

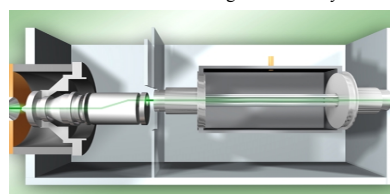
Analysis of Wastewater and Mine Tailing Samples Using Octopole Reaction System Agilent 7500cs for Sub Parts Per Billion Reporting Levels.

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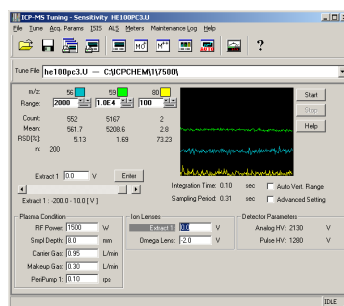
Environmental laboratories continue to seek high performance instruments to meet ever-changing EPA regulations and data quality objectives. Accurate analysis of wastewater without matrix bias is vital in today's environmental laboratory. Today's economics prohibits laboratories from financially investing in highly selectively methods and extraction techniques, such as atomic fluorescence and hydride generation-ICP-MS, for achieving required reporting levels for multiple metals. Today's environmental laboratory needs one instrument flexible enough to handle ever changing matrices and capable of sub parts per billion analysis.

North Creek Analytical, Inc., based in Bothell, Washington with five environmental laboratories located across the Pacific Northwest and Alaska, acquired the latest in ICP-MS technology, the Agilent 7500cs Octopole Reaction System. NCA with five ICP-MS systems, teamed with Agilent Technologies to take the proven high performance of the Agilent 7500cs out of the Clean Room and on to the environmental laboratory bench top. This new prototype Agilent 7500cs is designed with on-axis reaction cell (ORS) and equipped with high performance prototype extraction lens assembly. NCA experienced increases in sensitivity of 4-10 times for many analytes beyond current Agilent 7500i and HP 4500 performance. NCA found this new lens and Octopole Reaction System configuration was ideally suited for matrix elimination and long term stability.

Sample matrix elimination is performed with He & H₂ Reaction Gas Mode with Collisionally Induced Dissociation (CID) and Energy Discrimination (ED). The most common ICPMS mass interferences in wastewater analysis are ArC⁺, ClO⁺, ArO⁺ & ArCl⁺. These matrix interferences can be eliminated by selection of reaction gas for atomic collisions within the Octopole Reaction Cell. Energy Discrimination working in tandem with CID, continues to filter out the remaining interfering polyatomics, this is done by optimizing the Octopole and Quadrupole, a created potential well that allows the mass of interest to continue to the electron multiplier. This is easily demonstrated by analysis of 10 ppb Co & 1ppb Fe tune solution prepared in 1% HCl, where the ArO⁺ and ArAr are eliminated from the signal.



Agilent 7500cs Inductively Coupled Plasma Mass Spectrometer Octopole Reaction System



Instrument Conditions:

Agilent 7500cs Prototype

Plasma conditions:
 Plasma Power 1500 kW
 Reflected Power <1 W
 Ar Coolant 16 L/min
 Ar Aux Flow 1.0 L/min

Sampling conditions:
 PFA 100 nebulizer
 PFA 400 nebulizer
 pump rate @0.08 rpm
 ESI PC³ Spray chamber @14C
 Sample depth @ 8mm
 Long life shield torch system
 Ni Sample Cone
 Ni Skimmer Cone

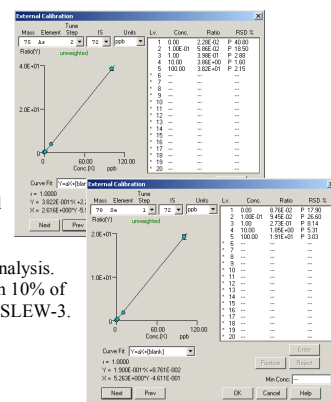
Reaction Cell conditions:
 Octopole Bias -14 to +6 V
 Q-pole Bias -9.2 to -3V
 Reaction gas -He 4.0 ml/min
 Reaction gas -H₂ 3.5 ml/min

Data acquisition:
 Peak hopping with 3 pts/peak
 Dwell time of 0.1 to 0.5 sec with 4 integrations



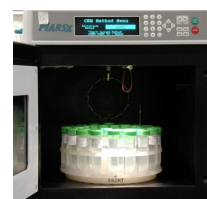
Calibration :

Multiple conditions were applied during method development, ranging from spray chambers, nebulizers, as well as reaction gas flow rates. Calibration curves were matrix matched to contain 1% HNO₃ & 0.5% HCl by volume. Linear calibration ranges were obtained for all trace metals up to masses at 0-1ppm. As and Se provide excellent sensitivity comparable to HG-ICP-MS analysis. NCA obtained results for As & Se within 10% of the certified value of CRM SLRS-4 and SLEW-3.



