AN APPLICATION REPORT FROM
SPECTRO ANALYTICAL INSTRUMENTS

ICP-77, Rev. 1

SPECTROBLUE FME36

Analysis of Environmental Samples Following the CLP ILM 05.3 Protocol by ICP-OES with Axial Plasma Observation

Introduction

To monitor pollution and protect the environment, the US EPA has been given the authority to develop standardized analytical methods for the measurement of pollutants in environmental samples.

The contract laboratory program CLP ILM 05.3, (Multi-Media, Multi-Concentration, Inorganic Analytical Service for Superfund) includes analytical methods for Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-OES), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Cold Vapor Atomic Absorption (CVAA), and colorimetric techniques, in order to provide data for the U.S. Environmental Protection Agency in support of the investigation and clean-up activities under the Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA) and the Superfund Amendments and Reauthorization Act of 1986 (SARA) [1], [2], [3].The methods cover 23 analyte metals, mercury and cyanide and are suitable for water, soil, sediment and aqueous samples.

The SPECTROBLUE with axial plasma observation offers a simple, fast, accurate, precise and cost efficient method for regulated analysis as required by CLP ILM 05.3. MDLs at sub ppb levels were measured and excellent recoveries were determined for the check samples required to be analyzed. In conjunction with an autosampler the SPECTROBLUE can be fully automated. Independent from the number of lines and elements, an analysis (including 2 replicates, pre-flush, and method rinse) can be performed in less than two and a half minutes.

The complete elimination of water cooling not only saves the costs for an external cooling system, as well as its operating costs, but also increases operational safety.

Thanks to UV PLUS the optical system does not consume any purge gases, which again considerably reduces operating costs.

To enable the production of data with known quality, the methods include a strict chain of custody and numerous validation and verification steps.

The CLP provides the methods to be used, specific reporting and contractual requirements, quality assurance, quality control and standard operating procedures. Participating laboratories must demonstrate the ability to meet the quality objectives prior to analyzing samples, e.g. document the methods used and determine MDLs. Analytical data from QC are used to estimate and evaluate analytical results and to determine the necessity for, or the effect of corrective action procedures.

The aim of this application report is to demonstrate that the SPECTROBLUE ICP-OES has all the analytical capabilities to perform analysis within the guidelines of the above mentioned program.

Instrumentation

All measurements were performed with the SPECTROBLUE inductively coupled plasma optical emission spectrometer with axial plasma observation. The SPECTROBLUE features a Paschen-Runge spectrometer mount, employing the proprietary Optimized Rowland Circle Alignment (ORCA) technique. Consisting of two hollow section cast shells, optimized small volume and 15 linear CCD detectors, the wavelength range between 165 and 770 nm can be analyzed, allowing complete spectrum capture within 4s. Due to the unique reprocessing capabilities of the system, a new measurement is not required even if additional elements or lines are to be determined at a later date. The optic is hermetically sealed and filled with argon, continuously circulated through a filter, which absorbs oxygen, water vapor and other species. High optical transmission in the UV is achieved, allowing the determination of non-metals as well as the use of prominent and interference free lines in this region. Utilizing SPECTRO's "Intelligent Calibration Logic" (iCAL), which normalizes the wavelength scale, the state of the optical system is automatically monitored. An air-cooled, 27.12 MHz, free running type LDMOS ICP-generator is installed, which ensures excellent stability of the forward power even in the case of rapidly changing sample loads. All relevant ICP operating parameters are software controlled, allowing easy selection of the optimum operating conditions. For sample introduction, a Modified Lichte nebulizer with a cyclonic spray chamber was used. The operating conditions are given in Table 1.

Table 1: ICP Operating Conditions

Power	1450 W
Coolant flow	13 L/min
Auxiliary flow	0.8 L/min
Nebulizer flow	0.7 L/min
Plasma Torch	Quartz, demountable
Injector tube	2.0 mm
Spray Chamber	Cyclonic
Nebulizer	Modified Lichte
Sample uptake rate	1.33 mL/min
Uptake rate for buffer	0.68 mL/min
Replicate read time	42 s per replicate

