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STANDARD OPERATING PROCEDURE

for

DETERMINATION OF METALS AND TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY (ICP-MS); EPA METHOD 6020

SOP No.: MET-6020

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	Laboratory Manager	3/19/10 Date

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Annual review of this SOP has been performed and the SOP still reflects current practice.
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DETERMINATION OF METALS AND TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY (ICP-MS) EPA METHOD 6020

1 SCOPE AND APPLICATION

1.1 This procedure is used to determine the concentrations of certain elements in water, soil, tissues, aqueous and non-aqueous wastes, and sediment samples using EPA Method 6020 or 6020A. Table 1 indicates analytes that are typically determined by this procedure and lists the standard Method Reporting Limits (MRLs) for each analyte in water and soil. Equivalent nomenclature for MRL includes Estimated Quantitation Limit (EQL) and Practical Quantitation Limit (PQL). Therefore, MRL=EQL=PQL. Project-specific MRLs may apply, and if lower than standard MRLs, it is demonstrated through method detection limit determinations and analysis of MRL standards that the MRL is achievable. Method Detection Limits (MDLs) that have been achieved are listed in Table 1. These may change as annual studies are performed.

1.2 The complexity of the technique generally requires outside study of appropriate literature as well as specialized training by a qualified spectroscopist. The scope of this document does not allow for the in-depth descriptions of the relevant spectroscopic principles required for gaining a complete level of competence in this scientific discipline.

2 SUMMARY OF METHOD

2.1 Prior to analysis, samples must be digested using appropriate sample preparation methods. The digestate is analyzed for the elements of interest using ICP-mass spectrometry (ICP-MS).

2.2 Methods 6020 and 6020A describe the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

3 DEFINITIONS

3.1 **Analysis Sequence** - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by sample digestates interspersed with calibration standards.

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3.2 **Independent Calibration Verification (ICV) -** ICV solutions are made from a stock solution which is different from the stock used to prepare calibration standards and is used to verify the validity of the standardization.

3.3 **Matrix Spike** (MS) - In the matrix spike analysis, predetermined quantities of standard solutions of certain analytes is added to a sample matrix prior to sample digestion and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the methods used for the analyses. Percent recoveries are calculated for each of the analytes detected.

3.4 **Matrix Spike Duplicate** (MSD) - In the matrix spike duplicate analysis, predetermined quantities of standard solutions of certain analytes are added to a sample matrix prior to sample digestion and analysis. The purpose of the matrix spike duplicate is to evaluate the effects of the sample matrix on the methods used for the analyses. Percent recoveries are calculated for each of the analytes detected. The relative percent difference between the matrix spikes is calculated and used to assess analytical precision.

3.5 **Duplicate Sample** (DUP) - A laboratory duplicate. The duplicate sample is a separate field sample aliquot that is processed in an identical manner as the sample proper. The relative percent difference between the samples is calculated and used to assess analytical precision.

3.6 **Method Blank -** The method blank is an artificial sample designed to monitor introduction of artifacts into the process. The method blank is carried through the entire procedure.

3.7 **Continuing Calibration Verification Standard (CCV) -** A standard analyzed at specified intervals and used to verify the ongoing validity of the instrument calibration.

3.8 **Instrument Blank (CCB) -** The instrument blank (also called continuing calibration blank) is a volume of blank reagent of composition identical to the digestates. The purpose of the CCB is to determine the levels of contamination associated with the instrumental analysis.

4 INTERFERENCES

4.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Attention should be given to circumstances where very high ion currents at adjacent masses may contribute to ion signals at the mass of interest. Matrices exhibiting a significant problem of this type may require resolution improvement, matrix separation, or analysis using another isoptope.

4.2 Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that

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could affect ICP-MS determinations have been identified in the literature. Refer to Method 6020/A for further discussion.

5 SAFETY

5.1 All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personnel protective equipment, such as, safety glasses, lab coat and the correct gloves.

5.2 Chemicals, reagents and standards must be handled as described in the CAS safety policies, approved methods and in MSDSs where available. Refer to the CAS Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method.

5.3 Hydrochloric and/or Nitric Acid are used in this method. These acids are extremely corrosive and care must be taken while handling them. A face shield should be used while pouring acids. And safety glasses should be worn while working with the solutions. Lab coat and gloves should always be worn while working with these solutions.

5.4 High Voltage - The RF generator supplies up to 2000 watts to maintain an ICP. The power is transferred through the load coil located in the torch box. Contact with the load coil while generator is in operation will likely result in death. When performing maintenance on the RF generator, appropriate grounding of all HV capacitors must be performed as per manufacturer.

5.5 UV Light - The plasma is an intense source of UV emission, and must not be viewed with the naked eye. Protective lenses are in place on the instrument. Glasses with special protective lenses are available when direct viewing of the plasma is necessary.

6 SAMPLE COLLECTION, CONTAINERS, PRESERVATION, AND STORAGE

6.1 Aqueous samples are typically collected in plastic containers. Aqueous samples are preserved with nitric acid (pH<2), then refrigerated at 4 ± 2°C from receipt until digestion. Soil or solid samples may be collected in plastic or glass jars. Non-aqueous samples are refrigerated at 4 ± 2°C from receipt until digestion.

6.2 Samples are prepared via procedures in SOPs MET-DIG, MET-3020A, or MET-3050 depending on matrix and project specifications.

6.3 Digestates are stored in the appropriate volumetric containers. Following analysis, digestates are stored until all results have been reviewed. Digestates are neutralized prior to disposal through the sewer system, 2 weeks after data is reviewed.

