Title: Agilent 7500ce Inductively Coupled Plasma Mass Spectrometer operation, data acquisition, processing and reporting		Copy No: ##
SOP No: 6.14/3.1 /S	Effective Date: May 13, 2013	Location: ###

QSM Approval: _____

Agilent 7500ce Inductively Coupled Plasma Mass Spectrometer operation, data acquisition, processing and reporting

1. INTRODUCTION AND SCOPE

1.1. This Standard Operating Procedure (SOP) provides procedures for the operation of the Agilent 7500ce Inductively Coupled Plasma Mass Spectrometer (ICP-MS), and for data acquisition, processing and reporting using the ChemStation software.

1.2. Agilent 7500ce ICP-MS system is restricted for use by, or under supervision of experienced and properly trained personnel.

2. INSTRUMENT START-UP

2.1. The shield torch must be used at all times when using ICP-MS. For installation of the Shield Torch, refer to the *Agilent 7500 Series ICP-MS Hardware Manual*.

2.2. The Agilent integrated autosampler (I-AS) should be properly installed and configured for automatic control using ChemStation software (refer to the *Agilent 7500 Series ICP-MS Hardware Manual)*. Turn the autosampler **ON.**

2.3. Click ***ICP-MS Top*** on the desktop, select ***Instrument*** from the top panel (or click ) and choose ***Instrument Control*** >> ***ALS*** >> ***Home***. Fill ***Bottle 1*** with tuning solution (5 µg/L Li, Y, Tl and Ce, in 2% HNO_3), ***Bottle 2*** with fresh double deionised water (DDW), and ***Bottle 3*** with fresh 1% HNO_3[1].

2.4. Ignite the plasma.

2.4.1 Open the liquid argon (Ar) gas valve and the hydrogen (H_2) and/or helium (He) gas cylinders valves. Make sure that the outlet pressure of liquid Ar Dewar is more than 100 psi (or Dewar is more than 30% full) and the gas cylinders pressures are not below 500 psi. **NOTE**: If the liquid Ar outlet pressure is lower than 100 psi, turn on the pressure-building valve on the Dewar; it may have to be kept open during the analysis.

2.4.2 Check the gas delivery pressures from the switchover gas line system. The Ar gas delivery pressure should be between 110 -120 psi. Adjust the knob on the switchover system and check the reading of the Ar pressure from the ChemStation until it is between 700 – 730 kPa. The H_2 or He gas outlet pressure should be 5 psi.

[1] Acid concentrations in this document are expressed as % (v/v)

2.4.3 Make sure that the chiller is **ON** and the water temperature is 12 to 15^{o}C. Visually check the cooling water filter compartment for change of color. The clean filter is white; if the filter is dark brown or black in color, it needs to be changed.

2.4.4 Check the drain vessel level and empty if necessary.

2.4.5 If the instrument is in ***STANDBY*** mode, the LED on the top right side of the top cover displays an orange light. **G**o to Step 2.2.7.

- If the instrument is in ***SHUTDOWN*** mode, turn on the instrument and the computer.
- Start the ***ChemStation*** software by double clicking ***ICP-MS Top*** on the desktop. Select ***Instrument*** from the top panel and click on ***Instrument Control***. The instrument control window will appear with a diagram of the instrument status.
- Click ***Vacuum*** from the top panel and select ***Vacuum ON***. Click ***Yes*** at the dialog box to confirm. It usually takes at least 40 minutes for the vacuum chamber to attain its correct pressure of 5 x 10^{-4} Pa, depending on how long the vacuum chamber has been open to the atmosphere. The LED on the top right side of the top cover will be flashing until the proper vacuum is achieved.

2.4.6 Check the condition of the peristaltic pump tubes and replace if necessary. Ensure that they are correctly clamped into the peristaltic pump.

2.4.7 Ensure that the autosampler needle is in the ***Bottle 2*** by selecting ***ALS*** from the top panel, and choosing ***Go To*** and ***2.***

2.4.8 Complete the "Standby Mode" section of the logbook. The typical values for Ar delivery pressure, backing pressure and analyser pressure are shown in Appendix A (Table A1).

2.4.9 Select ***Plasma*** >> ***Plasma ON*** or simply click  to ignite the plasma. Click ***Yes*** in the dialog box to confirm.

2.4.10 When changing to the Analysis mode is complete, the LED on the top right side of the top cover will display a green light.

2.5. Ensure that the drain is flowing.

2.6. Wait for at least 45 minutes for the system to stabilize. Then record in the "Analysis Mode" section of the logbook the following meter readings from the ChemStation software: Ar gas tank pressure, forward and reflected power, interface pressure (I/F pressure), backing pressure, analyzer pressure, cooling water flow rate at the interface (WC/IF) and the RF generator (RF/TP). The typical values for these parameters are shown in Appendix A (Table A2).

3. INSTRUMENT TUNING

3.1. Select ***Instrument*** >> ***Tune*** (or simply click ) to open the tuning window.

3.2. Start tuning in no gas mode (Reaction gas should be **OFF**). Make sure that the internal standard line is disconnected and the corresponding inlet of T-joint is plugged in. Refer to the *Agilent 7500 Series ICP-MS Tuning & Application Handbook* for detailed tuning procedure (page 1-38) and typical values of tuning parameters (page 1-49).

3.2.1 Make sure that the autosampler needle is in ***Bottle 1*** containing tuning solution. If not, select ***Instrument Control*** >> ***ALS*** >> ***Go To*** >> ***1***. Wait for about 3 minutes for the uptake of the solution to the nebulizer and stabilization of the signal. The peristaltic pump speed should be the same as that of analysis (e.g., 0.10 rps).

3.2.2 Select ***Tune*** >> ***Sensitivity*** (or click the shortcut button ) to adjust sensitivity and obtain high stable signal over the whole mass range. Click ***Start*** to monitor the signal (for ^{7}Li, ^{89}Y and ^{205}Tl) and view the numerical values in the real-time display. The typical values of sensitivity are shown in Appendix B (Table B1). The RSD should not exceed 5% and the background should be less than 10 counts per second (CPS) for all three masses.

