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SPECTRO**GREEN**

Analysis of Wastewater by ICP-OES With Dual Side-on Plasma Observation With a Focus on India

Introduction

The surveillance of the discharge of wastewater to surface or groundwater is an important part of environmental protection and the assurance of clean water. The handling, treatment, use and discharge of wastewater from industrial and urban sources is handled differently in different countries. This report describes the analysis of wastewater by ICP-OES in accordance with the standard IS 3025 applicable in India.

The handling of wastewater, treatment, reuse, and discharge poses a global challenge. Produced by industrial and urban sources, every country has its own regulations in place. Requirements for discharging wastewater to the environment vary largely from country to country.

In India, the central pollution control board issued standards for the emission and discharge of environmental pollutants, specifically adapted to different industrial branches, but also adapted to common effluent treatment plants [1]. Table 1 gives an overview of the applicable limit values from the environmental protection rules.

Due to its multi-element determination capability, high linear dynamic range and sensitivity, Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is widely used for the analysis of waste waters. Trace, minor, and major elements can be determined simultaneously ensuring low cost of analysis. The application is described in several ICP-OES standard procedures such as the IS 3025 [2] for the determination of 33 elements by ICP-OES which applies in India.

This report describes the principal methodology for the analysis of wastewater. It presents typical limits of detection for a wide range of elements as well as studies on precision and accuracy using spike recovery measurements and the analysis of a certified reference material. Measurements were made in accordance with the IS 3025.

Table 1: Applicable limit values for the discharge of wastewater to water bodies in India

Element	Concentration [mg/L]
Ag	5
Al	5
As	0.1
Cd	0.05
Co	0.2
Cr	0.1
Cu	0.05
Fe	2

Element	Concentration [mg/L]
Hg	0.01
Mn	1
Ni	0.1
Pb	0.05
Sb	0.1
Se	0.05
Sn	2
V	0.2
Zn	0.1

Instrumentation

All measurements were performed with the SPECTROGREEN ICP optical emission spectrometer (SPECTRO Analytical Instruments, Kleve, Germany) with Dual Side-on plasma observation. It enables an average factor 2 enhanced sensitivity compared to single radial plasma observation and a comparable sensitivity to vertical torch dual-view systems, while eliminating typical axial-view interferences. In addition, it offers a high matrix compatibility, linear dynamic range and precision without the need to change the plasma observation mode during analysis. The SPECTROGREEN 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 CMOS detectors, the wavelength range between 165 and 770 nm can be analyzed, allowing complete spectrum capture within 3 s. 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 point in time. 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.

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 SeaSpray nebulizer and a cyclonic spray chamber were used. The ICP operating conditions are given in Table 2.

Table 2: Typical ICP operating conditions

Plasma power	1150 W
Observation mode	Dual Side-on
Coolant flow	12.0 L/min
Auxiliary flow	0.80 L/min
Nebulizer flow	0.90 L/min
Plasma torch	Quartz, fixed 1.8 mm Injector tube
Spray chamber	Cyclonic
Nebulizer	SeaSpray
Sample aspiration rate	2 mL/min
Replicate read time	39 s per replicate

Table 3: Calibration Standards

Element	Calibration range
Ag	0 – 0.5 mg/L
As, B, Ba, Be, Cd, Co, Cr, Hg, Li, Mn, Mo, Ni, Pb, Sb, Se, Si, Sn, Sr, Tl, V	0 – 2 mg/L
Cu	0 – 5 mg/L
Al, K, P, Zn	0 – 10 mg/L
Fe	0 – 25 mg/l
Mg	0 – 50 mg/L
Ca, Na	0 – 200 mg/L

Calibration Standards

For calibration, a commercially available multi-element standard [3] and single element standards [4] were used and acidified with 1% HNO_3 (v/v) [5]. The calibration range is given in table 3.

Results and Discussion

Table 4 shows the selected wavelengths and the limits of detection (LOD) achieved. The LODs were calculated according to the equation [6]:

LOD = 3 RSDb c/100*SBR

Where:

RSD – relative standard deviation of 10 replicates of the blank [%]

c – concentration of the standard

SBR – signal to background ratio

Table 4: Typical Limits of Detection (LOD) for the selected lines with Dual Side-On plasma observation

Element	λ [nm]	LOD (3σ) [µg/L]	Element	λ [nm]	LOD (3σ) [µg/L]
Ag	328.068	0.9	Mn	257.611	0.06
Al	167.078	0.1	Mo	202.095	0.3
As	189.042	1.3	Na	589.592	5
As	193.759	2.1	Ni	221.648	0.4
B	249.773	0.4	Ni	231.604	0.5
Ba	455.404	0.1	P	177.495	1.0
Be	313.042	0.04	P	178.287	1.5
Ca	315.887	2.3	Pb	220.353	2.2
Cd	214.438	0.1	Sb	206.833	2.0
Cd	226.502	0.18	Se	196.090	3.2
Co	228.616	0.3	Si	251.612	0.9
Cr	267.716	0.5	Sn	189.991	0.7
Cu	324.754	0.8	Sr	407.771	0.03
Fe	259.941	0.3	Tl	190.864	1.9
Hg	184.950	0.6	Ti	334.941	0.3
Hg	194.227	0.7	V	311.071	0.7
K	766.491	17	Zn	213.856	0.1
Li	670.780	0.8	Zr	343.823	0.7
Mg	285.213	0.5			

Instrument Performance

Instrument performance must be monitored according to IS 3025 [2] by regularly analyzing calibration check and instrument performance check solutions. Table 5 displays the recovery of a multi-element standard [3].