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7 APPARATUS & EQUIPMENT

7.1 Instruments: Thermo Elemental ExCell (K-ICP-MS-02) Serial # EX191, and Thermo Elemental X-Series (K-ICP-MS-03) Serial # X0193.

7.2 Thermo Meinhard type (Part # 1201318)

7.3 Thermo Impact Bead Quartz Spray Chamber (Part # 3600170)

7.4 Thermo X7 Nickel Sample Cone (1.0 mm orifice) (Part # 3004661), or Xi sample cone (part # 3600812)

7.5 Thermo X7 Nickel Skimmer Cone (0.75 mm orifice) (Part # 3200860) or Xi skimmer cone(part # 3600811)

8 STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

8.1 All standards are prepared from NIST traceable standards. The expiration dates are assigned according to the EPA method and the vendor's assigned expiration dates. For example, working ICS solutions are prepared weekly in accordance with Method 6020, Section 5.6.1.

8.1.1 1000 ppm Single Element Stock Standard Solutions: Each stock standard is store at room temperature on shelves located in room 113 of the metals lab. The manufacturer, lot number, and expiration date of each stock standard is recorded in a bound logbook also located in room 113. Additionally each stock standard is given a unique, identifying name.

8.1.2 Intermediate Standard Solutions: Intermediate mixed stock solutions are made from the individual stock standards described above. The individual component of each mixed solution is recorded in a bound logbook located in the ICP-MS laboratory and mixed solution is given a unique, identifying name. The expiration date for the intermediate standard is the earlier of any one of its stock components.

8.1.3 Calibration Standards: Calibration standards are made fresh daily from the intermediate standard solutions. Each individual intermediate standard used in the calibration standard is recorded in a bound logbook located in the ICP-MS laboratory, and the calibration standard solution is given a unique, identifying name. The calibration standards unique name is used on the raw data to link the data to the subsequent prepared standards and ultimately the original purchased stock standard.

8.2 Standards Preparation

8.2.1 Expiration of all standard solutions defaults to the earliest expiration date of an individual component unless otherwise specified.

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8.2.2 Calibration Standards

The calibration standard is prepared from two intermediate stock solutions. These solutions are prepared in acid rinsed 1000 mL Class A volumetric flasks following the formulations laid out on the attached example standard sheet (see Attachments). The working calibration standard is made daily by aliquoting 2.5 mL of each of the intermediate solutions in to a 100 mL Class A volumetric flask and diluting to volume with 1% HNO3. This standard is also used as the Continuing Calibration Verification (CCV).

8.2.3 Initial Calibration Verification (ICV)

8.2.3.1 The ICV intermediate stock solution is prepared in an acid rinsed 100 mL Class A volumetric flask. The solution is prepared by adding 2.0 mL of Inorganic Ventures QCP-CICV-1, 1.0 mL each of QCP-CICV-2 and QCP-CICV-3, 0.5 mL of 1000 ppm Molybdenum stock solution, 0.5 mL of 1000 ppm Uranium stock solution and diluting to volume with 1% HNO3.

8.2.3.2 The working ICV solution is prepared by aliquoting 0.5 mL of the mixed ICV intermediate solution into an acid rinsed 100 mL Class A volumetric flask and diluting to volume with 1% HNO3.

NOTE: The ICV solution is not at the midpoint of the linear range which may be as high as 1000 µg/L for some elements. The ICV solution used is a premixed standard purchased from Inorganic Ventures and contains the elements of interest between 2.5 and 100 µg/L. This solution provides calibration confirmation at more representative levels, given that most ICP-MS analyses are quantifying analytes in the low-ppb to sub-ppb range.

8.2.4 Interference Check Solutions (ICSA and ICSAB)

8.2.4.1 The ICSA is prepared in an acid rinsed 50 mL Class B volumetric flask by aliquoting 1.0 mL of Elements ICSAm (CS-CAK02) solution and diluting to volume with 1% HNO3.

8.2.4.2 The ICSAB is prepared in an acid rinsed 50 mL Class B volumetric flask by aliquoting 1.0 mL of Elements ICSAm (CS-CAK02), 0.125 mL of Inorganic Ventures 6020ICS-9B, and 0.250 mL of 10 ppm Molybdenum solutions and diluting to volume with 1% HNO3.

8.2.5 Post-digestion spikes are performed by adding appropriate amounts of the calibration intermediate solutions to aliquots of the sample digestate. The volumes of each standard used vary based on the native concentrations found in the field samples. Refer to the post-digestion spike in Section 12 for details.

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8.2.6 Refer to the appropriate digestion SOP for details of LCSW and matrix spike solution composition and preparation.

8.2.7 Tuning / Mass Calibration Solution

8.2.7.1 A 10 ppm intermediate solution containing Ba, Be, Bi, Co, In, Li, Pb, Mg, Tl, and U is prepared by adding 10 mL of each from 1000 ppm stock standards to an acid rinsed 1000 mL volumetric flask and diluting to volume with 1% nitric acid. The expiration date for the intermediate solution is the earliest of any one of its stock components.

8.2.7.2 The working solution is prepared in two ways. For the ExCell (K-ICP-MS-02) a 1.0 ppb tune/mass calibration solution is prepared by adding 0.10 mL of intermediate solution to an acid rinsed 1000 mL volumetric flask and diluting to volume with 1% nitric acid. For the X-Series (K-ICP-MS-03) instrument a 5.0 ppb tune/mass calibration solution is prepared by adding 0.50 mL of intermediate solution to an acid rinsed 1000 mL volumetric flask and diluting to volume with 1% nitric acid. The expiration date for this solution is taken from the intermediate stock above.