3.2.3 Select ***Tune*** >> ***Oxide Ion*** (or click the shortcut button ). Click ***Start*** to monitor the signal (156/140 mass ratio) and view the numerical values in the real-time display. Tune the instrument so that the oxide ion ratio is lower than 1.5% when using Micro Mist Nebulizer, or lower than 2% if using other types of nebulizers. To promote the decomposition of oxide species:

- Increase the Sampling depth
- Decrease the Carrier gas and Make up gas flows (sum should be ~1 L/min)
- Increase the RF power
- Decrease the Sample flow rate

3.2.4 Select ***Tune*** >> ***Doubly Charged Ion*** (or click the shortcut button ). Click ***Start*** to monitor the signal (70/140 mass ratio) and view the numerical values in the real-time display. The ratio of doubly charged mass to the element mass should not be higher than 4% (ideally, it should be below 2%). In order to reduce the ratio of doubly charged ions, follow the same steps as 3.2.3.

3.2.5 Select ***Tune*** >> ***Resolution/Axis*** (or click the shortcut button ). Click ***Start*** to monitor the signal and view the spectra and numerical values in real-time

display. The resolution (W-10%) should be 0.65 - 0.85 AMU, and the axis should be within ± 0.05 of the selected mass.

3.2.6 When all tuning parameters are within acceptance criteria, go to step 3.8.

3.3. There is no necessity to re-tune the instrument, if the sensitivity is similar to or better than the typical values shown in Appendix B (Table B1), the oxide and double charged ion percentages are below the above-mentioned levels, and the resolution for each mass is reasonable. If a major tuning is needed, in the tuning window choose ***Tune*** >> ***Autotune***, and check the boxes next to the following parameters: ***Resolution/Axis***, ***Torch Vertical/Horizontal Position***, and ***Lens/Plasma***. Click ***OK***.

3.3.1 Repeat procedures 3.2.1 to 3.2.6 to perform fine tunes if necessary. **It is strongly recommended that ONLY the person with EXTENSIVE EXPERIENCE on ICP-MS adjust the parameters in *Advanced Setting*.** Typical values of tuning parameters are shown in Appendix B (Table B2).

3.4. Perform detector tuning **(set EM)** monthly using autotune setting.

3.4.1 Make sure that the autosampler needle is in ***Bottle 1.***

3.4.2 In the tuning window, select ***Tune >> Autotune;*** check the boxes of ***Hot***, ***EM*** and ***Adjust Discriminator***. Click ***Run***.

3.4.3 Record the ***Discriminator*** voltage, the ***Analog HV*** and ***Pulse HV*** in the ICP-MS Autotuning Log.

3.5. **Set P/A factor** once set EM has been performed.

3.5.1 Usually a standard solution that includes all analytes and will be used as one of the standard solutions to make calibration curves is used for tuning P/A Factors.

3.5.2 In the tuning window, select ***Tune >> P/A Factor Tuning***. A dialog box will appear; fill in the masses and elements selected, or load them from an acquired method.

3.5.3 Disable ***Merge in the Current Data*** box.

3.5.4 Enter the vial number of the autosampler in the ***ALS Tuning Solution Vial*** (e.g. vial 1001 for position 1 in autosampler tray). Click ***Run***.

3.5.5 After the P/A factor tuning is complete, print and keep the ICP-MS report together with the tuning report of the same day. Highlight the whole page, copy/paste to NOTEPAD and save it in C:\ICPCHEM\1\7500\PAFactor folder as **xx(year)xx(month)xx(date)** (e.g. 120610). Record the file name in the ICP-MS Autotuning Log.

3.5.6 Click **Yes** to the dialogue box: *Would you like to adopt new P/A factors*?

3.6. Tune the instrument in reaction/collision cell mode using He or H_2 gas, if needed. For details refer to *Agilent 7500 Series ICP-MS Tuning & Application Handbook*, page 1-51 and 1-55, respectively.

3.6.1 It is recommended to tune in He or H_2 mode after tuning in no gas mode. Autotune cannot be used in this mode. However, after using Autotune in no gas mode, edit the tune values and change only values necessary for He or H_2 mode (Table B2).

3.6.2 Turn ***Reaction Mode*** Check Box ***ON*** and set the value 4.5 mL/ min for the He or 5.0 mL/min for the H_2 gas flow rate.

3.6.3 Modify the other parameters according to Table B2.

3.6.4 Maximize the sensitivity of ^{89}Y by adjusting the Cell Entrance, QP focus and Cell Exit.

3.6.5 Aspirate fresh DDW and measure the background counts for mass 51 AMU (He mode) and 56 AMU (H_2 mode). If the counts of these masses are too high, increase the flow rate of He or H_2 gas (up to 6.0 mL/min); then repeat steps 3.6.3 and 3.6.4 to get the best sensitivity (table B2).

3.6.6 Record the analyzer pressure in the "Analysis Mode" section of the logbook.

3.6.7 When all the tuning parameters are within acceptance criteria, go to step 3.8.

3.7. Tune the instrument in the high matrix introduction (HMI) mode if analyses of lanthanoids (La to Lu) are required. It is recommended to tune in HMI mode after tuning in no gas mode.

3.7.1 Make sure the autosampler needle is in ***Bottle 1*** containing the tuning solution for lanthanoids (5 µg/L Ba, Pr, Dy, Tm, Lu in 2% HNO_3).

3.7.2 In the toolbar select ***HMI Option*** >> ***Preset HMI parameters*** >> ***Preset Mode*** >> ***Ultra Robust Low***.

3.7.3 The sensitivity should be within limits specified in Appendix B (Table B1) with a RSD of less than 5%; the oxide ratio should range between 0.5 and 1% and the doubly charged ion ratio should be less than 4%. If not, follow the steps as described in 3.2.3.

3.7.4 When all the tuning parameters are within acceptance criteria, go to step 3.8.

3.8. Select ***File*** >> ***Save Tune Values*** to save the tuning parameters. Type the tuning file name as xx(year)xx(month)xx(date) and a description of tuning mode (max. 8 characters, e.g. 120610HM for tuning in HMI mode).

3.9. Select ***File*** >> ***Generate Report***. Print and keep the Tuning Report as a record.

3.10. Record Sensitivities, Oxide and Doubly Charged Ions percentages.

3.11. Rinse the sample line and instrument between different tuning solutions using 2% HNO_3 followed by DDW or 1% HNO_3.

3.11.1 Select ***Tune*** >> ***ALS*** >> ***Rinse***; when the autosampler needle dips into the rinsing port, increase the peristaltic pump speed up to 0.30 rps and let it rinse for 2-3 minutes.