Table 2: Calibration standards

Element	Std. 0 [mg/L]	Std. 1 [mg/L]	Std. 2 [mg/L]	Std. 3 [mg/L]	Std. 4 [mg/L]	Std. 5 [mg/L]
Ag	0	0.005	0.05	0.5		
Al	0	0.1	1	10	50	100
As	0	0.1	1	10		
Ba	0	0.01	0.1	1		
Be	0	0.01	0.1	1		
Ca	0	0.1	1	10	50	100
Cd	0	0.02	0.2	2		
Co	0	0.02	0.2	2		
Cr	0	0.05	0.5	5		
Cu	0	0.02	0.2	2		
Fe	0	0.1	1	10	50	100
K	0	0.2	2	20	50	100
Mg	0	0.1	1	10	50	100
Mn	0	0.02	0.2	2		
Na	0	0.1	1	10	50	100
Ni	0	0.02	0.2	2		
Pb	0	0.1	1	10		
Sb	0	0.05	0.5	5		
Se	0	0.05	0.5	5		
Tl	0	0.05	0.5	5		
V	0	0.02	0.2	2		
Zn	0	0.05	0.5	5		
Sb	0	0.1	0.5	2		
Se	0	0.1	0.5	2		
Si	0	0.1	0.5	2		
Sn	0	0.1	0.5	2		
Sr	0	0.1	0.5	2		
Tl	0	0.1	0.5	2	5	
V	0	0.1	0.5	2	0	
Zn	0	0.1	0.5	2	0	

Calibration Standards

For calibration, commercially available standard solutions (Inorganic Ventures Christiansburg, VA, USA [6]) were used and diluted to the concentrations as given in Tab. 2. All solutions and samples were acidified with 1% HNO_3 and 5% HCl of suprapure quality. CsCl at a concentration of approximately 3400 mg/L was added as ionization buffer. The addition was performed online using a 10 g/L solution made form CsCl salt (99.995%), a Y-piece, an orange-white pump tube and the third channel of the instrument’s peristaltic pump.

Procedure

To demonstrate compliance with the method the following procedure and sample sequence was run. Prior to the calibration, method detection limits (MDL) and the linear range were determined. Various water samples were analyzed as unknown samples.

Sample	When	Specification	Control failure action
S0	Daily	None	
S1	Daily	None	
ICV	Directly after the calibration	90% - 110% recovery	Terminate, re-calibration
ICB	Directly after the calibration	± 1xCRQL	Terminate, re-calibration
CRI	Following ICV/ICB, at the end of the run, before the ICS analysis and once every 20 samples followed by the ICS/CCV-CCB analysis	70%-130% - 50%-150% (Sb, Pb, Tl) recovery	Re-analyze for failing elements, if fails again ->terminate
CCV	Frequency of 10% or every two hours, beginning and end of run	90% - 110% recovery	Terminate, re-calibration, re-analysis
CCB	After the CCV frequency of 10% or every two hours, beginning and end of run	+/- 1xCRQL	Terminate, re-calibration, re-analysis
ICSA	Beginning, end , not before the ICV, every 20 samples, followed by CCV/CCB	± 2x CRQL or 20% whatever is greater	Terminate and correct problem
ICSAB	Beginning, end, not before the ICV, every 20 samples, followed by CCV/CCB	± 2x CRQL or 20% whatever is greater	Terminate and correct problem
PB	Once with every sample batch	± 1x CRQL	Re-digest and re-measure all samples analyzed ≤10x of the relevant element
Spike	Once for every group of sample with similar matrix	75%-125% recovery (unless conc. of org sample is >5x spike)	Do post digestion spike @ 2x the indigenous or 2x CRQL whatever is greater
Duplicate	Once for every group of sample with similar matrix	20% relative difference for conc. >5x CRQL. If <5x CRQL, control limit	Flag all samples of the relevant batch
LCS	Once for every group of sample with similar matrix or for each batch digested, whatever is more frequent	= CRQL	Terminate and correct problem
Serial Dilution	Once for every group of sample with similar matrix or for each batch digested, whatever is more frequent	80%-120% recovery except Ag and Sb	Flag all samples of the relevant batch
LRS	At start of contract. Thereafter, quarterly	For concentrations >50x MDL, a 5xdiluted sample when corrected for dilution should give a result within 10% of the original sample	
MDL	At start of contract, annually and after instrument maintenance or changes	Within 5% of the true value to determine the upper limit of the ICP-OES linear range	

For an explaration of the sample abbreviations please see the glossary at page 12 of this report.

