^{137}Ba$ | < 3 % |
| $^{140}Ce^{16}O$ / $^{140}Ce$ | < 2 % |
| Bkg 4.5 | < 1 cps |
| Bkg 220.7 | < 2 cps |

Mass Calibration Verification:

$^{7}Li$: minimum peak width: 0.65 amu; maximum peak width: 0.85 amu

$^{59}Co$: minimum peak width: 0.65 amu; maximum peak width: 0.85 amu

$^{115}In$: minimum peak width: 0.65 amu; maximum peak width: 0.85 amu

$^{238}U$: minimum peak width: 0.65 amu; maximum peak width: 0.85 amu

### KINETIC ENERGY DISCRIMINATION (KED) PERFORMANCE REPORT LIMITS

| | |
|---|---|
| $^{59}Co$ | > 30,000 cps |
| $^{115}In$ | > 35,000 cps |
| $^{238}U$ | > 85,000 cps |
| $^{140}Ce^{16}O$ / $^{140}Ce$ | < 1 % |
| Bkg 4.5 | < 0.5 cps |
| Bkg 220.7 | < 2 cps |

Mass Calibration Verification:

$^{59}Co$: minimum peak width: 0.65 amu; maximum peak width: 0.85 amu

$^{115}In$: minimum peak width: 0.65 amu; maximum peak width: 0.85 amu

$^{238}U$: minimum peak width: 0.65 amu; maximum peak width: 0.85 amu

## APPENDIX E. APPENDIX OF SIGNIFICANT CHANGES

1. 1/18/2018 Gadolinium (Gd) added.


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