3.11.2 Select ***Tune*** >> ***ALS*** >> ***Go To*** >> ***3*** to move the autosampler needle to the 1% HNO_3 bottle and rinse for 1 minute.

3.11.3 Lower the peristaltic pump speed back to 0.10 rps before starting tuning or measuring.

4. ON-LINE INTERNAL STANDARD ADDITION SET-UP

The instrumental drifts and matrix-induced changes of sensitivity are corrected by the use of internal standards. Internal standard solution (containing Y, In, and Ho) is added on-line at the time of analysis for all samples, standards and blanks.

4.1. In the top panel of ***ICP-MS Top*** select ***ALS*** >> ***Go To*** >> ***2*** to move the autosampler needle to ***Bottle 2*** (DDW).

4.2. Make sure the peristaltic pump speed is set to 0.10 rps.

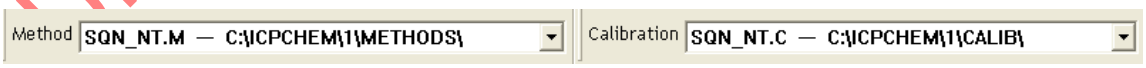
4.3. Connect the internal standard line to the corresponding inlet of the T-joint and make sure that the flow is steady.

4.4. Move the autosampler needle to ***Bottle 3*** (1% HNO_3).

4.5. Monitor the instrument signal for elements present in the internal standard solution, (see 3.2.2); make sure that the signal is stable (RSD <10%) before starting the analysis.

5. METHOD CREATION/EDIT

5.1. Usually, a new method is created by editing any existing method and saving the changes under a new name. A new calibration file with the same name will be created automatically. The name of the current method is displayed in the title box next to ***Method***.



5.2. In the top panel of ***ICP-MS Top***, select ***Methods*** >> ***Edit Entire Method*** and follow the dialog boxes to continue. For details refer to the *Agilent 7500 Series ICP-MS ChemStation (G1834B) Operator's Manual*. Select the following parameters:

Interference Correction Equation:	208: [208]*1+[206]*1+[207]*1
Acquisition mode:	Spectrum

Acquisition parameters	See Appendix B (Table B3)
Peristaltic Pump Program	See Appendix B (Table B4)

5.3. The peristaltic pump is programmed to uptake the solution under analysis at a higher speed (for example 0.30 rps) for the first 35 seconds, stabilize for 30 seconds, and start acquisition at a lower speed, which is usually 0.10 rps (Table B4).

NOTE: When samples or standards are sequentially analyzed, memory effect or carry-over may occur if large concentration differences are present. The extent of memory effect is affected by sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer. The rinse period between samples must be long enough to eliminate significant memory effects.

5.4. After all parameters are entered or edited, the ***Method Save Options*** dialog box will appear. Make sure that all options are checked and then click ***OK***.

5.5. The ***Specify File Name for Method and Calibration*** dialog box will appear. Type in the name (max. 8 characters) for the created method and calibration file and click ***OK***. It is recommended that both files be saved with the same name. **NOTE**: Save the modified method under a new name, i.e., giving a new version number.

6. SEQUENCE SET-UP

6.1. In the top panel of ***ICP-MS Top***, select ***Sequence*** >> ***Edit Sample Log Table;*** the ***Sample Log Table*** dialog box will appear. To create a sequence, edit the Sample Log Table for the sequence currently in memory. For details refer to the *Agilent 7500 Series ICP-MS ChemStation (G1834B) Operator's Manual* (Chapter 5).

6.2. Save the created sequence by selecting ***Sequence*** >> ***Save.*** The ***Save Sequence*** dialog box will appear. Enter the sequence name as the description of samples to be run. For example, an aqueous PM extract batch sequence is named: "TB**N" (No gas mode) or "TB**H2" (H_2 mode).

6.3. Print the sequence and load the autosampler with vials containing samples, blanks and standards (fill each vial to ~80% of max. volume). Typical sequence examples are given in Appendix C.

6.4. Finish the sequence with the **Wash.M** method (Vial #2). This method is designed to rinse the instrument after completing the sequence with DDW in two steps of 5 minutes each, with pump speed 0.30 and 0.10 rps, for the first and the second step, respectively.

6.5. In case the analysis cannot be completed before the end of working hours, the sequence should be finished by the ***Keyword: StandBy,*** which ensures that the plasma will turn off automatically at the end of the run.

6.6. A ***Chained Sequence*** may be set up when it is necessary to run a series of sequences without interruption.

6.6.1 Generate a sequence for each mode (method) and save using a proper name (see 6.1 and 6.2).

6.6.2 In the top panel of ***ICP-MS Top*** select ***Chained Sequence*** >> ***Edit and Run***.

6.6.3 Select proper sequences and the corresponding tuning files (for example, no gas mode tuning file should be selected for the sequence generated for no gas mode, and H_2 mode tuning file should be selected for the sequence generated for H_2 mode).

6.6.4 Enter the stabilization time between the operation modes switching as 900 seconds.

6.6.5 Check the box at the bottom next to ***Save Sequence after Run***.

6.6.6 Click ***Run.***

6.6.7 Using a chained sequence will not allow the analyst to type in the name for the data batches. The computer will generate the name as xx(year)Y(month, letter)zz(date)T(time, letter)00 (for example, the data generated on January, 01, 2012 at 5 pm will be named as 12A01r00).

7. METHOD INITIALIZATION

7.1. Ensure the proper sequence is loaded and select ***Sequence*** >> ***Run***.

7.2. The ***Start Sequence*** dialog box will appear. Under ***Method Sections To Run***, check ***Full Method*** option. Type the analyst's name in the box next to ***Operator Name***. In the box next to ***Data Batch Directory***, type in the data file name for the analysis: C\ICPCHEM\1\DATA\xx(year)xx(month)xx(date).B\ (max. 8 characters, e.g. 122506).

7.3. Click ***Run Sequence***.

7.4. To start the sequence from any desired position of the ***Sample Log Table***, click ***Sequence*** >> ***Position and Run***. Click the line of the ***Sample Log Table*** where you want to start. Click *OK*.

7.5. If a single sample will be analyzed using a specific method, make sure that the proper method and calibration are loaded. Select ***Methods*** >> ***Run***, fill out the dialog box and click ***Run Method***.