8.3 Internal Standards Stock Solution – Prepare a 10 µg/mL solution containing ^{71}Ga, ^{115}In, ^{6}Li, ^{175}Lu, ^{103}Rh ^{45}Sc, and ^{89}Y by adding 10.0 mL of each 1000 ppm single element stock solution to a acid rinsed 1000 mL volumetric flask and diluting to volume with 1% nitric. Use this solution for addition to blanks, calibration standards and samples at a ration of 0.5 mL of internal standard to 100 mL of solution, or dilute by an appropriate amount using 1% (v/v) nitric acid, if the internal standards are being added by peristaltic pump.

8.4 Additional Reagents

8.4.1 Reagent water, ASTM Type II

8.4.2 “OmniTrace Ultra” Concentrated Nitric Acid (EM Science # NX0408-2)

8.4.3 Argon (Airgas Industrial Grade – 99.999% pure, bulk delivered)

9 PREVENTIVE MAINTENANCE

9.1 All maintenance is documented in the instrument logbook. CAS/Kelso maintains a service contract with the instrument manufacturer that allows for an unlimited number of service calls and full reimbursement of all parts and labor.

9.2 Most routine maintenance and troubleshooting is performed by CAS staff. Preventive maintenance activities listed below should be performed when needed as determined by instrument performance (i.e. stability, sensitivity, etc.) or by visual inspection. Other

maintenance or repairs may, or may not require factory service, depending on the nature of the task.

- cone removal and cleaning
- removal and cleaning of ICP glassware and fittings
- checking and cleaning RF contact strips
- checking air filters and cleaning if necessary
- checking the oil mist filters and cleaning if necessary
- checking the rotary pump oil and adding or changing if necessary
- removal and cleaning of extraction lens
- removal and cleaning of ion lens stack
- replace the electron multiplier as necessary

10 RESPONSIBILITIES

10.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

10.2 It is the responsibility of the department supervisor/manager to document analyst training. Documenting method proficiency, as described in the SOP for Documentation of Training, is also the responsibility of the department supervisor/manager.

11 PROCEDURE

11.1 Refer to method 6020 (or 6020A) and the instrument manuals for detailed instruction on implementation of the following daily procedures preceding an analytical run.

11.2 After the instrument has been placed in the "Operate" mode, begin completing the daily instrument log (see Attachments). Refer to the instrument manuals for the optimum settings for each instrument.

11.3 The following parameters are monitored to assure awareness of changes in the instrumentation that serve as signals that optimum performance is not being achieved, or as indicators of the physical condition of certain consumable components (i.e. EMT and cones).

11.3.1 Multiplier Voltages

11.3.2 Gas Flows - Coolant Ar

11.3.3 The nebulizer and auxiliary flows are adjusted later as part of the optimizing procedure.

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11.4 Optimization

11.4.1 Gas Flows

11.4.1.1 Allow a period of not less than 30 minutes for the instrument to warm up.

11.4.1.2 Aspirate a mixed tune solution into the plasma and monitor the instrument output signal of In at mass 115 on the ratemeter. Adjust the nebulizer and auxiliary flows to obtain maximum signal. Adjust the tension screw on the peristaltic pump to obtain minimum noise in the analytical signal. Record flow rates and note any large variances.

Note: Significant differences in flow rates will be observed for different torches and cones.

11.4.2 Tuning

11.4.2.1 Ion Lens Setting - While monitoring the output signal of a mixed tune solution at mass 115 on the ratemeter, adjust the ion lenses to obtain maximum sensitivity. Refer to the instrument manual for details on performing the adjustments.

11.4.2.2 Mass Calibration - Aspirate the tune / mass calibration solution described in section 9.2.7.2 and perform the mass calibration using the instrument's Mass Calibration program. (Refer to the instrument manual for details pertaining to the mass calibration procedure.) The acceptance criteria for the mass calibration is <0.1 amu from the true value. If the mass calibration fails criteria re-tune the instrument and perform the mass calibration procedure again.

11.4.2.3 Resolution Check - Using the spectra created during the mass calibration procedure; perform the resolution check to assure the resolution is less than 0.9 AMU at 10% peak height. If the resolution does not pass criteria adjust the instrument's resolution settings, run a new scan of the mass calibration solution and recheck.

11.4.2.4 Stability Check - Using the tune / mass calibration solution, perform a short-term stability check as per EPA Method 6020 or 6020A. The relative standard deviations of five scans for each element in the tune solution must be < 5%. If the test does not pass criteria determine the cause (i.e. dirty cones, improper tune, etc.) correct the problem and re-run the test.

11.5 Analytical Run

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11.5.1 Calibrate the instrument using a calibration blank (Standard 0), composed of reagent water and 1% nitric acid, and the working calibration standard (8.2.2). The masses typically monitored and those used for quantification are listed in Table 1. These masses are set as defaults in the instrument's analytical procedures. To begin select the correct method. Nebulize Standard 0 (Blank) into the plasma. Allow 1-2 minutes for system to equilibrate prior to establishing baseline. Follow directions on computer screen to perform standardization. Nebulize the working calibration standard into the plasma. The operator must sign and date the first page of standardization.

11.5.2 After the first CCB and before the ICS standards a CRA (MRL / LLICV / LLCCV) standard is analyzed. Method 6020 requires the detection to be > the MDL but < 2x the MRL. For 6020A, the criteria are 70-130% recovery. For DoD projects, the CRA criteria are 80-120%.

Note: For 6020A the LLCCV must also be analyzed at the end on the analytical run sequence.

