Analysis of flue gas desulfurization wastewaters with the Agilent 7700x/7800 ICP-MS

Application note

Environmental

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Introduction

The U.S. Environmental Protection Agency (US EPA) is in the process of revising effluent guidelines for the steam electric power generating industry, due to increases in wastewater discharges as a result of Phase 2 of the Clean Air Act amendments. These regulations require SO_2 scrubbing for most coal-fired plants resulting in ‘flue gas desulfurization’ (FGD) wastewaters. The revised effluent guidelines will apply to plants ‘primarily engaged in the generation of electricity for distribution and sale which results primarily from a process utilizing fossil-type fuel (coal, oil or gas) or nuclear fuel in conjunction with a thermal cycle employing the steam water system as the thermodynamic medium’[1]. This includes most large-scale power plants in the United States. Effluents from these plants, especially coal-fired plants, can contain several hundred to several thousand ppm of calcium, magnesium, manganese, sodium, boron, chloride, nitrate and sulfate. Measurement of low ppb levels of toxic metals (including As, Cd, Cr, Cu, Pb, Se, Tl, V and Zn) in this matrix presents a challenge for ICP-MS,

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due to the very high dissolved solids levels and potential interferences from matrix-based polyatomic ions. Furthermore, FGD wastewater can vary significantly from plant to plant depending on the type and capacity of the boiler and scrubber, the type of FGD process used, and the composition of the coal, limestone and make-up water used. As a result, FGD wastewater represents the most challenging of samples for ICP-MS; it is very high in elements known to cause matrix interferences, and also highly variable. To address this difficult analytical challenge, in 2009 the EPA commissioned the development of a new ICP-MS method specifically for FGD wastewaters. This method was developed and validated at TestAmerica Laboratories, Inc. using an Agilent 7700x ICP-MS equipped with an Agilent ISIS-DS discrete sampling system.

Methods and materials

Instrumentation

The Agilent 7700x ICP-MS with ISIS-DS is uniquely suited to the challenge of developing a simple, robust analytical method for the analysis of regulated metals in uncharacterized high-matrix FGD wastewaters. Three attributes of the 7700x system are particularly critical and work together to enable reliable, routine analysis of large batches of variable high-matrix samples:

- Agilent's unique High Matrix Introduction (HMI) system enables controlled, reproducible aerosol dilution, which increases plasma robustness and significantly reduces exposure of the interface and ion lenses to undissociated sample matrix.
- The Octopole Reaction System (ORS^3) operating in helium collision mode eliminates matrix-based polyatomic interferences regardless of sample composition, without the need for time consuming sample-specific or analyte-specific optimization.
- The optional ISIS-DS discrete sampling system significantly reduces run time, while further reducing both matrix exposure and carryover.

Sample preparation

The samples were collected in HDPE containers and acidified with trace metal grade nitric acid to pH <2. Sample preparation was performed according to EPA 1638, Section 12.2 for total recoverable analytes by digestion with nitric and hydrochloric acid in a covered Griffin beaker on a hot plate. All calibrations were prepared in 2% HNO_3/0.5% HCl v/v as described in the method.

Analytical method

A standard Agilent 7700x ICP-MS with Micromist nebulizer and optional ISIS-DS was used. HMI aerosol dilution was set to medium, using the MassHunter ICP-MS software to automatically optimize the plasma parameters and robustness (CeO^+/Ce^+ ratio ~0.2%). MassHunter uses HMI optimization algorithms that take into account the type of nebulizer used, to ensure reproducible conditions from run to run and from instrument to instrument. Operating parameters are shown in Table 1.

Table 1. Instrument parameters used, illustrating simple, consistent instrument settings used for all analytes and all sample matrices

Parameter	Helium mode	Hydrogen mode
Instrument conditions		
HMI mode	Robust plasma, medium aerosol dilution	
Forward RF power (W)	1550	
Carrier gas flow (L/min)	0.56	
Dilution gas flow (L/min)	0.33	
Extraction lens 1 (V)	0	
Kinetic energy discrimination (V)	4	
Cell gas flow (mL/min)	4 (He)	4 (H_2)
Acquisition conditions		
Number of isotopes (including ISTDs)	25	3
Number of replicates	3	
Total acquisition time (s)	80 (total for both ORS modes)	
ISIS parameters		
Sample loop volume (µL)	600	
Online dilution factor	1:2	

The ORS[3] was operated in two modes: helium collision mode (He mode) for all analytes except selenium, which was measured in hydrogen reaction mode (H_2 mode). Twenty-five masses including internal standards were acquired, with typical integration times of 50 ms per replicate and three replicates per sample. Instrument detection limits (IDLs) were automatically calculated by the MassHunter software, based on the precision of the calibration blank measurement and the slope of the calibration plots (Table 2). Method detection limits (MDLs) (3σ) were calculated from 7 replicate analyses of a low-level spike of the synthetic FGD matrix solution.