8. DATA PROCESSING FOR QUANTITATIVE ANALYSIS OF TRACE ELEMENTS

8.1. The Agilent 7500ce allows for both quantitative (FullQuant) and semi quantitative (SemiQuant) modes of data acquisition and analysis. FullQuant is defined as the method where concentrations of unknown samples are calculated based on a

calibration curve that covers the expected concentration range for all analytes; in the SemiQuant method a single calibration standard that contains all analytes is used.

8.2. The SemiQuant[2] program allows the use of up to 4 internal standards at a time, thus ^{89}Y, ^{115}In, and ^{165}Ho are used. Depending on the intended analysis, other internal standard elements can be used.

8.3. Obtain SemiQ factors in ***Offline Data Analysis*** panel:

8.3.1 After the calibration standard is run, open ***Offline Data Analysis.***

8.3.2 Click ***Method*** >> ***Load*** and select the on-line method and calibration files.

8.3.3 Click ***Data file*** >> ***Load*** and select the current calibration standard data file.

8.3.4 Select ***SemiQuant*** >> ***Internal Standard Correction***; click the ***Browse*** button and select the current calibration standard data file. Make sure that the correct elements (e.g. Y, In and Ho) are selected as ***Internal Standard Elements***.

8.3.5 If a background correction is necessary (e.g. methods 6.11/*.*M and 6.13/*.*/M) select ***Method*** >> ***Data Correction*** and check the box next to ***Subtract Background.*** Click the ***Browse*** button and select the current calibration blank data file. Make sure that the correct masses (e.g. 89, 115 and 165) are selected as ***Rejected Masses.***

8.3.6 Click ***SemiQuant*** >> ***Edit SemiQuant Parameters.*** Enter the concentrations of analytes present in the calibration standard and select ***Correct by Current Data.*** NOTE: Do not click the ***Reset Correction*** button.

8.3.7 Select ***Method*** >> ***Run analysis method***. Look at the report and verify if the concentrations are the same as the calibration standard solution (i.e. about 20 µg/L for most elements).

8.3.8 Select ***Method*** >> ***Save*** to save the method to the root menu; then choose ***Save to Online***. From now on, all results will be processed using the updated SemiQ factors, background correction, and internal standard file.

8.3.9 Select ***SemiQuant*** >> ***Generate Report*** and print the report that contains the SemiQ factors for each element analyzed.

8.4. The ICP-MS method is always associated with a database, which is updated during the analysis and contains the results of current analysis.

8.4.1 To create a new custom report, select ***SemiQuant*** >> ***Edit Custom Report*** >>***Template*** >> ***New*** in the top panel of ***Offline Data Analysis.*** Two windows will open: Report Template (.sqt), and Database (.*sq*d).

[2] This SOP refers to SemiQuant method only. For details on the FullQuant method, refer to the *Agilent 7500 series ICP-MS Chemstation (G1834B). Operator's manual,* Chapter 11

8.4.2 Click ***Database*** >> ***Header,*** select ***Data File Path, Data File Name, Sample Name, Date Acquired*** and ***Acquisition Method*** and click ***Add***.

8.4.3 Go to ***All Elements*** >> ***Semi Quant Elements*** >> ***Isotope 1*** >> ***Concentrations*** >> ***Add***. For more details on how to create and edit a custom report, refer to *Agilent 7500 Series ICP-MS ChemStation (G1834B) Operator's Manual* (Chapter 10)

8.4.4 When all the necessary items are selected, click ***OK.*** Save the Custom Report Database in the designated sub-directory using the same name as the method, calibration and report files. Link the database to the current method file.

8.5. After all samples are analysed, go to the top panel of ***Offline Data Analysis*** and select ***SemiQuant*** >> ***Edit Custom Report***. Choose the database window, highlight the whole database and select ***Edit*** >> ***Copy***. Open an Excel spreadsheet and paste.

8.6. Save the Excel spreadsheet to ICPMSBackup$ drive in the yyyy Excel folder as "yyyymmdd_description of batch". The data in the spreadsheet can now be accessed by the analyst at his/her office computer for reporting.

8.7. Transfer raw data to the corresponding sub-directories in the ICPMSBackup$ shared drive immediately after the analysis is completed and before any reprocessing. The data are then copied to the analyst's computer for further reprocessing and reporting.

8.8. Remove the data from the local disk drive (C drive) and save them in the ICPMSBackup$ shared drive or the external hard drive every six months to ensure that the C drive has enough memory to perform all the steps of analysis.

8.9. In general, there is no need to reprocess data that have been obtained with the current SemiQ factor, background and internal standard correction.

8.9.1 To reprocess data files individually go to ***Offline Data Analysis.*** Load the data file that needs to be reprocessed and select ***Method*** >> ***Run*** >> ***Analysis Method***.

8.9.2 To reprocess data file as a batch:

- Go to ***ICP-MS Top***, click ***Method*** >> ***Load*** and select the method saved in the folder of the batch that needs to be reprocessed.
- Open the ***Offline Data Analysis*** panel and follow steps 8.3.1 to 8.3.9 to make the necessary changes.
- In the ***ICP-MS Top***, select ***Sequence*** >> ***Reprocess Data Batch*** and load the data batch that needs to be reprocessed. Continue with steps 8.5 to 8.8.

9. DATA REPROCESSING FOR LEAD ISOTOPES ANALYSIS

9.1. Open ***ICP-MS Top***, choose ***Sequence*** and load the sequence *results.s* file from the folder of the batch analyzed in no gas mode (for example C:\ ICPCHEM\ 1 \ DATA\ batchname\ results.s). NOTE: Check the attributes of this file using Windows Explorer (right-click the file) and uncheck the box ***Read Only.***

9.2. Click ***Sequence*** >> ***Edit Sample Log Table***. Change the method name to the isotopes ratio analysis method for all samples. Save the sequence table using the same name (*results.s*). NOTE: The isotopes ratio analysis method acquires only Pb isotopes, should not have any interference equation and should be linked to a database containing the counts (CPS) of ^{206}Pb, ^{207}Pb and ^{208}Pb.

9.3. Click ***Sequence*** >> ***Run.*** Under ***Method Sections to Run,*** check ***Reprocessing only*** and load the data batch directory that needs to be reprocessed.

9.4. When reprocessing is finished, click ***Data Analysis*** >> ***Main Panel***. In the new window that opens, select ***SemiQuant*** >> ***Edit Custom Report.*** The database will contain counts for all lead isotopes.