11.5.3 Perform the analysis in the order listed below. A daily run log of all samples analyzed is maintained.

Initial Calibration Verification (ICV)
Continuing Calibration Verification (CCV)
Initial Calibration Blank (ICB)
Continuing Calibration Blank (CCB)
CRA (MRL / LLICV / LLCCV)
ICSA
ICSAB
Analyze 10 Samples
CCV
CCB
Analyze 10 Samples
CCV
CCB
Repeat sequence as required to complete analytical run, analyzing CCVs/CCBs every 10 analyses and at the end of the run.

12 QA/QC REQUIREMENTS

12.1 Initial Precision and Recovery Validation

The accuracy and precision of the procedure must be validated before analysis of samples begins, or whenever significant changes to the procedures have been made. To do this, four LCS aliquots are prepared and analyzed. The average percent recovery of for each analyte must be 85-115% (for water, and within the LCS limits for soils) and the RSD <20%.

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12.2 Method Detection Limits

12.2.1 A method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike a minimum of seven blank matrices at a level near or below the MRL. Follow the procedures starting in Section 11 to analyze the samples. Refer to the CAS SOP for *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification (ADM-MDL)* details of performing the MDL study.

12.2.2 Calculate the average concentration found (x) and the standard deviation of the concentrations for each analyte. Calculate the MDL for each analyte using the correct T value for the number of replicates. MDL's must be verified annually or whenever there is a significant change in the background or instrument response.

12.3 For method 6020A, an LLQC sample (a CRA that is carried through the digestion) must be analyzed to verify accuracy at the MRL. The recovery must be 70-130%.

12.4 Instrument Detection Limits (IDLs) and linear ranges studies are performed quarterly. These will be calculated and made available to the ICP-MS operator. Linear range studies determine the Linear Dynamic Range (LDR) of the each instrument by analysis of a high concentration standard with results with ± 10% of the expected value. For non-DoD projects samples may be quantified between the MRL and 90% of the LDR without flagging. The Linear Calibration Range (LCR) is established by the highest calibration standard.

- **Note:** IDLs must be < LOD for DOD projects. DoD project samples with concentrations above the calibration standard must be diluted to bring results within the quantitation range. The LOQ and cal standard establish the quantitation range. The lab may report a sample result above quantitation range if the lab runs and passes a CCV that is > sample result.

12.5 The Initial Calibration Verification (ICV) standard is analyzed immediately after calibration. The results of the ICV must agree within ±10% of the expected value. If the control limits are exceeded, the problem will be identified and the instrument recalibrated.

12.6 A Continuing Calibration Verification (CCV) and Continuing Calibration Blank (CCB) are analyzed after calibration then every 10 samples thereafter with a final CCV/CCB closing the final samples of the analytical run.

12.6.1 The results of the CCV must agree within ±10% of the expected value.

12.6.2 The CCB measured values must be less than the MRL / LOQ for each element for standard applications. Other project-specific criteria may apply (for DoD QSM projects CCB can have no analytes > the LOD).

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12.6.3 If the control limits are exceeded, the problem will be identified and corrective action taken. The instrument recalibrated. The previous 10 samples must be reanalyzed.

12.7 The ICSA and ICSAB solutions are analyzed after calibration and before any field samples. The solutions are then reanalyzed every 12 hours. Results of the ICSA are used by the analyst to identify the impact of potential interferences on the quality of the data. Based on these results appropriate action should be taken when interferences are suspected in an field sample including, but not limited to, selecting and alternative isotope for quantification, manual correction of the data, elevating the MRL, selection of an alternative method (e.g. optical ICP, GFAA) or flagging the result as estimated when no other action is possible. Results for the spiked analytes in the ICSAB solution must agree with ± 20% of the expected value.

INTERFERENCE CHECK SAMPLE COMPONENTS AND CONCENTRATIONS

	Solution A Concentrations (mg/L)	Solution B Concentrations (mg/L)
Al	20.0	20.0
Ca	60.0	60.0
Fe	50.0	50.0
Mg	20.0	20.0
Na	50.0	50.0
P	20.0	20.0
K	20.0	20.0
S	20.0	20.0
C	40.0	40.0
Cl	424	424
Mo	0.05	0.05
Ti	0.40	0.40
As	0.0	0.025
Cd	0.0	0.025
Cr	0.0	0.050
Co	0.0	0.050
Cu	0.0	0.050
Mn	0.0	0.050
Ni	0.0	0.050
Se	0.0	0.025
Ag	0.0	0.0125
V	0.0	0.050
Zn	0.0	0.025

NOTE: The concentration of interfering elements in the ICSA and ICSAB solutions are spiked at levels 5 times lower than recommended in Table 1 of Method 6020A. Running the full strength solutions as described in 6020A introduces too much material approximately 0.35 % dissolved solids into the ICP-MS system when trying to conduct low level analysis. Since the ICP-MS instrumentation is able to handle a maximum of 0.2% solids, the 6020A ICSA

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solution is higher in interfering components than any sample that would run through the instrument. However, the ICS solutions will be analyzed at levels that will provide approximately 0.1% dissolved solids.

12.8 Internal standards are used to correct for physical interferences. Masses used as internal standards include; ^{71}Ga, ^{115}In, ^{6}Li, ^{175}Lu, ^{103}Rh ^{45}Sc, and ^{89}Y. These internal standards are used in combination to cover the appropriate mass ranges. Internal standard correction is applied to the analytical isotopes via interpolation of the responses form nearest internal standard isotopes. This function is performed in real-time by the instruments operating system. Internal standards must be run within 50 AMU of the masses that are analyzed. Internal standard recoveries must fall between 30% and 125% when running method 6020, or 70% to 125% when running method 6020A Revision 1. If not, then the sample must be reanalyzed after a fivefold or greater dilution has been performed.