Result and Discussion

Tab. 5 shows the selected wavelengths and the achieved instrument detection limits (IDL) as well as the determined method detection limits (MDL). The IDLs were calculated according to the equation [4]:

$$\mathbf{IOD = 3\ RSD_b\ c/100\ SBR}$$

Where:

RSD_b – relative standard deviation of 10 replicates of the blank (in %)
C – concentration of the standard
SBR – signal to background ratio

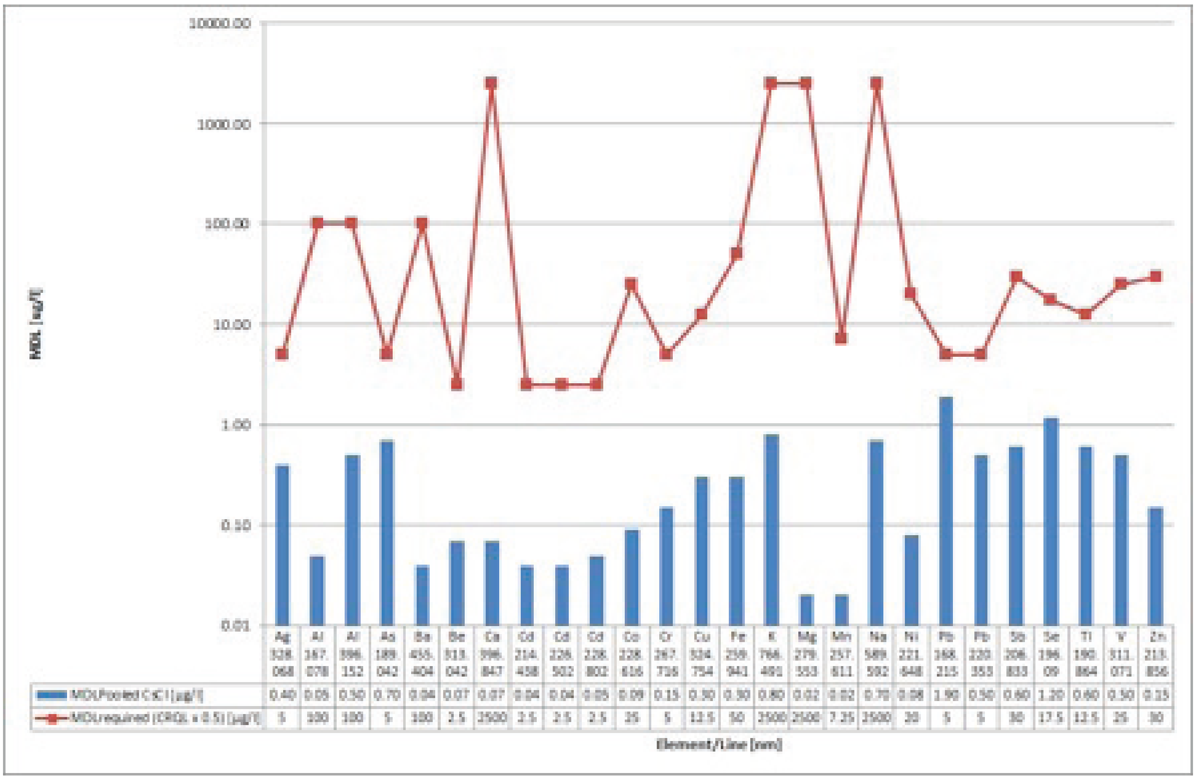
Table 4:
Sample Sequence

Step No.	Sample Sequence
1	S0
2	S1
3	ICV
4	ICB
5	CRI
6	ICSA
7	ICSAB
8	CCV
9	CCB
10	10 samples
11	CCV
12	CCB
13	7 samples
14	CRI
15	ICSA
16	ICSAB
17	CCV
18	CCB
19	10 samples
20	CCV
21	CCB
22	7 samples
23	CRI
24	ICSA
25	ICSAB
26	CCV
27	CCB
28	5 samples
29	CRI
30	ICSA
31	ICSAB
32	CCV
33	CCB

Table 5: ILDs and MDLs for selected lines and comparison to the contract required limits

Element/ Line [nm]	IDL [µg/l]	MDL Pooled [µg/l]	MDLrequired (CRQLx0.5) [µg/l]	CRQL [µg/l]
Ag 328.068	0.7	0.4	5	10
Al 167.078	0.04	0.05	100	200
Al 396.152	1.6	0.5	100	200
As 189.042	0.8	0.7	5	10
Ba 455.404	0.05	0.04	100	200
Be 313.042	0.08	0.07	2.5	5
Ca 396.847	0.07	0.07	2500	5000
Cd 214.438	0.07	0.04	2.5	5
Cd 226.502	0.09	0.04	2.5	5
Cd 228.802	0.09	0.05	2.5	5
Co 228.616	0.2	0.09	25	50
Cr 267.716	0.3	0.15	5	10
Cu 324.754	0.6	0.3	12.5	25
Fe 259.941	0.1	0.3	50	100
K 766.491	1.3	0.8	2500	5000
Mg 279.553	0.03	0.02	2500	5000
Mn 257.611	0.03	0.02	7.25	15
Na 589.592	0.3	0.7	2500	5000
Ni 221.648	0.3	0.08	20	40
Pb 168.215	1.4	1.9	5	10
Pb 220.353	1.1	0.5	5	10
Sb 206.833	1.6	0.6	30	60
Se 196.09	1.8	1.2	17.5	35
Tl 190.864	0.7	0.6	12.5	25
V 311.071	0.6	0.5	25	50
Zn 213.856	0.08	0.15	30	60