9.5. Copy and paste the database in an Excel Workbook. Perform the necessary calculations following the appropriate template (see NOTE). Save the Excel files and create the necessary backups (see 8.6 to 8.8).

- **NOTE**: All mass spectrometers exhibit a mass bias which changes with instrument conditions and drifts with time. In order to correct for the mass bias the bracketing method with SRM981 standard is used. The correction factors and corrected ratios are calculated as follows:
- Calculate the correction factor F(208) as:

$$F(208)= \frac{R^{Std.}_{Certified}\,(208)}{R^{Std.}_{Measured}\,(208)}$$

where F(208) is the correction factor and $R^{Std.}_{Certified}\,(208)$ and $R^{Std.}_{Measured}\,(208)$ are the certified and measured ^{208}Pb/^{206}Pb ratios for the SRM981 standard, respectively.

i. Calculated the corrected ratios as:

$$R_{Corrected}(208)= F(208)\times R_{Measured}(208)$$

where $R_{Corrected}(208)$ and $R_{Measured}(208)$ are the corrected and measured ^{208}Pb/^{206}Pb ratios, respectively; F(208) corresponds to the correction factor of the SRM981 standard acquired less than 10 measurements prior to the actual sample.

ii. Repeat calculations (i to ii) to correct the measured isotope ratios for $^{207}Pb/^{206}Pb$ for all samples.

10. PLASMA TURN-OFF

10.1. After completing the analysis, rinse the system with 2% HNO_3 at 0.30 rps peristaltic pump speed for 5 minutes, followed by rinsing with DDW for 5 minutes.

10.2. Lower the peristaltic pump speed back to 0.10 rps, then click ***Plasma*** >> ***Plasma OFF*****.** A dialogue box will appear confirming if you wish to turn off the plasma; click "Yes".

10.3. Close all gas line valves.

10.4. Turn off the chiller if the instrument will not be used for 3 days or longer.

11. AUTOSAMPLER TURN-OFF

11.1. Turn off the autosampler at the end of the analysis by turning off the power switch located at the back of the autosampler.

11.2. Cover the rinsing port with the plastic cap.

12. INSTRUMENT SHUT DOWN FOR MAINTENANCE

12.1. Shut down the instrument when maintenance inside the vacuum chamber is to be performed, or when the instrument will not be used for a prolonged period of time (e.g. 2 months and longer).

12.2. To shut down the instrument, THE VACUUM MUST BE TURNED OFF FIRST and THE ARGON SUPPLY MUST BE ON. Select ***Vacuum*** from the top panel of ***Instrument Control***, and choose ***Vacuum OFF***.

12.3. When the LED on the top right side of the top cover of the ICP-MS stops flashing (usually takes a few minutes), turn off the power by pushing the power switch located at lower right of the instrument. Unplug the power supply if necessary.

APPLICABLE DOCUMENTS

6.10/*.*/M "Determination of Trace Elements in Aqueous Extracts of Airborne Particulate Matter and Other Aqueous Solutions by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)"

6.11/*.*/M "Determination of Near-Total Trace Elements in Airborne Particulate Matter by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)"

6.13/*.*/M "Determination of Trace Elements and Lanthanoids in Airborne Particulate Matter by

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

SWP-001/*.*: Safe Working Procedures and Policies

REVISIONS

December 2004: Author, Heidi Chen. New document SOP 6.14/1.0/S

August 2005: Reviewer, Heidi Chen

Section 2.2.1: addition of "Open the hydrogen (H_2) gas cylinder valve, if applicable; and open the helium (He) gas cylinder valve if it is not already open". Section 3.2.2: last sentence "click OK" was changed to "click Run"; Section 3.7.4 change was made to the range of He flow rate, i.e., from "2.5 to 4.0 mL/min" changed to "2.5 to 4.5 mL/min"; Section 3.7.9 was modified to include more information; Section 6.4 was added; Section 8.2.5 was added, Table 1 in Appendix A, "Computer Reading" is added to the first cell in the table under "Meter"; Table 2 in Appendix A, Cooling water flow rate (WC/IF) changed from "1.1 to 2.0 L/min" to "1.1 to 2.1 L/min"; Table 3 in Appendix B, the "Count/10 ppb" for 7Li is changed to > 3000; Table 4 in Appendix B, the Adjustment Range for Cell Exit (V) is changed to "-15 to -5 (practically no more negative than -20)".

April 2007: Reviewer Valbona Celo and Irina Okonskaia

Section 2.2.3: "Record tank and outlet pressure values into appropriate log" is added Section 2.2.12: "Before Plasma Ignition" section of logbook was changed to "Stand By" section of logbook; Section 2.4: "Also record the analyzer pressure in H_2 mode if needed" is added; Section 3.3.3.4 is deleted; Section 3.3.6.1 and 3.3.6.2 are deleted; Sections 3.4.4 and 3.7.10: tune files names are changed to xx(month)xx(date)xx(year)N, xx(month)xx(date)xx(year)He and xx(month)xx(date)xx(year)H2; Sections 3.7.11 and 3.7.12; Section 4.3 is removed; Section 4.4 is changed; Section 6.3 is changed to: "Enter the name of sequence as description of samples to be run. For example, aqueous PM extract batch sequence is named: TB**N (Normal mode) or TB**H2"; Section 8.1 and 8.2 are combined in one; Section 8.5 is added; All sections and tables: the instrument operation conditions with no collision or reaction gas is always referred to as normal mode.