Table 2. Analytes and analytical figures of merit

Element	Mass	Int. time (s)	ORS mode	ISTD	IDPL (ppb)	3σ MDL* (µg/L)
V	51	0.05	He	Sc	0.08	0.42
Cr	52	0.05	He	Sc	0.17	-
Mn	55	0.05	He	Sc	0.44	0.68
Ni	60	0.05	He	Sc	0.17	0.45
Cu	63	0.05	He	Sc	0.15	0.48
Zn	66	0.05	He	Ge	0.94	2.04
As	75	0.1	He	Ge	0.49	0.61
Se	78	0.05	H_2	Ge	0.08	0.31
Ag	107	0.05	He	In	0.02	0.29
Cd	111	0.05	He	In	0.19	0.59
Sb	121	0.05	He	In	0.05	0.36
Tl	205	0.05	He	Ho	0.02	0.23
Pb	208	0.05	He	Ho	0.03	0.36

* MDL calculated as 3σ of low-level spike into synthetic FGD matrix sample (n=7). MDL not calculated for chromium due to significant contamination in the synthetic FGD matrix solution. Additional isotopes were acquired for internal confirmation, but not reported.

Quality control

The quality control used for the new FGD wastewater method was based on the typical protocols used in other EPA methods. Prior to commissioning for routine operation, initial method validation requires determination of method detection limits, linear ranges, and analysis of multiple, single-element interference check solutions, to assess the effectiveness of polyatomic interference removal under the collision/reaction cell conditions used in the method. In routine use, daily quality control in a typical analytical sequence includes the analyses outlined in Table 3.

The FGD wastewater method requires the analysis of two new QC samples: a synthetic FGD matrix sample and a fortified FGD matrix sample.

Prior to preparing the synthetic FGD matrix samples, each potential matrix component was analyzed as a separate single-element standard, in order to determine the source and magnitude of any potential contaminants and the effectiveness of He mode at removing matrix-based interferences. Results are shown in Table 4. Nearly all contaminants and interferences were sub-ppb. The most significant contaminants were Cr, Ni and Zn in the 10,000 ppm Ca solution, confirmed by measuring secondary or qualifier isotopes for the analytes. Approximately 2 ppb of V was detected in the 10% HCl solution. This was either due to contamination, a small residual interference from $^{35}Cl^{16}O$, or a combination of the two, but at less than 2 ppb it did not present a problem for this analysis.

After each matrix component was characterized individually, a mixed synthetic FGD solution was prepared with the composition shown in Table 5, together with a second solution with the same matrix components but additionally spiked with all the analyte elements at 40 ppb. These new FGD matrix samples are analogous to the interference check solutions ICS-A and ICS-AB required by EPA method 6020, except the synthetic FGD samples are much higher in total dissolved solids (TDS) than the ICS-A and AB solutions, and contain those matrix elements that are commonly high in actual FGD samples. The detailed composition of the FGD matrix samples, which contain a total of >1% (10,000 ppm) TDS, is listed in Table 5, and results from the analysis of the synthetic FGD matrix blank and synthetic FGD matrix spike are shown in Table 6.

Table 3. Typical FGD analytical sequence including all required quality control.

ICV: Initial Calibration Verification, ICB: Initial Calibration Blank,
CCV: Continuing Calibration Verification, CCB: Continuing Calibration Blank,
LCS: Laboratory Control Sample, MS/MSD: Matrix Spike/Matrix Spike Duplicate

Analytical sequence	
Warm up	Once per sequence
Tune instrument	
Perform mass calibration check	
Perform resolution check	
Validate tuning criteria	
Calibration blank	
Calibration standard 1	
Calibration standard 2	
Calibration standard 3	
ICV	
ICB	
Method (reagent) blank	
Synthetic FGD matrix interference check	
Laboratory fortified synthetic FGD matrix	
Reporting limit verification standard	
CCV	
CCB	
10 samples (which can include all sample types) Must include 1 LCS and 1 MS/MSD pair	Repeat
CCV	
CCB	

Table 4. Initial demonstration of interference removal in single-element matrix solutions. Analyte concentrations (ppb) for each matrix (sum of analyte impurity and residual spectral interference).