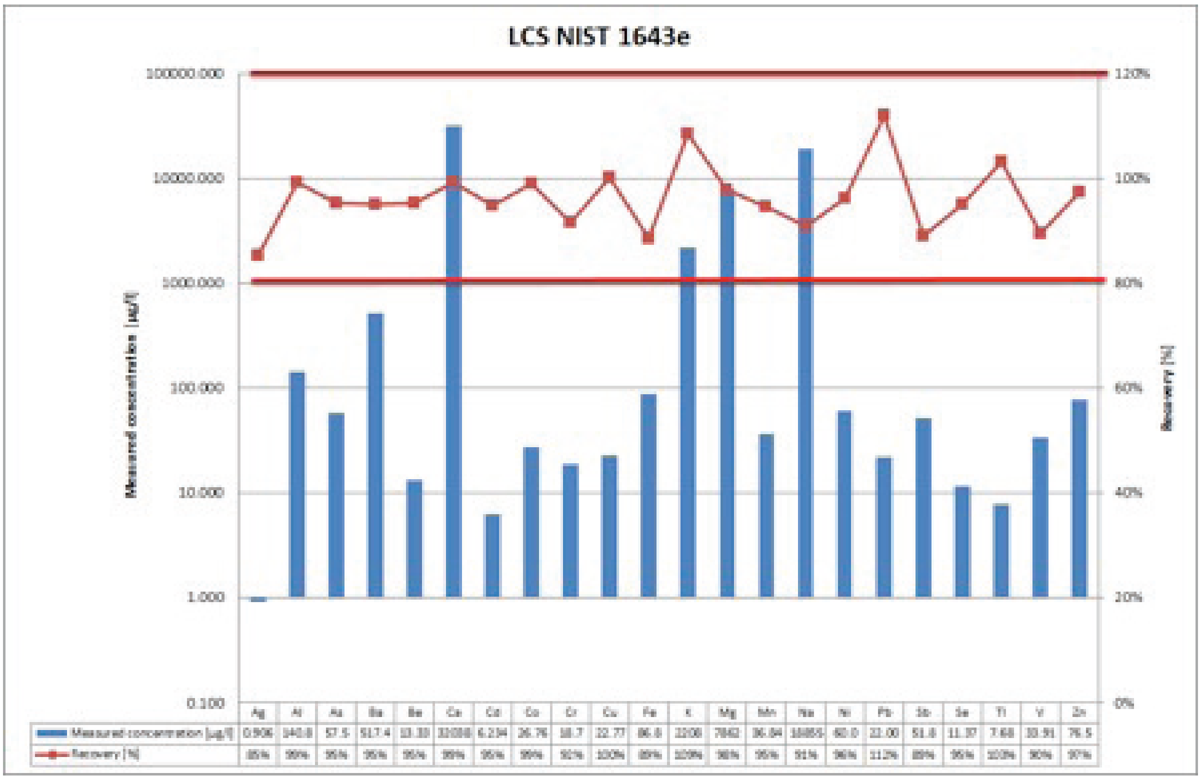
The MDLs where calculated according to 40 CFR 136 Appendix B [5]. All elements required to be determined, show MDLs at 1 µg/l, the great majority even considerably below 1 µg/l and thus are well below the required MDLs, defined as 50% of the contract required quantification limit (CRQL) (see Tab.5 and Fig.1). Even for the most critical element, arsenic, the SPECTROBLUE provides a factor 7 difference to the required MDL; ample performance to guarantee unobstructed routine operation. All required check samples could be analyzed without deviation. As examples the recoveries of NIST CRM 1643e (NIST, Gaithersburg, MD, USA [7]) used as the laboratory control sample, the CRI to prove performance at the CRQL and the interference check sample ICS AB are displayed in Fig. 2-4.