September 2009: Reviewers: Valbona Celo and Irina Okonskaia

The SOP is applicable to the operation of Agilent 7500 ce system and changes are made in the title and in the text, accordingly; Section 2.2.4.: "Make sure that the chiller is ON and the water temperature is 12 to 15^{o}C" is added; Section 2.4: the waiting time is changed to 45 min; recording of plasma gas flow rate and auxiliary gas flow rate, are removed;; Section 3.2 is changed to Section 3.4; Sections 3.3 and 3.4 are combined in Sections 3.2. and 3.3; Sections 3.2 to 3.4: The Chemstation buttons are added, the peristaltic pump speed is changed to 0.10 rps, concentration of tuning solution is changed to 5 □g/L. Section 3.3.3 is changed to: "Click *Start* and monitor the ratio of signals for mass 156/140 which should be lower than 1.5% when using Micro Mist Nebulizer and

lower than 2% if using other types of nebulizers"; Section 3.3.6: Table 4 is changed to Table B1 (Appendix B); Section 3.4.1: "Make sure that the internal standard line is disconnected and the corresponding inlet of T-joint is plugged in" is added; Section 3.5: concentration of the multielement solution is changed to 50 ppb; Section 3.7 is changed according to requirements of the new instrument configuration; Section 4.3: "Connect the internal standard line at corresponding inlet of T-joint" is added; Sections 5.4 to 5.7 are changed according to requirements of the new instrument configuration; Section 6.1 "For details refer to *Agilent 7500 Series ICP-MS ChemStation (G1834B) Operator's Manual*" is added; Section 6.2 is removed; Section 6.4.4: Stabilization time between operation modes is changed to 600 seconds; Section 6.3.8: The Chained Sequence Simulation is added; Section 7.5 is added; Section 8.5: "Turn off the chiller if the instrument will not be used for 3 days or more" is added; All tables are changed to reflect typical values for the new instrument configuration and to add values of parameters in reaction gas mode. All sections and tables: the instrument operation conditions in normal mode are referred to as no gas mode.

May 2011: Reviewer Valbona Celo

No changes were made

May 2013: Reviewer Valbona Celo, Irina Okonskaia

Title is revised; Small editorial changes are made throughout the text; Section 1.1: "the data acquisition, processing and reporting using the ChemStation software", is added; Section 1.2 is moved to Section 2; Section 1.3 is changed to: "Agilent 7500ce ICP-MS system is restricted for use by, or under supervision of, properly experienced and trained personnel"; Section 2 title is changed; Sections 2.1 and 2.2 are changed; Section 3.2.2: "The RSD should not exceed 5% and background should be less than 10 counts per second (CPS) for all three masses" is added; these values are removed from Table B1 (Appendix B); Sections 3.2.6, 3.3.2 and 3.6.6 are changed to "When all the tuning parameters are within acceptance criteria, go to step 3.8"; Sections 3.2.7, 3.3.3 and 3.6.7 are deleted and Section 3.8 is added instead; Section 3.7 is added; Section 4: "The instrumental drifts and matrix-induced changes of sensitivity are corrected by the use of internal standards. Internal standard solution (containing Y, In, and Ho) is added on-line at the time of analysis for all samples, standards and blanks" is added; Section 4.5 is added; Section 5.2: the table of parameters is added; Section 6.3 is added; Sections 8 and 9 are added; Appendix B, Table B1: sensitivity values for H2 and HMI modes is added; values for RSD% and Background signal are added in the text; Appendix B, Table B2: tuning parameters for HMI mode are added; Tables B3, B4 and Appendix C are added

REFERENCES

Agilent Technologies, *Agilent 7500 Series ICP-MS ChemStation (G1834B) Operator's Manual*, Rev.A, September 2007

Agilent Technologies, *Agilent 7500 Series ICP-MS Tuning & Application Handbook*,

Rev. A, May 2008.

Agilent Technologies, *Agilent 7500 Series ICP-MS Hardware Manual*, Rev. A, September 2008

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Appendix A

Table A1. Typical Range for 7500 ce instrument parameters in Standby Mode

Meter	Typical Range	Recommended range
Ar Gas Delivery Pressure	720 - 730 kPa	700 - 730 kPa
Backing Pressure	1 to 2 Pa	0.3 to 5 Pa
Analyzer Pressure	1 x 10^{-5} to 6 x 10^{-5} Pa	3 x 10^{-5} to 6 x 10^{-4} Pa

Table A2. Typical Range for 7500 ce instrument parameters in Analysis Mode

Meter	Typical Range	Recommended Range
<u>Ar gas flow</u> Plasma gas flow rate Auxiliary gas flow rate	 15 L/min 0.89 L/min	 15 L/min 0 to 1.0 L/min
<u>RF generator</u> Forward power Reflected power Cooling water flow rate (RF/TP)	 1200 to 1500 W < 2 W 2.0 to 2.3 L/min	 700 to 1600 W < 20 W 1.1 to 3.0 L/min
<u>Interface</u> Interface pressure (I/F pressure) Cooling water flow rate (WC/IF)	 250 to 350 Pa 1.9 L/min	 250 to 490 Pa 1.1 to 2.1 L/min
Backing pressure	290 – 350 Pa	250 – 490 Pa
Analyzer Pressure	2 to 4 x 10^{-4} Pa in no gas mode 4 to 9 x 10^{-3} Pa in reaction gas mode	3 x 10^{-4} to 2 x 10^{-3} Pa (no gas mode)

Appendix B

Table B1. Typical Values of Sensitivity (CPS)[(a)]

No gas mode		H_2/He mode		HMI mode	
^{7}Li	10 to 20 $\times 10^3$	^{56}Fe/^{51}V	< 1000	^{138}Ba	5 to 10 $\times$ 10^3
^{89}Y	20 to 40 $\times 10^3$	^{89}Y	10 to 20 $\times$ 10^3	^{162}Dy	3 to 5 $\times$ 10^3
^{205}Tl	10 to 20 $\times 10^3$			^{175}Lu	8 to 15 $\times$ 10^3

[(a)]Signal of a solution containing 5 µg/L of each analyte and integration time 0.1 sec

Table B2. Typical Values of Tuning Parameters

Parameter	Typical Values	Adjustment range
RF Power (W)	1300 to 1500 (-1600 W in HMI mode)	Normally use 1500
Sampling Depth (mm)	6.5 to 7.5 (10 in HMI mode)	6 to 10
Carrier Gas (L/min)	0.6 to 0.8 (0.35 in HMI mode)	Normally use 0.6
Makeup Gas (L/min)	0.2 to 0.4 (0.60 in HMI mode)	0.1 to 0.3
Nebulizer pump (rps)	0.10	Normally use 0.10
S/C Temp (°C)	2	Normally used at 2 °C
Extract 1 (V)	0	0 to 6
Extract 2 (V)	-130	-150 to -70
Omega Bias-ce (V)	-28 to -22	-30 to -12
Omega Lens-ce (V)	1 to 2	-2 to 2
Cell Entrance (V)	-40 to -35	-40 to -30
Cell Exit (V)	-45 to -35	-50 to -30
QP Focus	5 (-8 in reaction gas mode)	1 to 5
OctP RF (V)	140 to 150	140 to 200
OctP Bias (V)	-6 (-18 in reaction gas mode)	Normally use -6
QP Bias (V)	-3 (-16 in reaction gas mode)	-3 to -1 (3 V more positive than OctP Bias)