12.9 A method blank is digested and analyzed with every batch of 20 (or fewer) samples to demonstrate that there are no method interferences. If the method blank shows any hits above the MRL for standard applications, or >½ the MRL for DoD projects or > 1/10 the sample result, corrective action must be taken. The MB can only be rerun once. Corrective action includes recalculation, reanalysis, system cleaning, or re-extraction and reanalysis.

12.10 Laboratory Control Samples are analyzed at a frequency of 5% or one per batch, whichever is greater. See the Attachments for a listing of control limits. For method 6020A, the LCS recovery limits are 80-120%. If statistical in-house limits are used, they must fall within the 80-120% range. Project, QAPP, or client-specific control limits may supersede the limits listed, but laboratory limits should be consistent with specified limits in order to establish that the specified limits can be achieved. If the control limits are exceeded, the associated batch of samples will be redigested and reanalyzed.

12.11 A digested duplicate and matrix spike are analyzed at a frequency of 5% or one per batch, whichever is greater. The matrix spike recovery and relative percent difference will be calculated while analysis is in progress. See the Attachments for a listing of control limits. Project, QAPP, or client-specific control limits may supercede the limits listed. If the control limits are exceeded, the samples will be redigested and reanalyzed, unless matrix interference or sample non-homogeneity is established as cause. In these instances, the data and the report will be flagged accordingly.

12.12 A Matrix Spike sample is digested one per batch, or per 20 samples (i.e. 5%). Default spike concentrations are listed in the sample digestion SOPs. Spike concentrations may be adjusted to meet project requirements. The matrix spike recovery will be calculated while the job is in progress. Where specified by project requirements, a matrix spike duplicate may be required. Matrix spike recovery criteria are derived from lab data and are listed in Table 2. For method 6020A, the recovery limits are 75-125%. If statistical in-house limits are used, they must fall within the 75-125% range. In some cases, project-specific QC limits may be required. Unless specified otherwise, for DoD QSM projects the project LCS criteria will be used for evaluation of matrix spikes. If an analyte recovery is outside acceptance limits proceed

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with the additional quality control tests described in sections 12.13 and 12.14. Based on results of these tests, the physical nature of the sample (e.g. homogeneity), and any specific project requirements, a determination can then be made as to appropriate corrective action (e.g. redigestion, reporting with a qualifier, alternative methodologies, etc.). If the analyte concentration is >4x the spike level the spike control limit is no longer applicable and no action is required. For specifics on the preparation and composition of matrix spike solutions refer to the appropriate digestion SOP.

Note: For DOD projects a MS/MSD is required with every extraction batch. The %RSD should be < 20%.

12.13 Post Digestion Spike Test: When analysis is conducted via 6020 a post digestion spike must be performed for each matrix and each batch of sample. The prepared sample or its dilution is spiked for each element of interest at a concentration sufficiently high to be observed. Typically 20 µL of 10,000 ppb intermediate stock is added to a 10 mL aliquot of sample. If analyte concentrations are elevated in the sample, spiking at a higher concentration may be required. The post spike should be recovered to within 75-125% of the known value or within the laboratory derived acceptance criteria. When analysis is conducted via 6020A, the post digestion spike test is performed whenever matrix spike or replicate criteria are exceeded. An analyte spike is added to a portion of a prepared sample, or its dilution, and should be recovered to within 80% to 120% of the known value. If this spike fails, then the dilution test (Sec. 12.14) should be run on this sample. If both the matrix spike and the post digestion spike fail, then matrix effects are confirmed.

12.14 Dilution Test: When analysis is conducted via 6020, a serial dilution test must be performed for each matrix and each batch of sample. For sample concentrations that are sufficiently high (minimally, a factor of greater than 100 times the MDL), the analysis of a fivefold (1+4) dilution must agree within ± 10% of the original determination. When analysis is conducted via 6020A, the dilution test is performed whenever matrix spike or replicate criteria and post digestion spike criteria are exceeded. If the dilution test fails then a chemical or physical effect should be suspected. Corrective action can include additional dilution of the sample, the use of alternate methodologies, etc. or the data can be flagged and reported. The exact course of action will be dependent on the nature of the samples and project requirements and should be discussed with the project manager.

12.15 Instrument blanks should be evaluated for potential carryover and rinse times need to bring the analyte signal to within the CCB criteria discussed above in section 12.4. Results from instrument blanks run after standards or control samples should be used to establish levels at which carryover in samples may occur. Samples exhibiting similar effects of carryover should be reanalyzed.

12.16 Refer to the Quality Control section of EPA Methods 6020 and 6020A for additional information describing required QA/QC. Note that the nomenclature of certain QC samples in the method differs from that of the CLP SOW, but the function of those samples is equivalent in both cases.

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13 DATA REDUCTION, REPORTING, AND REVIEW

13.1 Calculations

Calculate sample results using the data system printouts and digestion information. the digestion and dilution information is entered into the data system. The data system then uses the calculations below to generate a sample result.

Aqueous samples are reported in µg/L:

$$\mu g / L\ (Sample) = C^{*}\ x\ Digestion\ Dilution\ Factor\ x\ Post\ Digestion\ Dilution\ Factor$$

C*= Concentration of analyte as measured at the instrument in ug/L (in digestate).

Solid samples are reported in mg/Kg:

$$mg/Kg\ (Sample) = C^{*}\ x\ Post\ Digestion\ Dilution\ Factor\ x\ \frac{Digestion\ Vol\ (ml)}{Sample\ wt\ (g)}\ x\ \frac{1mg}{1000ug}\ x\ \frac{1L}{1000ml}\ x\ \frac{1000g}{1Kg}$$

C*= Concentration of analyte as measured at the instrument in ug/L (in digestate).