Element/Line [nm]	Ag 328.068	Al 167.078	Al 396.152	As 189.042	Ba 455.404	Be 313.042	Ca 396.847	Cd 214.438	Cd 226.502	Cd 228.802	Co 228.616	Cr 267.716	Cu 324.754
MDLPooled C:C I [µg/l]	0.40	0.05	0.50	0.70	0.04	0.07	0.07	0.04	0.04	0.05	0.09	0.15	0.30
MDLrequired (CRQL x 0.5) [µg/l]	5	100	100	5	100	2.5	2500	2.5	2.5	2.5	25	5	12.5

Element/Line [nm]	Fe 259.941	K 766.491	Mg 279.553	Mn 257.611	Na 589.592	Ni 221.648	Pb 168.215	Pb 220.353	Sb 206.833	Se 196.09	Tl 190.864	V 311.071	Zn 213.856
MDLPooled C:C I [µg/l]	0.30	0.80	0.02	0.02	0.70	0.08	1.90	0.50	0.60	1.20	0.60	0.50	0.15
MDLrequired (CRQL x 0.5) [µg/l]	50	2500	2500	7.25	2500	20	5	5	30	17.5	12.5	25	30

Figure 1: Required versus determined MDLs



	Ag	Al	As	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe
Measured concentration [µg/l]	0.906	140.8	57.5	517.4	13.33	32038	6.234	26.76	18.7	22.77	86.8
Recovery [%]	85%	99%	95%	95%	95%	99%	95%	99%	92%	100%	89%

	K	Mg	Mn	Na	Ni	Pb	Sb	Se	Tl	V	Zn
Measured concentration [µg/l]	2208	7842	36.84	18855	60.0	22.00	51.8	11.37	7.68	33.91	76.5
Recovery [%]	109%	98%	95%	91%	96%	112%	89%	95%	103%	90%	97%