Table B3. Example of Data Acquisition parameters

Isotope	Integration Time (sec/point)			Interference Equation & Notes
	No gas mode	H_2 Mode	He Mode	
^{9}Be	0.2	--	--	Interference Equation: $^{208}Pb = {}^{206}Pb + {}^{207}Pb + {}^{208}Pb$ Notes: (a) If no interference is suspected, Cr can be determined in no gas mode, where ^{52}Cr or ^{53}Cr is acquired. (b) Lead isotopes ^{206}Pb and ^{207}Pb are acquired for the use of interference equation. ^{208}Pb is reported for quantitative determination of Pb (c) Bi can be determined if not added to the mixed internal standard solution (d) Lanthanoids (La to Lu) are analyzed in HMI mode with an Integration time 0.2 sec/point
^{27}Al	0.1	--	--	
^{47}Ti	0.1	--	--	
^{51}V	0.1	--	0.3	
^{52}Cr	0.1[(a)]	0.1	0.3	
^{53}Cr	0.3[(a)]	--	0.3	
^{55}Mn	0.1	--	--	
^{56}Fe	--	0.05	0.1	
^{59}Co	0.2	--	--	
^{60}Ni	0.2	--	--	
^{65}Cu	0.1	--	--	
^{66}Zn	0.3	--	--	
^{69}Ga	0.2	--	--	
^{72}Ge	0.2	--	--	
^{75}As	0.2	--	0.3	
^{78}Se	--	0.2	--	
^{85}Rb	0.1	--	--	
^{88}Sr	0.1	--	--	
^{89}Y (ISTD)	0.1	0.1	0.1	
^{90}Zr	0.2	--	--	
^{93}Nb	0.2	--	--	
^{95}Mo	0.2	--	--	
^{107}Ag	0.2	--	--	
^{111}Cd	0.3	--	--	
^{115}In (ISTD)	0.1	0.1	0.1	
^{118}Sn	0.2	--	--	
^{121}Sb	0.2	--	--	
^{137}Ba	0.1	--	--	
^{139}La	0.2	--	--	
^{140}Ce	0.2	--	--	
^{165}Ho	0.1	0.1	0.1	
^{182}W	0.2	--	--	
^{205}Tl	0.1	--	--	
^{206}Pb	0.2[(b)]	--	--	
^{207}Pb	0.2[(b)]	--	--	
^{208}Pb	0.2[(b)]	--	--	
^{209}Bi	0.1[(c)]	--	--	
^{238}U	0.1	--	--	

Table B4. Typical peristaltic pump program

Probe Rinse (2% HNO_3 in autosampler rinsing bottle)		**Vial Rinse (1% HNO_3)*in Bottle 3 of the autosampler**	
Speed (rps)	0.30	Speed (rps)	0.30
Sample Rinse Time (sec)	75	Vial No.	3
Standard Rinse Time (sec)	75	Rinse Time (sec)	45

Appendix C

Table C1. Proposed Sequence for the analysis of water-soluble metals in PM using the SemiQuant method (Method 6.10/*.*/M)

Method	Type	Vial	DataFile[3]	Sample Name[4]	Dil/ Level
SQN_WS.M	Sample	3	Blank1	Blank1	1
SQN_WS.M	Sample	1080	Calblk1	Calblk1	1
SQN_WS.M	Sample	1083	Cstd10-1	Cstd10-1	1
SQN_WS.M	Sample	1084	Cstd50-1	Cstd50-1	1
SQN_WS.M	Sample	1081	LCS-WS	MES4-1	1
SQN_WS.M	Sample	1082	CS-WS	MES-1	1
SQN_WS.M	Sample	3	Blank2	Blank2	1
SQN_WS.M	Sample	1001	ICPblk1	ICPblk1	1
SQN_WS.M	Sample	1002	ICblkR1	ICblkR1	1
SQN_WS.M	Sample	1003	ICblkM1	ICblkM1	1
SQN_WS.M	Sample	1004	FieldBlk-1	FieldBlk-1	1
SQN_WS.M	Sample	1005	FieldBlk-2	FieldBlk-2	1
SQN_WS.M	Sample	1006	FieldBlk-3	FieldBlk-3	1
SQN_WS.M	Sample	1007	LabBlk-1	LabBlk-1	1
SQN_WS.M	Sample	1080	Calblk2	Calblk2	1
SQN_WS.M	Sample	1008	ICPspk1	ICPspk1	1
SQN_WS.M	Sample	1009	MDLspk1	MDLspk1	1
SQN_WS.M	Sample	1085	LTM-1	LTM-1	1.07
SQN_WS.M	Sample	1010	ICspk1	ICspk1	1
SQN_WS.M	Sample	1011	ICspk2	ICspk2	1
SQN_WS.M	Sample	1012-1021	Sample1 to 10	Sample1 to 10	1
SQN_WS.M	Sample	1086	MTM-1	MTM-1	1.07
SQN_WS.M	Sample	3	Blank3	Blank3	1
SQN_WS.M	Sample	1022-1026	Sample11 to 15	Sample11 to 15	1
SQN_WS.M	Sample	1012	Sample1d	Sample1 duplicate	1
SQN_WS.M	Sample	1027-1030	Sample16 to 19	Sample16 to 19	1
SQN_WS.M	Sample	1082	MES-2	MES-2	1
SQN_WS.M	Sample	3	Blank4	Blank4	1
SQN_WS.M	Sample	1031-1041	Sample20 to 30	Sample20 to 30	1
SQN_WS.M	Sample	1026	Sample15s	Sample15 spiked	1
SQN_WS.M	Sample	1088	HTM-1	HTM-1	1.07
SQN_WS.M	Sample	3	Blank5	Blank5	1
SQN_WS.M	Sample	1079	VS10	VS10	1
SQN_WS.M	Sample	1081	VS50	VS50	1
SQN_WS.M	Sample	3	Blank6	Blank6	1

[3] Data file name can have only 8 characters

[4] A more detailed description of the sample can be added here

Table C2. Proposed sequence for the analysis of acid extracted trace elements and lead isotopes in PM using the SemiQuant method (Method 6.11/*.*/M and 6.13/*.*/M)