NOTE: If results are to be reported on a dry weight basis, determine the dry weight of a separate aliquot of the sample, using the SOP for Total Solids.

13.2 Common isobaric interferences are corrected using equations equivalent to those listed in EPA Methods 6020, 6020A, and 200.8. Monitoring of multiple isotopes for a single element provides a mechanism for identifying isobaric interferences. Refer to the Interferences section of EPA methods for additional descriptions of possible interferences and the mechanisms required for adequately compensating for their effects.

13.3 Data Review and Reporting

13.3.1 The ICP-MS operator reviews the MS data and signs and dates the Data Review Form. A qualified senior staff spectroscopist performs a secondary review of the data and the Data Review Form is signed and dated. The data is then delivered to the report generation area where it is filed in the service request file. Once all of the data for the service request is complete, a CAR is generated.

13.3.2 The data is saved on the local hard drive and is also copied to the appropriate directory on the network. The data directories are located at r:\icp\wip\data. The data is kept on the local directory for 1 month. The network files are periodically backed up on disc or network tape.

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13.3.3 For "non-production" work (such as method development or research/development studies) the analyses are performed under the direction of a senior spectroscopist. All associated data is scrutinized by the senior spectroscopist. Original raw data and associated records are archived in the analytical project file.

13.3.4 The final review and approval of all data is performed by qualified spectroscopists.

14 CONTENGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Corrective action measures applicable to specific analysis steps are discussed in the applicable section of this (and other applicable) SOP(s). Also, refer to the SOP for *Nonconformity and Corrective Action* for correct procedures for identifying and documenting such data. Procedures for applying data qualifiers are described in the SOP for *Report Generation* or in project-specific requirements.

15 METHOD PERFORMANCE

This method was validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional available method performance data.

The method detection limit (MDL), limit of detection (LOD) and limit of quantitation (LOQ) are established using procedures described in the SOP for *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification (ADM-MDL).* Method Reporting Limits are established for this method based on MDL studies and as specified in the CAS Quality Assurance Manual.

16 TRAINING

16.1 A minimum of two senior level spectroscopists are to be maintained on staff at all times. Senior spectroscopists are defined as individuals with a minimum of ten years combined education and experience in, or related to atomic spectroscopy. Of those ten years, a minimum of two years of ICP-MS experience is required.

16.2 All technical staff is encouraged to attend one technical seminar per year. In addition to the technical seminars, senior spectroscopists are required to complete a one week training session offered by the instrument manufacturer.

16.3 Training outline

16.3.1 Review literature (see references section). Read and understand the SOP. Also review the applicable MSDS for all reagents and standards used. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

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16.3.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

16.3.3 Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

16.4 Training and proficiency is documented in accordance with the SOP ADM-TRANDOC.

17 POLLUTION PREVENTION

It is the laboratory's practice to minimize the amount of solvents and reagents used to perform this method wherever technically sound, feasibly possible and within method requirements. Standards are prepared in volumes consistent with the laboratory use in order to minimize the volume of expired standards to be disposed of. The threat to the environment from solvents and/or reagents used in this method may be minimized when recycled or disposed of properly.

18 WASTE MANAGEMENT

The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and disposal restrictions as specified in the laboratory Safety Manual, Sections 6 and 7.

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19 CHANGES SINCE THE LAST REVISION

19.1 Updated entire SOP to comply with EPA method 6020A requirements.

19.2 Sec 6.2 – Removed outdated information "Samples are generally received in the ICP-MS laboratory as 1-15% Nitric Acid digestates. Digestates originating from soil samples with greater than 60% solids are diluted prior to instrumental analysis by a factor of 5. This allows the analysis to achieve maximum sensitivity which results in optimum MRLs"

19.3 Sec 11.5.2 Added low level CRA acceptance criteria for 6020A.

19.4 The note at end of Sec 11.5.2 is new.

19.5 Sec 11.5.3, Added (MRL/LLICV/LLCCV) next to CRA.

19.6 Sec 12.2.1 and 12.2.2 Updated MDL SOP reference and requirements.

19.7 Sec 12.6.2, Added LOQ and removed NOTE from previous SOP from this section.

19.8 Sec 12.8, Added internal standard recovery criteria for method 6020A.

19.9 Sec 12.13 and 12.14 are new.

19.10 Remove Method EPA 200.8 from reference section

20 REFERENCES

20.1 USEPA, Test Methods for Evaluating Solid Waste, SW-846, 3rd Edition, Update III Method 6020, Revision 0, September 1994.

20.2 USEPA, Test Methods for Evaluating Solid Waste, SW-846, Update IV, Method 6020A, Revision 1, February 2007.

20.3 VG and Thermo Elemental Instrument Manuals

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TABLE 1
Method Reporting Limits and Method Detection Limits – Water Matrix