Figure 2: Recoveries for the laboratory control sample (LCS) NIST 1643e

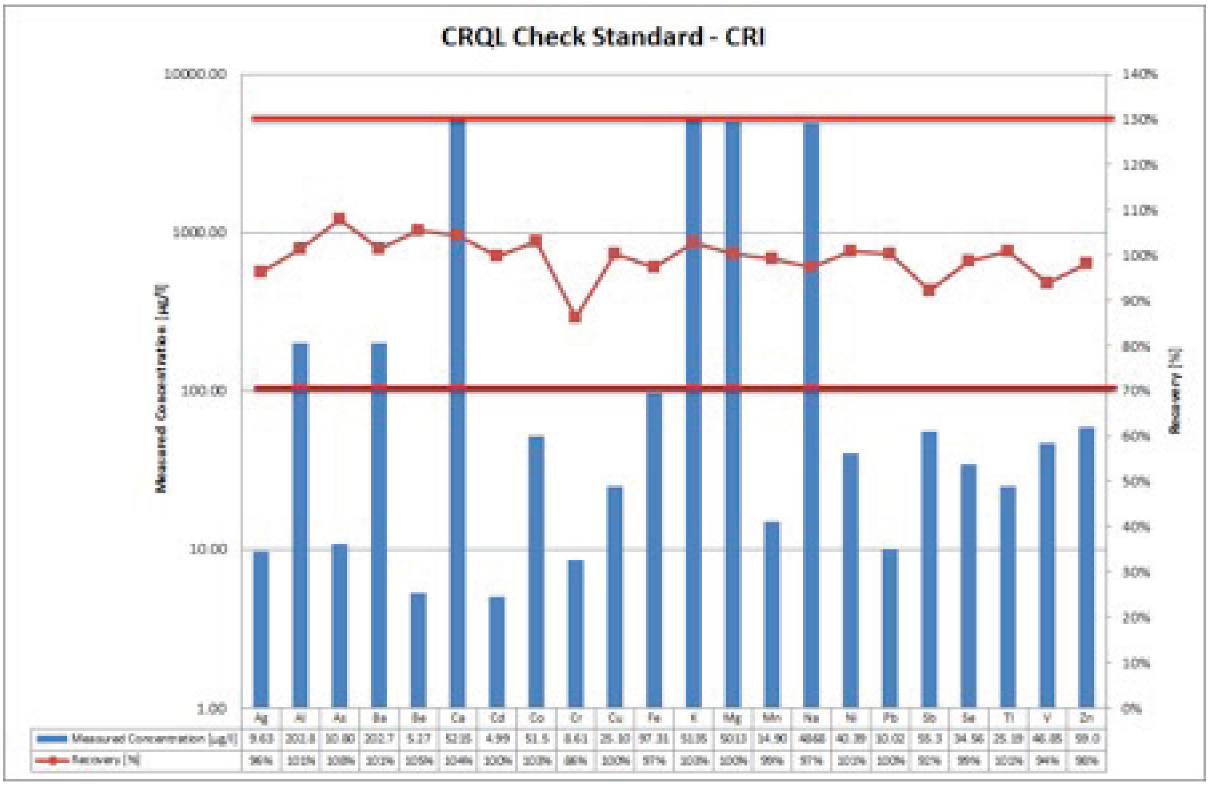


Figure 3: 3 Recoveries for the "Contract Required Quantitation Limit Check Standard (CRI)

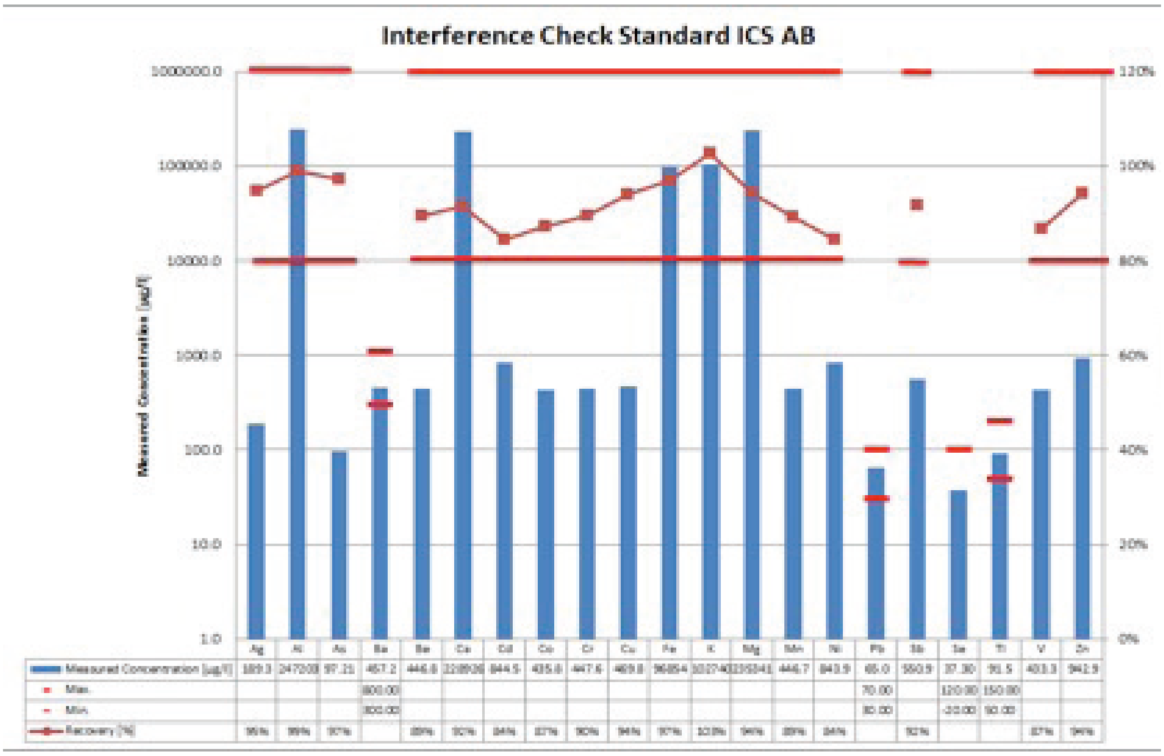


Figure 4: Recoveries for the Interference Check sample (ICS AB)

The interference check sample ICS A, as well as the results for the duplicate, spike and dilution sample measurements are displayed in Table 6 and 7 (next page).

The measurements demonstrate that the combination of high sensitivity with high resolution provide excellent recoveries at trace levels, even in the presence of higher amounts of alkali, earth alkali elements and metals, as contained in the interference check standard ICSAB.

