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

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according to NEN7777.

place on the same day.

carousel (picture 1).

Sample preparation:

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

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

Digestions for wastewater samples were performed

Sample (25mL waste water)

6 mL conc HCI + 2mL conc HNO

MW digestion:

0°C to 155°C in 30 min

Hold at 155°C for 25 min. Cooling cycle sfer to sample tube and make to 50mL with UP H-C

Picture 1. CEM Mars Microwave used for the sample

digestions of waste water samples.

with a CFM Mars microwave with a 40 position

materials for each run, blanks and unknown samples.

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Introduction

Eurofins Analytico in the Netherlands is a major, highthroughput 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.

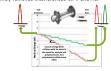
Previously this had not been possible due to the specific detection limit requirements in actual waste water aqua regia digests particularly for elements such as Hg.

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 NH₂ to meet LOD requirements. No need to avoid chloride in digest matrix, since OBS3 cell in helium mode effectively removes interferences on V and As.



Experimental

The final digest solutions containing 12% HCI / 4% HNO The full method validation protocol involved the 5) (v/v) were directly analyzed on an Agilent 7700x ICP-MS digestion and analysis of 18 different sample types on incorporating High-Matrix Introduction capability. 10 different days throughout a 30 day trial period. 6) ICP-MS conditions:



Picture 2. The Agilent 7700x at Eurofins Analytico and close-u the HMI bardware (insert).



Calibration ranges:

0 – 2 µg/L Ho 0 – 250 µg/L Ag 0 - 500 ug/L Li Be Ti Se. Sr. Mo. 0 – 1 ma/L Zr. W



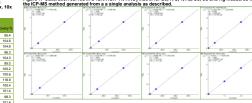
8) The total analysis time per sample (including uptake, ri and multiple isotopes per element for confirmation) was 5 minutes

Table 1. Method detection limits achieved, compared to required MDLs and spike recovery data for artificial waste waters at approx. 10x and more than 100x of the required reporting limit.

	Analyte	Unit	MDL (3o)	MDL required	Spike added	Recovery %	Spike added
	*Be	[ug/1]	0.80	1	10	108.6	1000
	11B	[ug/1]	25.6	60	500	95.8	10000
	23Na	[mg1]	0.12	0.2	1	108.8	20
	²⁴ Mg	[mg1]	0.03	0.1	1	102.3	20
	27AI	[mg1]	0.05	0.1	1	105.3	20
	31P	[mg1]	0.03	0.05	0.4	102.7	20
	з×S	[mg1]	0.83	1	5	102.9	100
	з≋К	[mg/l]	0.18	0.2	1	102.5	20
	44Ca	[mg1]	0.22	0.2	1.5	132.2	20
	eTi	[ug/1]	9.10	20	150	103.5	1000
	a:V	[ug/1]	2.80	10	100	103.7	1000
p of	^{sz} Cr	[ug/l]	1.89	5	40	104.8	1000
por	**Mn	[ug/1]	0.004	0.02	0.15	101.8	1
-	MFe	[ug/1]	0.03	0.05	0.5	102.0	20
	100.	formed 3	0.04	40	400	400.0	4000

Figure 1. Calibration curves in a 12% HCI / 4% HNO, matrix for Be, P, S, V, As, Se, Cd and Hg measured with

Results



ta from the original certification study, by ISE (1), the current PT a) (2) and prior data from Eurofins internal QC control charts (3).

ed (%)	Measured 1.68 35.10	Certified	Recovery (%)	Certificate	Recovery (%)	Target	Recovery
		1.52					(%)
	35.10		110.5				
	0.33	0.333	97.7			0.374	87.0
	9.15	9.4	97.3				
	28.42	25.6	111.0			29.873	95.1
	2.45	2.52	97.3			2.74	89.5
	0.91	1.23	74.1				
	6.42	5.25	122.2			7.172	89.5
	35.47	38.5	97.2				
	504.79						
	64.03	55.8	114.7				
0 96.5	193.66	180	107.6	186	104.1	197	98.3
5 96.2	1.03	1.05	98.5				
	35.54	35.2	101.0				
3 91.2	19.03	18.4	103.4	18.8	101.2		
1 89.4	56.81	54	105.2	53.8	105.6	57.1	99.5
7 92.3	151.27	153	98.9	158	95.7		
0 91.8	1019.10	1020	99.9	1009	101.0		
	44.62	41.6	107.3	43.7	102.1		
	1.80	1.71	105.1				
	139.88	129	108.4				
	0.00	0.00141	103.7				
	3.06	2.75	111.2				
3 90.4	8.30	8.24	100.8	8.5	97.7	8.05	103.1
							102.3
	24.32	22.2	109.6			23.8	102.2
	24.32	22.2 3.28	109.6 78.0			23.8 3.07	102.2
5	3 91.2 51 89.4 77 92.3 60 91.8	3 91.2 35.54 11 80.4 56.81 17 92.3 151.27 10 91.8 1019.10 44.62 1.80 13 90.4 3.86 3 90.4 8.30	3 915 44 55.2 1 9003 151.27 153 0 91.4 56.81 54.4 17 92.3 151.27 153 0 91.8 1019.10 1020 1 144.62 41.6 1 138.8 129 0.00 0.0004 0.00141 3 90.4 8.30 3 90.4 8.30	3 9254 9554 952 9100 1 884 58.81 54 450.4 10 884 58.81 54 450.2 10 91.84 151.27 153 88.9 11 44.62 41.66 107.3 11 130.85 12.9 106.4 12 130.85 12.9 106.4 130.85 12.9 108.4 130.85 12.9 108.4 130.85 2.75 1112.7 3 0.4 8.30 8.24	35.64 35.25 10.10 91.2 10.03 10.48 10.04 16.84 11 86.44 56.64 16.62 55.64 12 92.3 15.77 15.0 66.06 10.64 10 92.3 15.77 15.0 66.06 10.64 10 92.4 10.04 64.81 10.93 10.00 10 92.4 10.04 64.81 10.93 10.00 10 92.6 10.05 10.05 10.05 42.97 10 92.6 10.05 10.05 10.05 42.97 10 92.6 92.05 10.05 10.05 10.05 10 92.6 92.05 10.05 10.05 10.05 10 92.6 92.05 10.05 10.05 10.05 10 92.6 92.6 10.05 10.05 10.05 10 92.6 10.05 10.05 10.05 10.05 10.05	354 352 9101 91111 0F2 1903 164 1103 1164 1012 1 0F44 5643 564 1552 5534 1552 1 0F43 1517 153 0556 0572 153 0566 10 0F43 1518 0516 053 0566 0573 10 0F43 10163 0400 0403 1000 0516 11 4528 4171 1013 423 0101 1014 12 4529 05914 1010 1000 0514 1010 1000 14 4529 05914 1010 1017 1014 1014 1014 1014 15 05926 1027 1010 1017 1014 1014 1014 1014 1014 1014 1014 1014 1014 1014 1014 1014 1014 1014 1014 1014 1014 1014	55.64 55.25 101.0 10.4 10.4 00.2 1 94.2 100.3 10.4 10.8 10.7 1 86.4 56.81 56.4 50.22 50.88 10.62 1 92.3 15.77 15.0 60.96 10.01 10.0 1 92.4 10.01 10.00 60.00 10.01 10.0 1 92.4 10.81 10.10 10.00 60.00 10.01 10.00 1 92.4 10.81 10.10 10.00 40.27 10.01 10.00 1 1.01.00 10.00 10.00 40.27 10.01