	Water (ug/L)			**Water (ug/L)**			**Seawater (ug/L)**		
	CLP Digestion			3020 Digestion			Reductive Precipitation		
Analyte	MRL (DoD)	**MRL**	**MDL**	MRL (DoD)	**MRL**	**MDL**	MRL (DoD)	**MRL**	**MDL**
Aluminum	2	**2**	**0.3**	2.4	**2**	**0.8**	-	**-**	**-**
Antimony	0.09	**0.05**	**0.03**	0.09	**0.05**	**0.03**	-	**-**	**-**
Arsenic	0.5	**0.5**	**0.08**	0.5	**0.5**	**0.07**	0.5	**0.5**	**0.02**
Barium	0.06	**0.05**	**0.02**	0.12	**0.05**	**0.04**			
Beryllium	0.02	**0.02**	**0.008**	0.02	**0.02**	**0.006**	0.02	**0.02**	**0.0007**
Bismuth	0.1	**0.1**	**0.02**	-	**-**	**-**	-	**-**	**-**
Boron	0.9	**0.5**	**0.3**	-	**-**	**-**	-	**-**	**-**
Cadmium	0.02	**0.02**	**0.008**	0.06	**0.02**	**0.02**	0.02	**0.02**	**0.006**
Chromium	0.2	**0.2**	**0.07**	0.2	**0.2**	**0.05**	0.2	**0.2**	**0.03**
Cobalt	0.02	**0.02**	**0.005**	0.02	**0.02**	**0.005**	0.02	**0.02**	**0.001**
Copper	0.1	**0.1**	**0.02**	0.21	**0.1**	**0.07**	0.1	**0.1**	**0.03**
Lead	0.03	**0.02**	**0.009**	0.06	**0.05**	**0.02**	0.02	**0.02**	**0.003**
Manganese	0.06	**0.05**	**0.02**	0.05	**0.05**	**0.01**	-	**-**	**-**
Molybdenum	0.09	**0.05**	**0.03**	0.09	**0.05**	**0.03**	-	**-**	**-**
Nickel	0.2	**0.2**	**0.07**	0.2	**0.2**	**0.05**	0.2	**0.2**	**0.03**
Selenium	1.2	**1**	**0.4**	1	**1**	**0.2**	-	**-**	**-**
Silver	0.03	**0.02**	**0.009**	0.03	**0.02**	**0.009**	0.02	**0.02**	**0.004**
Thallium	0.02	**0.02**	**0.003**	0.02	**0.02**	**0.004**	0.02	**0.02**	**0.0009**
Tin	0.1	**0.1**	**0.04**	-	**-**	**-**	-	**-**	**-**
Uranium	0.02	**0.02**	**0.005**	0.02	**0.02**	**0.004**	-	**-**	**-**
Vanadium	0.2	**0.2**	**0.08**	0.2	**0.2**	**0.05**	-	**-**	**-**
Zinc	0.5	**0.5**	**0.1**	0.6	**0.5**	**0.2**	0.5	**0.5**	**0.04**

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TABLE 1 (continued)
Method Reporting Limits and Method Detection Limits – Solid Matrix

	Soil/Sediment (mg/kg)			**Tissue (mg/kg, dry basis)**		
	3050 Digestion			PSEP		
Analyte	MRL (DoD)	**MRL**	**MDL**	MRL (DoD)	**MRL**	**MDL**
Aluminum	2	**2**	**0.5**	2	**2**	**0.4**
Antimony	0.09	**0.05**	**0.03**	0.06	**0.05**	**0.02**
Arsenic	0.5	**0.5**	**0.1**	0.5	**0.5**	**0.05**
Barium	0.09	**0.05**	**0.03**	0.15	**0.05**	**0.05**
Beryllium	0.06	**0.02**	**0.02**	0.02	**0.02**	**0.005**
Bismuth	0.1	**0.1**	**0.02**	-	**-**	**-**
Cadmium	0.02	**0.02**	**0.008**	0.03	**0.02**	**0.01**
Chromium	0.2	**0.2**	**0.04**	-	**-**	**-**
Cobalt	0.02	**0.02**	**0.003**	0.02	**0.02**	**0.006**
Copper	0.3	**0.1**	**0.1**	0.1	**0.1**	**0.03**
Lead	0.06	**0.05**	**0.02**	0.02	**0.02**	**0.006**
Manganese	0.12	**0.05**	**0.04**	0.06	**0.05**	**0.02**
Molybdenum	0.15	**0.05**	**0.05**	0.06	**0.05**	**0.02**
Nickel	0.2	**0.2**	**0.05**	0.2	**0.2**	**0.03**
Selenium	2	**1**	**0.4**	-	**-**	**-**
Silver	0.06	**0.02**	**0.02**	0.02	**0.02**	**0.006**
Thallium	0.02	**0.02**	**0.003**	0.02	**0.02**	**0.005**
Tin	0.2	**0.1**	**0.06**	-	**-**	**-**
Uranium	0.02	**0.02**	**0.004**	0.02	**0.02**	**0.007**
Vanadium	0.2	**0.2**	**0.04**	0.2	**0.2**	**0.04**
Zinc	0.6	**0.5**	**0.2**	1.2	**0.5**	**0.4**

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ATTACHMENTS

List of Target Element Masses

Example Standard Sheet

QC Acceptance Criteria

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Analyte	ISOTOPES ANALYZED	ISOTOPE REPORTED
Aluminum	27	27
Antimony	121,123	123
Arsenic	75	75
Barium	135,137,138	137
Beryllium	9	9
Cadmium	111,112,114	111
Chromium	52,53	52
Cobalt	59	59
Copper	63,65	65
Lead	206,207,208	208
Manganese	55	55
Molybdenum	95,97,98	98
Nickel	60,61,62	60
Selenium	77,78,82	82
Silver	107,109	107
Thallium	203,205	205
Uranium	238	238
Vanadium	51	51
Zinc	66,67,68	66

METALS SPIKE FORM

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Service Request #_____

Q.C. Sample #_____

Circle type of digest: GFAA ICP FAA ICP-MS Other:_____ Initials / Date:_____/_____