Table 6: Recoveries/results for the Interference Check Sample (ICS A)

Element	Unit	Measured	Expected	Recovery	Min	Max
Ag	[µg/l]	-4.62	0		-20.00	20.00
Al	[µg/l]	248876	250000	100%	80%	120%
As	[µg/l]	-0.17	0		-10.00	10.00
Ba	[µg/l]	-0.07	0		-200.00	200.00
Be	[µg/l]	0.05	0		-20.00	10.00
Ca	[µg/l]	232562	250000	93%	80%	120%
Cd	[µg/l]	5.33	0		-10.00	10.00
Co	[µg/l]	0.60	0		-100.00	100.00
Cr	[µg/l]	-1.01	0		-20.00	20.00
Cu	[µg/l]	0.65	0		-50.00	50.00
Fe	[µg/l]	98096	100000	98%	80%	120%
K	[µg/l]	105505	100000	106%	80%	120%
Mg	[µg/l]	237090	250000	95%	80%	120%
Mn	[µg/l]	4.02	0		-30.00	30.00
Na	[µg/l]	1.50	0		-1000.00	1000.00
Ni	[µg/l]	2.61	0		-80.00	80.00
Pb	[µg/l]	16.15	0		-20.00	20.00
Sb	[µg/l]	1.13	0		-120.00	120.00
Se	[µg/l]	-7.93	0		-70.00	70.00
Tl	[µg/l]	1.36	0		-50.00	50.00
V	[µg/l]	-0.41	0		-100.00	100.00
Zn	[µg/l]	11.25	0		-120.00	120.00

The green color includes compliance to the method.

Table 7: Duplicate, Spike and Dilution sample results

Element	Sample [µg/l]	Duplicate [µg/l]	Difference [µg/l]	Spec. ± [µg/l]	Sample [µg/l]	Spike[µg/l]	Conc. [µg/l]	Recovery [%]	Min [%]	Max [%]	Sample [µg/l]	Dilution [µg/l]	Difference [%]	Spec. ± [%]
Duplicate Sample					**Spike Sample**						**Dilution Sample**			
Ag	<DL	<DL	0	10	<LOD	49.55	50	99	75	125	48.38	48.23	0.3	10
Al	<DL	<DL	0	200	26.69	1039	1000	101	75	125	1008	1053	-4.5	10
As	4.63	4.78	0.16	10	3.16	1041	1000	104	75	125	1004	913	9.1	10
Ba	19.98	19.75	-0.23	200	18.85	121.5	100	103	75	125	103.3	97.2	5.9	10
Be	<LOD	<LOD	0	5	<LOD	105.1	100	105	75	125	102.0	105.5	-3.4	10
Ca	38695	38003	1.8	20							1002	1034	-3.1	10
Cd	<LOD	<LOD	0	5	<LOD	206.5	200	103	75	125	203.5	191.8	5.7	10
Co	<LOD	<LOD	0	50	0.184	204.1	200	102	75	125	198.8	207.9	-4.6	10
Cr	<LOD	<LOD	0	10	0.365	510	500	102	75	125	505	502	0.6	10
Cu	63.0	53.4	-9.6	25	44.54	259.2	200	107	75	125	200.9	189.8	5.5	10
Fe	<LOD	<LOD	0	100	23.07	1039	1000	102	75	125	1023	1038	-1.5	10
K	1483	1458	-25	5000							2100	2037	3.0	10
Mg	6539	6355	-184	5000							1041	1103	-5.9	10
Mn	0.386	0.371	-0.02	15	1.534	205.9	200	102	75	125	201.7	185.9	7.9	10
Na	12718	12500	-218	5000							1010	1011	-0.1	10
Ni]	9.02	8.99	-0.04	40	14.41	218.4	200	102	75	125	203.5	214.0	-5.1	10
Pb	8.81	8.65	-0.16	10	2.51	1045	1000	104	75	125	1033	1081	-4.6	10
Sb]	1.02	0.836	-0.18	60	1.23	522	500	104	75	125	506	465	8.2	10
Se	2.98	2.72	-0.26	35	<LOD	531	500	106	75	125	504	465	7.9	10
Tl	0.275	0.324	0.05	25	<LOD	517	500	103	75	125	514	497.7	3.1	10
V	<LOD	<LOD	0	50	<LOD	207.7	200	104	75	125	202.1	196.9	2.6	10
Zn	125.2	123.8	-1.4	60	104.2	589	500	97	75	125	502	511	-1.8	10

Conclusion

The SPECTROBLUE with axial plasma observation offers a simple, fast, accurate, precise and cost efficient method for regulated analysis as required by CLP (Contract Laboratory Program) ILM 05.3. MDLs (Method Detection Limits) at sub ppb levels were measured and excellent recoveries were determined for the check samples required to be analyzed. In conjunction with an autosampler the SPECTROBLUE can be fully automated. Independent from the number of lines and elements an analysis (including 2 replicates, pre-flush, and method rinse) can be performed in less than two and a half minutes. The complete elimination of water cooling not only saves the costs for external cooling system as well as its operating costs, but also increases operational safety.

