

TITLE: QUANTITATIVE MEASUREMENT OF ACIDIC SOLUTIONS FOR ELEMENTAL COMPOSITION USING INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY		
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INTRODUCTION

Aqueous samples or acid digests are diluted with a solution containing internal standard(s) to give a final acid strength generally from 1% to 25% (v/v). These solutions are nebulised and passed through a high energy argon plasma to create ions from the fine aerosol. The ions are then measured by a mass spectrometer. Unknown element concentrations are quantified by automated comparison with instrument response to calibration solutions.

SCOPE

Analysis of acidic solutions for elemental composition using an inductively coupled plasma mass spectrometer (ICP-MS).

This procedure can be used to analyse samples to either ISO17025 or GLP criteria.

Only the Agilent 7700x should be used for GLP work.

SAFETY

Users must ensure that they are trained in the procedures described and that they have read and declared their understanding of the COSHH risk assessment associated with this procedure.

MATERIALS

Chemicals & Solutions

Note: Chemicals should be of the stated quality although equivalent or higher quality reagents are permitted.

Nitric acid - concentrated, AristaR.

Hydrochloric acid - concentrated, AristaR.

10,000 ppm stock solution - BDH SpectrosoL, Sigma or Aldrich AAS Standard, Fisons Standard Metal Solution, Johnson Matthey Specpure or equivalent grade solution containing known levels of the element(s) of interest.

1,000 ppm stock solution - BDH SpectrosoL, Sigma or Aldrich AAS Standard, Fisons Standard Metal Solution, Johnson Matthey Specpure or equivalent grade solution containing known levels of the element(s) of interest.

10 ppm stock solution - Spex Multi-element Plasma Standard. Equivalent grade solution(s) containing known levels of the element(s) of interest are permitted.

Water - Double deionised, distilled deionised or equivalent.

ICP-MS tune stock (1 mg/L standard) - Transfer \approx 95 ml of water into a 125 ml bottle. Pipette 5.0 ml of nitric acid into the bottle followed by 100 μ l each of the element stocks which that are used for tuning the instrument. Cap the bottle tightly and shake well.

Note: The element tune list may change over time and the current selection will be clearly written on the bottle.

ICP-MS tune solution (1 μ g/L standard) - Transfer \approx 492 ml of water into a 500 ml bottle. Pipette 5.0 ml of nitric acid, 2.5 ml of hydrochloric acid into the bottle followed by 0.50 ml of tune stock. Cap

the bottle tightly and shake well. Mark each preparation with a new alphabetical letter for ease of identification.

Equipment

(* denotes acid cleaned apparatus)

Suitable plastics for general purpose use are polyethylene (PE), high density polyethylene (HDPE) and polypropylene (PP). Fluoro-polymers can also be used where required (PTFE, PFA, FEP).

Bottles* - Nalgene or equivalent, leak proof, wide mouthed, screw capped

Pipettors - Finnpiquette or similar, suitable for dispensing volumes over the range 0.5 µl - 10.0 ml

Pipette - Multi-pipette, Eppendorf or similar, 1 - 5 ml

Pipette tips - suitable for use with Finnpiquettes

Test tubes* - plastic (16 mm Ø, ~ 23 ml volume), graduated at 10 ml, with caps

Auto-sampler tubes* - plastic (13 mm Ø, ~ 13 ml volume), or specific Agilent vials

Test tube racks - suitable for use with test tubes and auto-sampler tubes

Vortex mixer

ICP-MS - Agilent 7500ce or Agilent 7700x

Measuring cylinders* – Nalgene or equivalent, plastic, various volumes, suited to application

Auto-sampler tubes* - Specific Agilent vials, nominal capacity 7 ml

PROCEDURE

1. For the Agilent 7700x, the set of tubes comprising the sample batch and associated calibration should be placed into one or more Agilent auto-sampler racks, following the current layout (check previous batches for guidance).
2. For the Agilent 7500ce, these solutions should be decanted into Agilent auto-sampler vials and placed in the auto-sampler rack following the current layout (check previous batches for guidance).

Operation of the ICP-MS

Note: Only authorised users can operate the ICP-MS systems.

Agilent 7700x

This instrument is functioning to GLP conditions and only persons qualified to GLP status have the authority to operate this instrument.