Circle type of sample: Soil Water Misc. Sludge Oil Other:_____

Solution Name	Element	mLs of 1000ppm Solution	Final Volume	Solution Conc. mg/L	Enter mls Added	
K-MET SS1 ID#14929	HNO3	50.0	1000ml	-		Expires:05/01/2010
	Al	100*	1000ml	200		
	Ag	100*	1000ml	5		
	Ba	100*	1000ml	200		
	Be	100*	1000ml	5		
	Cd	100*	1000ml	5		
	Co	100*	1000ml	50		
	Cr	100*	1000ml	20		
	Cu	100*	1000ml	25		
	Fe	100*	1000ml	100		
	Pb	100*	1000ml	50		
	Mn	100*	1000ml	50		
	Ni	100*	1000ml	50		
	Sb	50	1000ml	50		
	V	100*	1000ml	50		
	Zn	100*	1000ml	50		
K-MET SS2 ID#11468	HNO3	25.0	500ml	-		Expires:4/2010
	As	2.0	500ml	4		
	Cd	2.0	500ml	4		
	Pb	2.0	500ml	4		
	Se	2.0	500ml	4		
	Tl	2.0	500ml	4		
	Cu	2.0	500ml	4		
K-MET SS3 ID#15279	HNO3	25.0	500ml	-		Expires:05/2010
	As	50.0	500ml	100		
	Se	50.0	500ml	100		
	Tl	50.0	500ml	100		
K-MET SS4 ID#14962	HNO3	25	500ml	-		Expires:7/30/2010
	B	50	500ml	100		
	Mo	50	500ml	100		
K-MET SS5 ID#15720	HNO3	10.0	200ml	-		Expires 3/29/10
	K**	20	200ml	1000		
	Na**	20	200ml	1000		
	Mg**	20	200ml	1000		
	Ca**	20	200ml	1000		
K-MET GFLCSW ID# 15022	HNO3	10.0	1000ml	-		Expires: 07/01/10
	As, Pb, Se, Tl	5.0	1000ml	2.5		
	Cd	-	-	1.25		
	Cu	2.5	1000ml	2.5		
K-MET QCP-CICV-1 ID# 12779	Ca, Mg, Na, K	no dilution	-	2500		Expires:10/01/10
	Al, Ba	no dilution	-	1000		
	Fe	no dilution	-	500		
	Co, Mn, Ni, V, Zn	no dilution	-	250		
	Cu, Ag	no dilution	-	125		
	Cr	no dilution	-	100		
	Be	no dilution	-	25		
K-MET QCP-CICV-2 ID# 12778	Sb	no dilution	-	500		Expires: 12/10
K-MET QCP-CICV-3 ID#14972	As, Pb, Se, Tl	no dilution	-	500		Expires:12/1/10
	Cd	no dilution	-	250		

* Denotes volume of mixed stock standard.

** Denotes 10,000 ppm individual stock standards.

Standard	mls of standard	ppm	Logbook #	Exp. Date

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METALS ANALYSES

Method	Prep Method	Matrix	Analyte	LCS Accuracy (% Rec.)	Matrix Spike (% Rec.)	Precision (RPD)
6020	3050B	Soil	Aluminum	41-158	75-125*	20
6020	3050B	Soil	Antimony	50-150	10-103	20
6020	3050B	Soil	Arsenic	78-122	57-133	20
6020	3050B	Soil	Barium	81-119	54-173	20
6020	3050B	Soil	Beryllium	83-117	64-133	20
6020	3050B	Soil	Boron	67-133	75-125*	20
6020	3050B	Soil	Cadmium	81-119	68-137	20
6020	3050B	Soil	Chromium	80-119	34-175	20
6020	3050B	Soil	Cobalt	82-118	74-118	20
6020	3050B	Soil	Copper	83-116	22-181	20
6020	3050B	Soil	Lead	79-121	27-178	20
6020	3050B	Soil	Manganese	81-119	75-125*	20
6020	3050B	Soil	Molybdenum	75-125	53-143	20
6020	3050B	Soil	Nickel	81-118	59-132	20
6020	3050B	Soil	Selenium	80-120	65-125	20
6020	3050B	Soil	Silver	66-134	62-131	20
6020	3050B	Soil	Thallium	79-120	70-128	20
6020	3050B	Soil	Uranium	80-120*	75-125*	20
6020	3050B	Soil	Vanadium	79-121	59-142	20
6020	3050B	Soil	Zinc	73-121	37-162	20
6020	CLP/3020A	Water	Aluminum	85-120	56-143	20
6020	CLP/3020A	Water	Antimony	91-112	66-133	20
6020	CLP/3020A	Water	Arsenic	89-112	72-129	20
6020	CLP/3020A	Water	Barium	92-111	86-117	20
6020	CLP/3020A	Water	Beryllium	81-122	73-125	20
6020	CLP/3020A	Water	Cadmium	92-111	87-113	20
6020	CLP/3020A	Water	Chromium	88-113	60-136	20
6020	CLP/3020A	Water	Cobalt	87-114	84-115	20
6020	CLP/3020A	Water	Copper	89-113	62-130	20
6020	CLP/3020A	Water	Lead	90-112	76-117	20
6020	CLP/3020A	Water	Manganese	89-115	25-180	20
6020	CLP/3020A	Water	Molybdenum	66-135	67-138	20
6020	CLP/3020A	Water	Nickel	89-113	78-117	20
6020	CLP/3020A	Water	Selenium	87-115	47-150	20
6020	CLP/3020A	Water	Silver	64-134	55-136	20
6020	CLP/3020A	Water	Thallium	78-123	75-121	20
6020	CLP/3020A	Water	Vanadium	87-113	82-119	20
6020	CLP/3020A	Water	Zinc	86-119	65-126	20