Thanks to UV PLUS the optical system does not consume any purge gases, which again considerably reduces operating costs.

With the SPECTROBLUE ergonomics and ease of operation is a principle point. Components which require regular user maintenance can be quickly mounted and dismounted, e.g. by the use of bayonet connections. All critical parts are self-aligning, the plasma torch is tubeless. The newly developed, App-like SMART USER INTERFACE only includes few buttons and no menus. Even users unfamiliar with the instrument are able to quickly learn to operate the ICP routinely.

However, also the use of established techniques offers advantages: compared to the Echelle type optical systems, the Paschen-Runge design used in the SPECTROBLUE offers a more uniform optical resolution over a wide spectral range. The result: fewer interferences, which need correction.

All of this makes the SPECTROBLUE, which has been particularly designed for environmental work, the perfect instrument for the application.

References

[1] US-EPA Contract Laboratory Program, Statement of Work for Inorganic Analysis, CLP ILM 05.3,March 2004, Exhibit A-C
[2] US-EPA Contract Laboratory Program, Introduction to Analytical Methods, Exhibit D
[3] US-EPA Contract Laboratory Program, Quality Assurance Program, Exhibit E-H
[4] P. W. J. M. Boumans, Spectrochim. Acta 46B, 431 (1991)
[5] 40 CFr 136 Appendix B, Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11, 26th March 2010
[6] Inorganic Ventures, Christiansburg, VA, USA
[7] National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA

Glossary

CLP	Contract Laboratory Program
CLP ILM 05.3	Multi-Media, Multi-Concentration, Inorganic Analytical Service for Superfund
MDL	Method Detection Limit
IDL	Instrument Detection Limit
CRM	Certified Reference Material
CRQL	Contract Required Quantification Limit
S0	Calibration Blank Standard
S1	Calibration Standard
ICV	Initial Calibration Verification check standard
ICB	Initial Calibration Blank check standard
CRI	Contract Required Quantitation Limit Check Standard
CCV	Continuing Calibration Verification check standard
CCB	Continuing Calibration Blank check standard
ICSA	Interference Check Sample A
ICSAB	Interference Check Sample AB
PB	Preparation Blank sample
Spike	Spike sample
Duplicate	Duplicate sample
LCS	Laboratory Control Sample
Serial Dilution	Serial Dilution Sample
LRS	Linear Range Standard

SPECTRO
AMETEK
MATERIALS ANALYSIS DIVISION

www.spectro.com

GERMANY
SPECTRO Analytical Instruments GmbH
Boschstrasse 10
D-47533 Kleve
Tel: +49.2821.892.0
Fax: +49.2821.892.2202
spectro.sales@ametek.com

U.S.A.
SPECTRO Analytical Instruments Inc.
91 McKee Drive
Mahwah, NJ 07430
Tel: +1.800.548.5809
+1.201.642.3000
Fax: +1.201.642.3091
spectro-usa.sales@ametek.com

CHINA
AMETEK Commercial
Enterprise (Shanghai) CO., LTD.
Part A1, A4 2nd Floor Building No.1 Plot Section
No.526 Fute 3rd Road East; Pilot Free Trade Zone
200131 Shanghai
Tel.: +86.21.586.851.11
Fax: +86.21.586.609.69
spectro-china.sales@ametek.com

Subsidiaries: ▶**Hong Kong:** Tel. +852.2976.9162, Fax +852.2976.9132, spectro-ap.sales@ametek.com, ▶**FRANCE:** Tel +33.1.3068.8970, Fax +33.1.3068.8999, spectro-france.sales@ametek.com, ▶**GREAT BRITAIN:** Tel +44.1162.462.950, Fax +44.1162.740.160, spectro-uk.sales@ametek.com, ▶**INDIA:** Tel +91.22.6196 8200, Fax +91.22.2836 3613, sales.spectroindia@ametek.com, ▶**ITALY:** Tel +39.02.94693.1, Fax +39.02.94693.650, spectro-italy.sales@ametek.com, ▶**JAPAN:** Tel +81.3.6809.2405, Fax +81.3.6809.2410, spectro-japan.info@ametek.co.jp, ▶**SOUTH AFRICA:** Tel +27.11.979.4241, Fax +27.11.979.3564, spectro-za.sales@ametek.com, ▶**SWEDEN:** Tel +46.8.5190.6031, Fax+46.8.5190.6034, spectro-nordic.info@ametek.com.
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