Sample Preparation :

Wastewater samples are prepared for ICP-MS analysis by CEM microwave system. Cleaned 50ml centrifuge tubes digest 45 ml of sample with the addition of 1ml HNO₃ & HCl with total program for 40 digests is <1 hour. The sample digests along with method blank, method blank spike, sample duplicate and sample matrix spike were analyzed after particulate was allowed to settle overnight. Method Detection Limits MDL studies were performed with 6 replicates of method blank spikes at 50, 100, 200 ng/l (ppt).

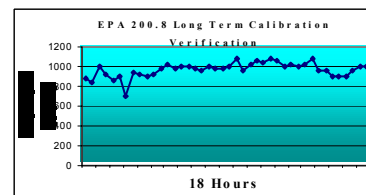


Results :

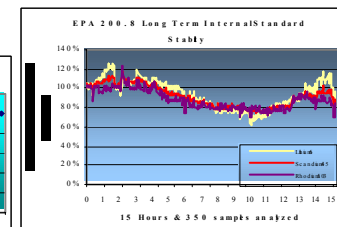
NCA found that the PFA 100 nebulizer combined with the PC³ spray chamber provided improved detection limits and provided much quicker washout times of 100 ppm analytes, Table 1. Comparative data in Table 1 illustrates the accuracy between this new method compared to traditional environmental analysis (HP 4500 ICPMS, ¹ICP-OES, ²HG-ICP-MS). Chloride content in the wastewater and mine tailings samples were <50 ppm. Sulfate concentrations were 50 ppm and 2800 ppm respectively, while the total dissolved solids were 175 ppm & 3800 ppm. NCA observed that Zn was extremely linear up to 100 ppm, as seen by the undiluted Agilent 7500cs results and the diluted 400 fold results from the HP 4500. Calibration blank check samples passed with <5 ppb Zn after analysis of the mine tailing samples.

NCA found exceptional long term stability with the PFA PC³ combinations. Graph 1 & 2 demonstrates overnight unattended analysis of >350 environmental samples. Graph 2 shows acceptable internal standard recoveries of 60-120% for 15 hours. The prototype Agilent 7500cs provided complete batch analysis within 3 hours, which includes calibration and quality control check samples. Traditionally, results would take 3 for each method, ICP-MS, ICP-OES and HG-ICP-MS.

Graph 1:



Graph 2:



Conclusions :

- Environmental laboratories now have a single technique capable of analyzing all metals simultaneously in the sub parts per billion range, 100 ng/l (ppt) a 10 fold decrease industry standard high matrix analysis.
- NCA has improved its linear calibration working range for As & Se with out extra analysis time of Hydride Generation-ICP-MS.
- NCA has expanded its ICP-MS environmental metals analysis with the newly enhanced prototype Agilent 7500cs ORS ICP-MS which outperforms non-ORS ICP-MS systems and traditional ICP-OES applications in detection limit and an extended working range..

Acknowledgements & References:

- Steve Wilbur, Emmett Soffey & Doug Martin, Agilent Technologies, Bellevue, WA.
- Ed McCurdy, Agilent Technologies "Optimizing Reaction Cell ICP-MS for Real World Application."
- USEPA, 1996. Determination of Trace Elements in Water and Wastes by Inductively Coupled Plasma-Mass Spectrometry, EPA Method 200.8, Revision 5.4.
- USEPA, 1994. Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, "Inductively Coupled Plasma-Mass Spectrometry, Method 6020.", SW-846, 2nd Edition.

Table 1:

	Gas	MDL	7500cs Result, ppb	Traditional Result, ppb	Gas	7500cs Result, ppb	Traditional Result, ppb
Na 23	H ₂	2.0	7400	8100 ¹	H ₂	120000	150000 ¹
Mg 24	-	2.0	9800	9900 ¹	-	92000	97000 ¹
Al 27	-	2.0	47	50 ¹	-	12	< 10 ¹
K 39	-	1.0	400	430 ¹	-	5900	7900 ¹
Ca 40	H ₂	2.1	45000	63000 ¹	H ₂	220000	320000 ¹
V 51	He	0.019	0.4	< 2.0	He	< 0.1	< 2.0
Cr 52	He	0.12	0.31	< 2.0	He	< 0.1	< 2.0
Mn 55	-	0.02	3.9	4.0 ¹	-	11000	150 ¹
Fe 56	H ₂	1.7	130	130 ¹	H ₂	5100	150 ¹
Ni 60	He	0.016	0.6	< 2.0	He	160	180
Cu 63	He	0.051	0.83	< 2.0	He	1.4	< 2.0
Zn 66	-	0.14	51	52	-	35000	37000
As 75	He	0.024	0.17	< 2.0	He	0.43	< 5.0
Se 78	H ₂	0.020	1.5	1.4 ²	H ₂	1.01	1.4 ²
Ag 107	-	0.006	< 0.05	< 2.0	-	0.08	< 2.0
Cd 111	-	0.010	0.27	< 2.0	-	11	9
Sb 121	-	0.010	4.4	< 2.0	-	0.29	< 2.0
Ba 137	-	0.036	150	150 ¹	-	12	12
Tl 205	-	0.059	0.66	< 2.0	-	2	< 2.0
Pb 208	-	0.015	4.2	< 10	-	7	< 10