

Performance evaluation of Helium Mode ICP-MS for high-matrix sample types in a high-throughput European laboratory.

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Introduction

Eurofins Analytico in the Netherlands is a major, high-throughput laboratory with extensive expertise in the analysis of soil, sludge, groundwater, wastewater, air, building materials and residual analysis.

Previously a microwave digestion/ICP-MS analysis method has been validated for the analysis of aqua-regia soil digests according to Dutch regulation AS3000 by Agilent 7500cx ICP-MS with High Matrix Introduction (HMI) capability (Agilent Technologies application note 5989-7929EN).

A similar combined approach was needed for the direct analysis of more than 30 elements including Be, P, S, Ti, V, Cr, As, Se, Cd and Hg in wastewater samples prepared according to the aqua regia digestion approach of AS3000.

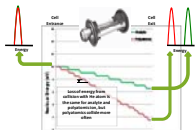
Previously this had not been possible due to the specific detection limit requirements in actual waste water aqua regia digests particularly for elements such as Hg.

An Agilent 7700x ICP-MS incorporating a newly designed ORS³ cell was applied to this very challenging application. The 7700x offers the following capabilities:

- 1) HMI system handles high TDS levels – no need to further dilute the samples after digestion – increased productivity.



- 2) Improved helium mode with ORS³ cell – all analytes measured with a single cell gas; no need for reactive gases (or gas mixtures) such as H₂ or NH₃ to meet LOD requirements. No need to avoid chloride in digest matrix, since ORS³ cell in helium mode effectively removes interferences on V and As.

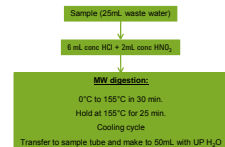


- 3) No need for ICP-OES, AFS or Hg analyzers.

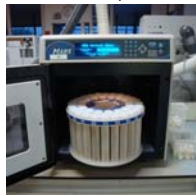
Experimental

- 1) The full method validation protocol involved the digestion and analysis of 18 different sample types on 10 different days throughout a 30 day trial period, according to NEN7777.
- 2) Sample types included artificial waste-waters to assess the method detection limits in a difficult matrix, spiked artificial wastewaters at 10x and more than 100x the required reporting limits and different QC materials for each run, blanks and unknown samples.
- 3) For the low and high-level spikes, the spikes were carried out at least 48 hours before the digestions. Digestions and ICP-MS measurement always took place on the same day.
- 4) Sample preparation: Digestions for wastewater samples were performed with a CEM Mars microwave with a 40 position carousel (picture 1).

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Picture 1. CEM Mars Microwave used for the sample digestions of waste water samples.



- 5) The final digest solutions containing 12% HCl / 4% HNO₃ (v/v) were directly analyzed on an Agilent 7700x ICP-MS incorporating High-Matrix Introduction capability.
- 6) ICP-MS conditions:

ICP-MS	Agilent 7700x
Nebulizer	Burgener MiraMist
RF Power	1600 W
Sampling gas	10.0 mm
Carrier gas	0.6 L/min
HMI dilution gas	0.4 L/min
KED voltage	3V
He flow rate	4.3 mL/min

Picture 2. The Agilent 7700x at Eurofins Analytico and close-up of the HMI hardware (insert).



- 7) Calibration ranges:
 - 0 – 2 µg/L Hg
 - 0 – 250 µg/L Ag
 - 0 – 500 µg/L Li, Be, Ti, V, Cr, Mn, Ni, Co, Cu, Zn, As, Se, Sr, Mo, Cd, Sn, Sb, Te, Ba, Ce, Ti, Pb
 - 0 – 1 mg/L Br, W
 - 0 – 2.5 mg/L B
 - 0 – 10 mg/L Br, In
 - 0 – 50 mg/L Na, Fe, K, Ca, Al, Mg
 - 0 – 100 mg/L P, S
 - 0 – 1000 mg/L C
- 8) The total analysis time per sample (including uptake, rinse and multiple isotopes per element for confirmation) was 5 minutes.

Results

Figure 1. Calibration curves in a 12% HCl / 4% HNO₃ matrix for Be, P, S, V, As, Se, Cd and Hg measured with the ICP-MS method generated from a single analysis as described.

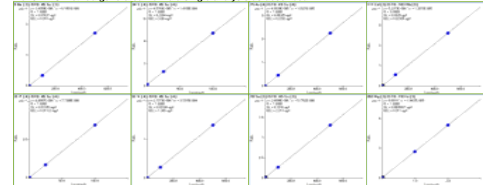
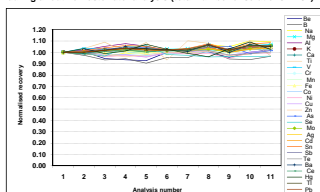


Table 2. CRM analysis data for BCR-145R (Sewage Sludge) and FeNeLa (Dutch River Clay). The FeNeLa data are evaluated against round-robin data from the original certification study, by ISE (°), the current PT data (Q1 2009 data) (†) and prior data from Eurofins Internal QC control charts (‡).