1. Check the argon gas supply is switched on (nominally 95 p.s.i.).
2. Check the recirculating chiller is switched on.
3. Check the alignment of the peristaltic pump tubing and clamp up the tubing.
4. Check the drain reservoir and empty the contents if necessary.
5. Check there is enough solution in the rinse reservoirs, normally positions 1 to 3 on the autosampler and a large container of water external to the autosampler. Check there is enough tune solution in position 7 (typically > 10 ml). Uncap all containers on the auto-sampler.
6. A simple schematic of the 7700x Compliance routines are given in the Appendix. A user must be proficient in the instrument software before working unaided.

Note: The software can take time to complete tasks. Users should be familiar with the correct final display for their actions, thus avoiding leaving the software in limbo. This is especially important when unlocking and relocking the software whilst the instrument is acquiring data.

7. From the Home Tab, click the 'Plasma On' icon, click 'yes' to the prompt message to run 'Startup' and allow the automated sequence to change the instrument status from 'Standby' to 'Analysis' and complete a performance check after a pre-set warm up period. Move the auto-sampler probe to position 1101 to aspirate water wash. If the instrument fails to achieve the requested task, another two attempts can be initiated before seeking advice from a more experienced operator. Once in 'Analysis' state, check that liquid is flowing correctly in the drain tubing.
8. The MassHunter software will complete a performance check and results displayed in the instrument screen (right click on the instrument icon to select this information).

Note: The current data obtained should be like previous records from successful runs. If there is a marked change (usually a loss of signal) the matter should be referred to a more experienced authorised operator unless there is an obvious and user-correctable problem observed.

9. The instrument is now in an acceptable state to measure samples.
10. Create a new batch from the template list, naming it by the format "####n" where #### is the batch code, n is the acquisition number. Ensure the elements required have been selected and auto-sampler positions are correct in the 'Sample List'.
11. Add the batch to the instrument Queue.

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12. Ensure "Plasma Off at End" is checked.
 13. **IMPORTANT** - Lock MassHunter software when leaving the workstation unattended.
 14. When the ICP-MS has finished the acquisition, the instrument will revert to the standby state. All accessories can then be switched off.

Note: Multiple batches can be run consecutively, but again, care must be exercised to ensure correct auto-sampler positions are entered.

Export of results – (Agilent 7700x)

15. Re-enter the locked MassHunter session (See Appendix for guidance).
16. Select "Online Data Analysis" to process the current batch. Use "Offline Data Analysis" to process older batches.
17. Select the batch from the list and wait for this to load. Confirm no serious issues occurred during the run by viewing the internal standard response plot.
18. Highlight all the data and export it. MassHunter exports to a fixed location: C:\

Processing of results

19. Process results using a verified macro, or if this facility is not available, calculations can be performed manually. The internal standard signal should be monitored for stability, large fluctuations e.g. more than $\pm 25\%$ of the response observed in the standards should be highlighted for consideration in the assessment of the results. Complete the calibration routine and check each graph for accuracy (correlation coefficient >0.995). If this value is not achieved and there are signs of discrepancy in the upper part of a calibration, check the detector calibration is not at fault (look at recorded detector mode).

Agilent 7500ce

1. Check the argon gas supply is switched on (nominally 95 p.s.i.).
2. Check the heat exchanger is switched on.
3. Check the alignment of the peristaltic pump tubing and clamp up the tubing.
4. Check the drain reservoirs and empty the contents if necessary.
5. Check there is enough solution in the rinse reservoirs to cover the planned run (a large bottle for the wash station and alkali/acid bottles in auto-sampler positions 1 and 2 respectively).
6. If the ChemStation software is already open skip to step 9. To open the software, click on the 'ICP-MS top' icon on the desktop.
7. Open the instrument screen and click on the 'ignite plasma' icon, click 'yes' to the two prompt messages and allow the automated sequence to change the instrument status from 'Standby' to 'Analysis'. Move the auto-sampler probe to position 2 to aspirate acid wash. If the instrument fails to achieve the requested task, another two attempts can be initiated before seeking advice from a more experienced operator. Once in 'Analysis' state, check that liquid is flowing correctly in the drain tubing and leave for at least 30 min to allow the interface and spray chamber temperatures to stabilise before continuing with tuning the instrument.
8. Click on the 'Enter the Tune Panel' icon, and record the background signal at mass 7, 89, and 205 before aspirating the tune standard. Record the uptake time, the signal response obtained for the tune at the same masses, plus oxide and double charged percentages. Fill in the logbook which is kept adjacent to the instrument.
9. Move the probe to the rinse station of the auto-sampler for about 30 seconds, then back to position 2.