Mass & analyte	10,000 ppm Ca	10,000 ppm S	10% HCl / 2% HNO_3
51 V	-0.631	0.236	1.934
52 Cr	0.771	0.000	0.171
55 Mn	0.019	0.137	0.647
60 Ni	1.115	0.740	0.078
63 Cu	-0.095	0.187	0.178
66 Zn	2.706	0.160	-0.126
75 As	0.689	-0.154	0.271
78 Se	0.029	0.213	0.320
107 Ag	0.012	0.040	0.002
111 Cd	-0.005	-0.031	-0.044
121 Sb	0.656	0.028	0.542
205 Tl	0.062	0.013	-0.003
208 Pb	0.058	0.135	0.037

Table 5. Composition of synthetic FGD matrix sample. Laboratory fortified synthetic FGD sample is spiked with 40 ppb of each of the target elements (400 ppb for zinc and 4000 ppb for aluminum).

Matrix component	Concentration
Chloride	5000 mg/L
Calcium	2000 mg/L
Magnesium	1000 mg/L
Sulfate	2000 mg/L
Sodium	1000 mg/L
Butanol	2 mL/L

Table 6. Analysis of mixed matrix FGD interference check sample and spiked FGD matrix solution. CCV expected value: 50 ppb.

Mass/ Analyte	FGD Matrix Check	Fortified FGD Recovery	Carryover Check	CCV (ppb)	CCB (ppb)
51 V	-0.187	102.2%	-0.068	48.885	0.101
52 Cr	12.699*	96.6%	0.015	48.851	0.117
55 Mn	-0.101	94.3%	-0.328	48.435	0.100
60 Ni	0.247	88.4%	-0.009	48.535	0.154
63 Cu	0.094	91.6%	0.096	47.316	0.115
66 Zn	3.181	86.1%	-0.302	49.804	0.100
75 As	0.107	110.0%	-0.043	48.205	0.009
78 Se	0.538	120.2%	-0.144	49.605	0.186
107 Ag	0.145	94.3%	0.010	47.632	0.003
111 Cd	0.039	98.9%	-0.017	48.695	0.017
121 Sb	0.181	98.4%	0.015	50.806	0.031
205 Tl	0.021	90.3%	0.000	48.108	0.008
208 Pb	0.436	92.1%	0.003	48.381	0.008

* Cr contamination verified by secondary isotope.

Results

Initial performance verification indicated that the 7700x with HMI was able to analyze the very high matrix samples, and He mode successfully eliminated matrix-based spectroscopic interferences, while the use of ISIS-DS helped to minimize memory effects (Table 6). Accuracy, both in terms of calibration stability (CCV) and for spike recoveries in the matrix (spiked FGD solution), were well within the standard operating procedure (SOP) requirements (CCV ± 15%, matrix spike recoveries ± 30%).

When running real FGD samples in a long sequence, continuing instrument performance must be monitored according to typical EPA criteria. Each group of 10 samples must include one laboratory control sample (LCS) of known concentration, and one matrix spike/matrix spike duplicate (MS/MSD) pair in addition to 7 unknown samples.

After each block of 10 samples, calibration and blank levels were verified through the analysis of a CCV and CCB standard (Figure 1). Additionally, internal standards were monitored for all samples and easily met the requirement to fall within 60 to 125% of the intensity measured in the calibration blank (Figure 2). Internal standard recoveries provide information on sample-specific matrix effects as well as longterm instrument drift.

Internal standard recoveries for the 88 sample validation sequence are shown in Figure 2. All samples met the ISTD QC requirements of 60 to 125% recovery and total instrument drift over the course of the sequence was less than 10% as indicated by the ISTD response for the final CCV sample.

In the complete sequence, a total of six MS/MSD pairs were analyzed and the relative percent difference (RPD) calculated for each pair is shown in Table 7. The method limit for RPD is < 20% which includes both measurement and sample preparation errors. Only silver proved to be problematic late in the sequence, most likely due to chemical stability/solubility problems in samples containing high and variable levels of chloride.