Analyte	Unit	BCR-145R		FeNeLa		ISE (°)		FeNeLa (‡)		Internal Control charts (†)	
		Measured	Certified	Measured	Certified	Recovery (%)	Certificate	Recovery (%)	Target	Recovery (%)	
°Be	[µg/L]	0.41	0.41	1.68	1.52	110.5					
°B	[µg/L]	18.72	35.10								
°Ba	[µg/L]	9.65	9.33	0.33	0.37				0.374	87.0	
°Br	[µg/L]	5.32	9.15	3.4	97.3						
°Ca	[µg/L]	21.48	28.42	25.8	111.0				29.873	95.1	
°Cd	[µg/L]	11.80	2.48	2.52	97.3				2.74	89.9	
°Ce	[µg/L]	12.33	0.91	1.23	74.1						
°Cr	[µg/L]	1.38	6.42	5.26	122.2				7.192	89.5	
°Cu	[µg/L]	45.61	35.47	36.5	97.2						
°Fe	[µg/L]	204.64	504.79								
°Hg	[µg/L]	28.55	84.03	55.8	114.7						
°In	[µg/L]	289.57	300	96.5	107.6				186	104.1	
°K	[µg/L]	0.14	0.145	96.2	1.03	1.05	96.5				
°Li	[µg/L]	12.54	35.54	35.2	101.0						
°Mn	[µg/L]	4.63	5.3	91.2	19.03	18.4	103.4		18.8	101.2	
°Ni	[µg/L]	224.33	251	89.4	58.81	54	105.2		53.8	105.6	
°P	[µg/L]	652.40	707	92.3	151.27	153	98.9		158	95.7	
°Pb	[µg/L]	1963.83	2140	91.8	1019.10	1020	99.9		1009	101.0	
°S	[µg/L]	8.01	44.62	41.8	107.3	43.7	102.0				
°Se	[µg/L]	8.38	1.80	1.71	105.1						
°Sn	[µg/L]	294.20	139.88	129	108.4						
°Sr	[µg/L]	0.01	0.00	0.00141	103.7						
°Tl	[µg/L]	13.39	3.06	2.75	111.2						
°Ti	[µg/L]	3.10	3.43	90.4	8.30	8.24	100.8		8.5	97.7	
°V	[µg/L]	68.22	24.32	22.2	109.6				23.8	102.2	
°W	[µg/L]	12.00	0.40	0.26	3.28	78.0			3.07	83.4	
°Zn	[µg/L]	-0.03	0.28								
††Be	[µg/L]	2446.58	857.95	797	107.6	821	104.5				
††B	[µg/L]	18.90	89.62								
††Ba	[µg/L]	1.84	1.99	92.5	3.64	3.81	95.6		4.07	89.5	
††Br	[µg/L]	0.18	1.25	1.3	114.2						
††Ca	[µg/L]	256.17	282	90.8	291.08	283	102.6		279	104.3	
††Cd	[µg/L]										
††Ce	[µg/L]										
††Cr	[µg/L]										
††Cu	[µg/L]										
††Fe	[µg/L]										
††Hg	[µg/L]										
††In	[µg/L]										
††K	[µg/L]										
††Li	[µg/L]										
††Mn	[µg/L]										
††Ni	[µg/L]										
††P	[µg/L]										
††Pb	[µg/L]										

Figure 2. Stability plot for CCV samples analyzed over a 104-hour period, during a routine wastewater analysis (total number of solutions = 137).



Discussion

- 1) The method detection limits (Table 1.) based on artificial wastewater testing and calculated according to the Dutch requirements over 10 different analysis days meet and for most elements far exceed the required limits, including challenging elements such as Hg (2x lower than required limit).
- 2) The interference removal efficiency of the ORS³ cell operating in He mode is demonstrated by the accuracy achieved for CRM analysis (Table 2.), with excellent agreement with certified/consensus-mean values for interfered elements such as P, V, Cr, Mn, Fe, Ni, Cu, Zn, As and Se in the high-acid, high-matrix digests without the need for mathematical correction equations.
- 3) All analytes as well as secondary confirmation isotopes we analyzed in the aqua regia digests, enabling the simultaneous determination of major elements (Na, Ca, P, S, K) as well as more than 20 trace elements including Hg, As and Se (Fig.1)
- 4) The spike recovery data (Table 1.) is within the required limits of 80 – 110% for all analytes except Ca. Most analytes were ± 5%.
- 5) Repeat analysis of CCV standards in a 12 hour sample run (Fig. 2.) indicate very good performance and meet the 90 – 110% target requirement.

Conclusions

The method validation has been successfully completed for all the elements tested including P, S, V, As, Se and Hg in wastewater digest with aqua regia required by Dutch regulations.

The combination of HMI and the performance of the ORS³ cell in the 7700x in terms of both sensitivity and interference removal have facilitated this combined approach for the first time.

The aqua regia digestion combined with direct analysis by Agilent 7700x ICP-MS is now routinely used at Eurofins Analytico for wastewater analysis.