Note: The current data obtained should be like the previous record from a successful run. If there is a marked change (usually a loss of signal) the matter should be referred to a more experienced authorised operator unless there is an obvious and user-correctable problem observed.

10. The instrument is now in an acceptable state to measure samples.
11. Select a previous method of similar conditions and modify the element list if necessary. Save this method with the batch code for this run.
12. Edit the sample log via the 'Sequence' drop down menu. Use the layout of a previous run as a format. Ensure 'Datafile' column has the correct batch code along with the relevant method. Multiple batches can be run consecutively, but care must be exercised to ensure correct auto-sampler positions are entered, especially if standards are not shared. For an overnight run, ensure that the auto shut down is activated on the ICP-MS. This involves a 'keyword' called 'standby' entered at end of log. (Omitting this step does not affect the analysis but will be wasteful).

Export of results – (Agilent 7500ce)

13. From the desktop, click on the 'Fileview32' icon and open the folder 'Data' in the LHS window to reveal all data subfolders. Open the relevant subfolder, the contents of which will be displayed in the middle window. The RHS window should be empty. Select the files required in the calculations and click on the button '→' to move them into the RHS window. Click on the button 'process' to generate an export file. From the 'Counts info' drop down menu, select 'Counts/second{det.mode}'. From the 'Tools' drop down menu, select 'Copy selected area to CSV file'. Select a suitable destination and save the file as ####ndmod (where ### = batch code, n = acquisition number).
14. The format of the Export file requires extensive modification to work with the macro. This is best accomplished using a previous conversion file as a starting point.

Note: Unless the instrument PC is connected to the network, the file will require transfer to a PC that has this facility, via a USB memory device.

Processing of results

15. Process results using a verified macro, or if this facility is not available, calculations can be performed manually. The internal standard signal should be monitored for stability, large fluctuations e.g. more than $\pm 25\%$ of the response observed in the standards should be highlighted for consideration in the assessment of the results. Complete the calibration routine and check each graph for accuracy (correlation coefficient >0.995). If this value is not achieved and there are signs of discrepancy in the upper part of a calibration, check the detector calibration is not at fault (look at recorded detector mode).

Instrument method guidelines

Cell Mode selection:

As a rule: No-Gas mode for below mass 20 and above mass 85. He mode for the rest. HEHe or H2 mode for specific elements e.g. Se. If in doubt, select all available modes and compare QC results.

Dwell time:

Typically, 0.1 sec is sufficient but if signal is low, increasing this value will benefit measurement. Elements known to require longer dwell times are As, Se and Hg.

Peri-pump timings:

		7500ce	7700x	
Pre Run	Uptake speed (nebulizer pump)	0.06	0.30	r.p.s
	Uptake Time*	5	25	sec
	Stabilise	0	20	sec
Post Run	(Probe Rinse)			
	Rinse Speed (nebulizer pump)	0.06	0.30	r.p.s
	Rinse at Rinse Port (Sample)	30	30	sec
	Rinse at Rinse Port (Std)	0	20	sec
Post Run	(Rinse)			
	Rinse Vial 1 1			
	Rinse Speed (nebulizer pump)	0.06	0.30	r.p.s
	at Rinse Vial (Step 1)	90	30	sec
	Rinse at Rinse Port (Step 1)	20	10	sec
	Rinse Vial 2 2			
	Rinse Speed (nebulizer pump)	0.06	0.30	r.p.s
	Rinse at Rinse Vial (Step 2)	150	30	sec
	Rinse at Rinse Port (Step 2)	10	10	sec
	Rinse Vial 3 3			
	Rinse Speed (nebulizer pump)	0	0.30	r.p.s
	Rinse at Rinse Vial (Step 3)	0	120	sec
	Rinse at Rinse Port (Step 3)	0	10	sec
	Intelligent Rinse	Off	Off	
	Preemptive Rinse	10		sec

Move to the next rinse step at acquisition complete No No

* Most important this value allows the sample to reach the plasma. For the 7500ce, the Uptake time and Stabilise is a combination of Cell stabilisation time and the value given here (typically 60 sec is the stabilisation time for H2, the first cell mode. Therefore, the total time would be 65 sec).

DOCUMENTS / RECORDS REFERRED TO

APPENDICES