857.95 797 107.6 821 104.5

89.62

1.25

90.8 291.08 283

102.9 279 104.3 206

Discussion

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).

- The interference removal efficiency of the ORS3 cell 21 operating in He mode is demonstrated by the accuracy achieved for CRM analysis (Table 2.), with excellent agreement with certified/consensusmean 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.
- 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 OBS³ cell in the 7700x in terms of both sensitivity and interference removal have facilitated this combined approach for the first time.

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

	128Te	[ug/1]	0.87	
	138Ba	[ug/1]	4.47	
	14Ce	[ug/l]	3.57	
	201Hg	[ug/l]	0.05	
	203TI	[ug/1]	3.08	
	208Pb	[ug/1]	2.73	
		 Stabil a routine 		
	1.	20		
V, Cr, Mn, Ni, Co, Cu, Zn, As,	1.			
, Cd, Sn, Sb, Te, Ba, Ce, Tl, Pb	1/	00	-	-
, 64, 61, 65, 16, 54, 66, 11, 15	_ 0.	90		-
	§ 0.			
	\$ 0. 8 0.			
		70		
		70 60		

138Ba [ug1] 2446.58

19.00

0.16

1.84 1.99 92.5 3.64 3.81 95.6 4.07 89.5 3.98 91.5

142Ce [ug1]

201Ho [uot]

2007] [Igu]

204Pb [ugit] 256.17 282

		101.4	1	101.8	0.15	0.02	0.004	[ug/1]	**Mn
CRM analy	Table 2	99.6	20	102.0	0.5	0.05	0.03	[ug/1]	MFe
evaluated		99.7	1000	100.3	100	10	2.01	[ug/l]	^{sn} Co
2009 data		96.2	1000	102.2	40	5	1.99	[ug/l]	^{eo} Ni
	(97.8	1000	99.8	40	5	1.03	[ug/l]	43Cu
		98.1	1000	98.6	100	10	6.03	[ug/1]	#Zn
B		99.6	500	100.1	15	2	1.22	[ug/1]	™As
Unit M	Analyte	103.4	1000	100.5	15	2	1.78	[ug/1]	7#Se
[up!]	"Be	106.3	1000	106.4	100	10	3.60	[ug/1]	**Sr
[ugi]	11B	103.1	1	106.7	0.1	0.01	0.002	[ug/1]	**Mo
[001]	···B	100.9	1000	104.3	15	2	0.41	[ug/]]	107Ag

Low level spike High level spike

**Se #*Sr #*Mo 107Ag

118Sn	[ug/1]	1.77	10	100	106.4	1000	104.5
121 Sb	[ug/1]	1.35	2	10	99.3	1000	103.0
128Te	[ug/1]	0.87	1	10	101.0	1000	104.6
заВа	[ug/1]	4.47	10	100	105.2	1000	103.3
144Ce	[ugi]	3.57	10	100	102.1	1000	100.8
²⁰¹ Hg	[ugi]	0.05	0.1	1	95.4	10	95.3
203TI	[ug/1]	3.08	10	100	101.4	1000	104.3
208Ph	[100/1]	2.73	5	40	101.8	1000	103.1

CV samples analyzed over a 12-hour period analysis (total number of solutions = 137).

8 0.80 8 0.70 8 0.60 9 0.60 9 0.40							0.90 0.80
3 0.60							
E 0.30							0.50
0.30						-	
0.20						-	

101.8

	100.4	1000	103.5	150	20
	101.4	1000	103.7	100	10
alle alle alle alle alle alle alle alle	98.3	1000	104.8	40	5
	101.4	1	101.8	0.15	1.02
Table 2, CRM analysis data for BCR-145R (S	99.6	20	102.0	0.5	1.05
data are evaluated against round-robin data	99.7	1000	100.3	100	10

Sewage Sudge) and FeNeLab (Dutch River Clay). The FeNeLab