Table 5: Recovery of an instrument performance check (IPC) solution

Element	Measured [mg/L]	Expected [mg/L]	Recovery [%]	Element	Measured [mg/L]	Expected [mg/L]	Recovery [%]
Ag	0.52	0.5	104	**Mg**	2.03	2	102
Al	2.06	2	103	**Mn**	2.0	2	100
As	1.93	2	97	**Mo**	2.05	2	103
B	1.93	2	97	**Na**	1.96	2	98
Ba	2.03	2	102	**Ni**	2.04	2	102
Be	1.92	2	96	**P**	10.0	10	100
Ca	1.95	2	98	**Pb**	2.04	2	102
Cd	1.95	2	98	**Sb**	1.95	2	98
Co	2.00	2	100	**Se**	1.98	2	99
Cr	2.06	2	103	**Si**	2	2	100
Cu	2.00	2	100	**Sn**	1.91	2	96
Fe	2.02	2	101	**Sr**	2.02	2	101
Hg	1.94	2	98	**Tl**	2.06	2	103
K	9.85	10	99	**V**	1.92	2	96
Li	1.95	2	98	**Zn**	1.96	2	98

The accuracy and precision of the method were additionally by analyzing a spiked wastewater sample and the reference material ERM-CA713 [7].

Table 6 shows the measured concentrations of the original wastewater sample, the spiked concentrations, which were added to the sample using a multi-element standard [3] and the measured concentrations of the spiked sample. Excellent spike recoveries were found for all analyzed elements.

The recovery of the certified concentrations of the reference material ERM-CA713 are presented in table 7, along with the relative standard deviation (RSD) of the replicate measurements. High precision could be achieved for all analyzed elements with RSDs below 0.5% and the reference material was analyzed in perfect agreement with the certified values.

Table 6: Recovery of a spiked wastewater sample

Element	Sample Concentrations [mg/L]	Spiked Concentrations [mg/L]]	Measured Concentrations [mg/L]	Spike Recovery [%]
Ag 328.068	< LOD	0.025	0.025	98.0
Al 167.078	0.142	0.100	0.237	95.0
As 189.042	< LOD	0.050	0.050	100.4
B 249.773	0.06	0.100	0.159	99.0
Ba 455.404	0.178	0.100	0.275	97.0
Be 313.042	< LOD	0.100	0.100	99.7
Ca 317.933	41.9	1.10	42.95	95.5
Cd 214.438	< LOD	0.005	0.005	100.4
Co 228.616	< LOD	0.100	0.099	98.5
Cr 267.716	0.0004	0.025	0.024	96.0
Cu 324.754	0.994	0.050	0.145	91.2
Fe 238.204	0.102	0.100	0.196	94.0
Hg 184.950	< LOD	0.100	0.098	98.3
K 766.491	22.8	1.50	24.21	94.0
Li 670.780	< LOD	0.100	0.106	98.9
Mg 279.079	2.75	0.100	2.840	90.0
Mn 257.611	< LOD	0.100	0.100	98.8
Mo 202.095	< LOD	0.100	0.099	97.4
Na 589.592	184.6	5.0	189.5	98.0
Ni 231.604	0.003	0.050	0.048	90.0
P 177.495	0.675	0.500	1.160	97.0
Pb 220.353	0.001	0.020	0.020	91.9
Sb 206.833	< LOD	0.100	0.102	101.8
Se 196.090	< LOD	0.100	0.104	103.3
Sn 189.991	< LOD	0.100	0.091	91.1
Sr 407.771	0.146	0.100	0.245	99.0
Tl 190.864	< LOD	0.050	0.046	92.8
V 311.071	< LOD	0.100	0.101	99.0
Zn 213.856	0.0291	0.100	0.133	103.9

Table 7: Recovery of the reference material ERM-CA713

Element	Certified Value [µg/L]	Measured Concentrations [µg/L]	Recovery [%]	RSD [%]
As 189.042	10.8 ± 0.3	11.0	101.7	0.415
Cd 214.438	5.09 ± 0.20	5.1	100.2	0.316
Cr 267.716	20.9 ± 1.3	22.2	106.3	0.063
Cu 324.754	101 ± 7	102	101.3	0.200
Fe 259.941	445 ±27	442	99.4	0.321
Hg 184.950	1.84 ±0.11	1.85	100.5	0.451
Mn 257.611	95 ± 4	92.9	97.8	0.282
Ni 231.604	50.3 ± 1.4	50.8	101.1	0.284
Pb 220.353	49.7 ± 1.7	50.4	101.4	0.167
Se 196.090	4.9 ± 1.1	5.1	103.3	0.430
Zn 213.856*	78	81.0	103.8	0.066

** non-certified concentration, for information only*

Conclusion

The SPECTROGREEN with Dual Side-on plasma observation offers a simple, fast, accurate, precise and cost-efficient method for the analysis of wastewater. Low limits of detection could be achieved across elements. Excellent precision and recoveries were determined for a spiked wastewater sample and for the reference material ERM-CA713. In conjunction with an autosampler, the SPECTROGREEN can be fully automated. Independent from the number of lines and elements, an analysis (including three replicates and pre-flush) can be performed in less than four minutes.

References

[1] Pollution control Law Series 7th edition, 2021 – The environment (protection) rules, 1986

[2] IS 3025 – Methods of sampling and test (physical and chemical) for water and wastewater – determination of 33 elements by inductively coupled plasma atomic emission spectroscopy

[3] Bernd Kraft GmbH Duisburg, Germany

[4] Inorganic Ventures, Christiansburg, Virginia

[5] HNO3 Suprapur®, 65%, Merck, Darmstadt, Germany

[6] P. W. J. M. Boumans, Spectrochim. Acta 46B, 431 (1991)

[7] European Commission, Joint Research Centre (JRC), Directorate F - Health, Consumers and Reference Materials, Geel, Belgium

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