Method	Type	Vial	DataFile	Sample Name	Dil/ level
SQN_NT.M	Sample	3	Blank1	Blank1	1
SQN_NT.M	Sample	1080	Calblk1	Calblk1	1
SQN_NT.M	Sample	1080	Calblk2	Calblk2	1
SQN_NT.M	Sample	1082	Calstd1	Calstd1	1
SQN_NT.M	Sample	1081	LCS-NT	LCS-NT	1
SQN_NT.M	Sample	1087	981-1	981-1	1
SQN_NT.M	Sample	3	Blank2	Blank2	1
SQN_NT.M	Sample	1001	Vialblk1	Vialblk1	1
SQN_NT.M	Sample	1002	Reagblk1	Reagblk1	1
SQN_NT.M	Sample	1003	Methblk1	Methblk1	1
SQN_NT.M	Sample	1004	GLBxxx	GLBxxx	1
SQN_NT.M	Sample	1088	982-1	982-1	1
SQN_NT.M	Sample	1005- 1007	Sample1 to 3	Sample1 to 3	1
SQN_NT.M	Sample	1087	981-2	981-2	1
SQN_NT.M	Sample	1008-1014	Sample4 to 10	Sample4 to 10	1
SQN_NT.M	Sample	1088	982-2	982-2	1
SQN_NT.M	Sample	1084	LTM-1	LTM-1	xxx
SQN_NT.M	Sample	3	Blank3	Blank3	1
SQN_NT.M	Sample	1015-1019	Sample11 to 15	Sample11 to 15	1
SQN_NT.M	Sample	1087	981-3	981-3	1
SQN_NT.M	Sample	1005	Sample1d	Sample1d	1
SQN_NT.M	Sample	1021-1023	Sample16 to 18	Sample16 to 18	1
SQN_NT.M	Sample	1085	MTM-1	MTM-1	xxx
SQN_NT.M	Sample	1088	982-3	982-3	1
SQN_NT.M	Sample	1024-1030	Sample19 to 25	Sample19 to 25	1
SQN_NT.M	Sample	1087	981-4	981-4	1
SQN_NT.M	Sample	1031-1035	Sample26 to 30	Sample26 to 30	1
SQN_NT.M	Sample	1083	MES-2	MES-2	1
SQN_NT.M	Sample	1036	Sample16 spk	Sample16 spk	1
SQN_NT.M	Sample	1088	982-4	982-4	1
SQN_NT.M	Sample	1037-1041	Sample31 to 35	Sample31 to 35	1
SQN_NT.M	Sample	3	Blank4	Blank4	1
SQN_NT.M	Sample	1042	MDLspk1	MDLspk1	1
SQN_NT.M	Sample	1043	Spike1	Spike1	1
SQN_NT.M	Sample	1044	Spike2	Spike2	1
SQN_NT.M	Sample	1045	HTM-1	HTM-1	xxx
SQN_NT.M	Sample	1046	NIST-1_dil	NIST-1_dil	xxx
SQN_NT.M	Sample	1047	NIST-1	NIST-1	10
SQN_NT.M	Sample	1087	981-5	981-5	1
SQN_NT.M	Sample	1082	VS1	VS1	1
SQN_NT.M	Sample	3	Blank5	Blank5	1
SQN_NT.M	Sample	2	wash	wash	1

Table C3. Proposed sequence for analysis of lanthanoids in PM using the SemiQuant method (Method 6.13/*.*/M)

Method	Type	Vial	DataFile	Sample Name	Dil./ Level
OS_HMI.M	Sample	3	Blank1	Blank1	1
OS_HMI.M	Sample	1080	Calblk1	Calblk1	1
OS_HMI.M	Sample	1080	Calblk2	Calblk2	1
OS_HMI.M	Sample	1081	Calstd	Calstd	1
OS_HMI.M	Sample	3	Blank2	Blank2	1
OS_HMI.M	Sample	1082	LCS-LA1	LCS-LA1	1
OS_HMI.M	Sample	1001	Methblk1	Methblk1	1
OS_HMI.M	Sample	1002	Methblk2	Methblk2	1
OS_HMI.M	Sample	1003	Methblk3	Methblk3	1
OS_HMI.M	Sample	1004	GLBxxx	GLBxxx	1
OS_HMI.M	Sample	1005	FieldBlk-1	FieldBlk-1	1
OS_HMI.M	Sample	1006	FieldBlk-2	FieldBlk-2	1
OS_HMI.M	Sample	1007	FieldBlk-3	FieldBlk-3	1
OS_HMI.M	Sample	1008	Spike1	Spike1	1
OS_HMI.M	Sample	1009	Spike2	Spike2	1
OS_HMI.M	Sample	1082	CMS1-2	CMS1-2	1
OS_HMI.M	Sample	3	Blank3	Blank3	1
OS_HMI.M	Sample	1010-1019	Sample1 to 10	Sample1 to 10	1
OS_HMI.M	Sample	1083	CMS5-1	CMS5-1	1
OS_HMI.M	Sample	3	Blank4	Blank4	1
OS_HMI.M	Sample	1019-1023	Sample11 to 15	Sample11 to 15	1
OS_HMI.M	Sample	1010	Sample 1d	Sample 1d	1
OS_HMI.M	Sample	1025-1027	Sample16 to 18	Sample16 to 18	1
OS_HMI.M	Sample	1083	CMS5-2	CMS5-2	1
OS_HMI.M	Sample	3	Blank5	Blank5	1
OS_HMI.M	Sample	1028 - 1037	Sample19 to 28	Sample19 to 28	1
OS_HMI.M	Sample	1082	CMS1-3	CMS1-3	1
OS_HMI.M	Sample	3	Blank5	Blank5	1
OS_HMI.M	Sample	1038	Sample 16 spk	Sample 16 spk	1
OS_HMI.M	Sample	1039 -1045	Sample29 to 35	Sample29 to 35	1
OS_HMI.M	Sample	1083	CMS5-3	CMS5-3	1
OS_HMI.M	Sample	1046	NIST-1	NIST-1	1
OS_HMI.M	Sample	1047	BCR-1	BCR-1	1
OS_HMI.M	Sample	3	Blank4	Blank4	1
OS_HMI.M	Sample	1081	VS	VS	1
SQN_NT.M	Sample	2	wash	wash	1