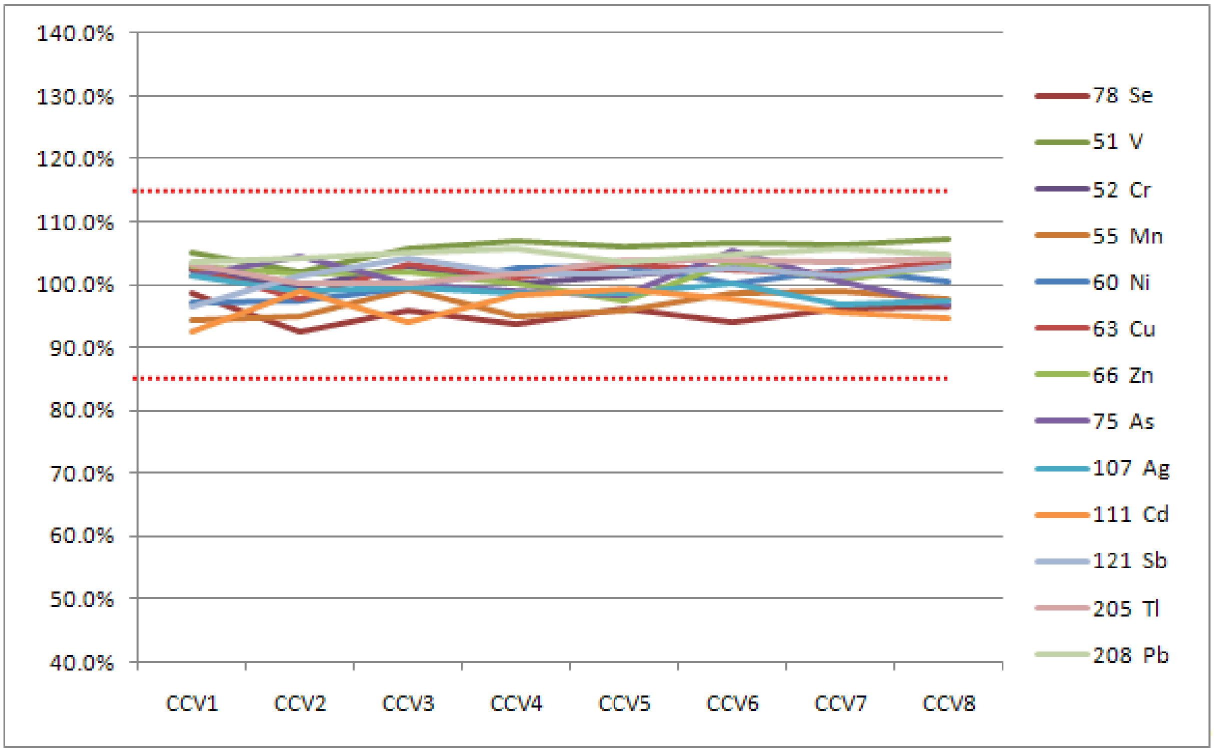

Figure 1. CCV recoveries over a sequence of 88 analyses including real FGD samples, all required QC samples and synthetic FGD matrix samples. Control limits (85–115%) are indicated in red.

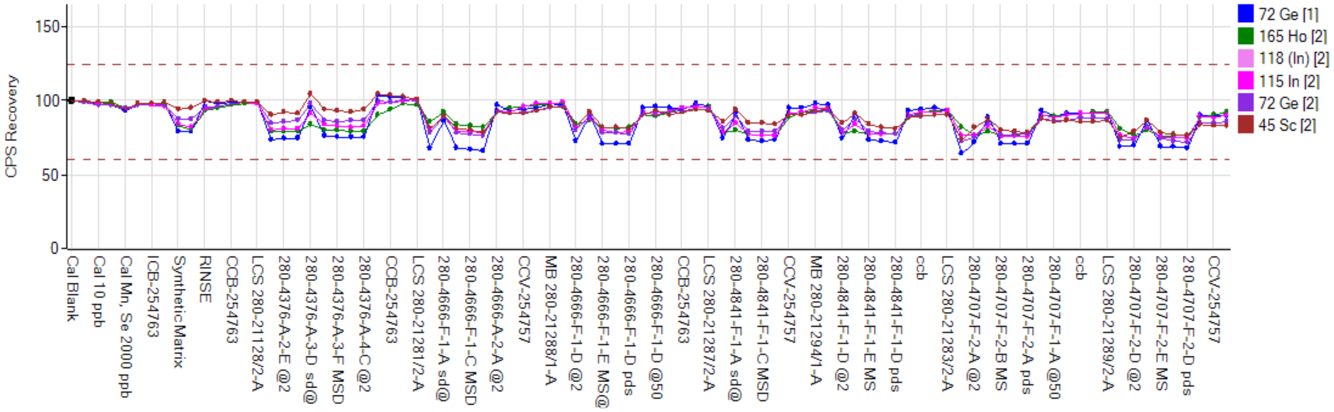

Figure 2. Internal standard recoveries for entire 88 sample sequence. Control limits (60–125%) are indicated by red dashed lines.

Table 7. Matrix spike (MS) and matrix spike duplicate (MSD) results and relative percent differences (RPD) for the sequence of 88 analyses. Spike concentration was 20 ppb except silver, which was 5 ppb.

Mass & element	Spike 1	Spike duplicate	RPD (%)	Spike 2	Spike duplicate	RPD (%)	Spike 3	Spike duplicate	RPD (%)
78 Se	21.60	22.05	2.1%	8425.29	8478.66	0.6%	1927.89	1948.11	1.0%
51 V	21.93	21.65	-1.3%	493.85	501.30	1.5%	25.07	24.92	-0.6%
52 Cr	20.04	20.62	2.9%	506.40	518.59	2.4%	20.26	20.32	0.3%
55 Mn	148.52	151.49	2.0%	34308.04	34217.28	-0.3%	33316.73	33152.16	-0.5%
60 Ni	18.25	18.90	3.6%	674.91	679.58	0.7%	486.75	489.42	0.5%
63 Cu	17.97	19.28	7.3%	537.18	545.67	1.6%	33.96	34.80	2.5%
66 Zn	19.66	20.96	6.6%	666.47	675.99	1.4%	69.48	66.64	-4.1%
75 As	23.74	21.64	-8.8%	97.51	95.70	-1.9%	26.40	25.67	-2.8%
107 Ag	19.67	19.75	0.4%	2.58	2.52	-2.7%	4.97	9.97	100.5%
111 Cd	20.58	19.31	-6.1%	23.73	24.12	1.6%	19.93	21.46	7.7%
121 Sb	20.51	20.32	-0.9%	52.84	51.56	-2.4%	22.79	23.79	4.4%
205 Tl	20.24	20.07	-0.8%	20.68	20.25	-2.1%	24.87	25.82	3.8%
208 Pb	19.79	20.14	1.8%	150.09	150.06	0.0%	20.27	19.74	-2.6%

Mass & element	Spike 4	Spike duplicate	RPD (%)	Spike 5	Spike duplicate	RPD (%)	Spike 6	Spike duplicate	RPD (%)
78 Se	1056.43	1064.35	0.8%	1038.18	1049.50	1.1%	1100.59	1076.18	-2.2%
51 V	21.43	21.99	2.6%	22.20	21.85	-1.6%	21.31	22.08	3.6%
52 Cr	20.08	20.19	0.5%	20.95	19.55	-6.7%	20.44	20.15	-1.4%
55 Mn	5093.08	5097.50	0.1%	5060.45	5121.08	1.2%	5444.41	5340.90	-1.9%
60 Ni	25.17	20.08	-20.2%	19.00	23.07	21.4%	20.53	19.39	-5.5%
63 Cu	19.26	19.53	1.4%	19.45	18.73	-3.7%	19.22	19.23	0.1%
66 Zn	21.44	21.27	-0.8%	20.47	21.73	6.1%	21.02	18.23	-13.3%
75 As	25.71	22.84	-11.2%	24.07	24.08	0.0%	24.18	22.80	-5.7%
107 Ag	6.02	2.87	-52.3%	5.75	8.30	44.3%	5.22	6.02	15.2%
111 Cd	17.69	20.06	13.4%	17.48	18.19	4.0%	19.00	18.71	-1.5%
121 Sb	21.42	22.69	5.9%	21.61	21.65	0.2%	22.38	21.82	-2.5%
205 Tl	20.79	20.45	-1.7%	20.44	20.54	0.5%	21.08	20.53	-2.6%
208 Pb	19.40	19.62	1.1%	19.47	19.73	1.3%	19.30	19.27	-0.2%

Conclusions

Flue gas desulfurization (FGD) wastewater samples are extremely challenging due to their high and variable matrix composition and the fact that most of the required analytes can suffer from overlap from matrix-based polyatomic interferences. However, the new EPA method development and validation has demonstrated that these difficult sample matrices can be routinely analyzed for trace metal contaminants using the Agilent 7700x ICP-MS with optional ISIS-DS discrete sampling accessory.

Based on extensive initial validation and strict ongoing EPA mandated quality control, the new method has been shown to be simple, robust, and reliable. Using the combined advantages of a highly robust plasma, HMI aerosol dilution, helium collision mode to eliminate interferences, and discrete sampling, this method has achieved performance comparable to that normally expected when analyzing much simpler samples such as waters and soil digests.

References

1. Technical Support Document for the Preliminary 2010 Effluent Guidelines Program Plan, 40 CFR Part 423.10, www.epa.gov

Note

Results presented in this document were obtained using the 7700x ICP-MS, but performance is also validated for the 7800 ICP-MS.

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