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SPECTRO**GREEN**

Analysis of Wastewater by ICP-OES With Dual Side-on Plasma Observation With a Focus on the European Union

Introduction

Environmental protection is essential to ensure the future availability of resources like water and soil. Especially in the water sector, the treatment and reuse of wastewater are important building blocks to ensure a working cycle. The handling, discharge, treatment, and reuse of wastewater produced by industrial and urban sources are regulated in legislation. This report describes the principal methodology for the analysis of wastewater samples in Europe according to DIN EN ISO 11885.

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 from country to country. In Europe, the corresponding regulations are the Council Directives 91/271/EC and 2010/75/EC [1],[2]. Member states of the European union must incorporate these regulations to their individual legislation but can also tighten the rules according to the present infrastructure.

In France, the European directive was implemented by the Environmental Code [3] and different ministerial orders, amongst others the order of 24th of August 2017 on the discharge of hazardous

substances to water [4], stating limit values for the discharge to surface water for different industries. Also, the conditions under which a laboratory may be approved to carry out analyses for monitoring purposes is regulated by law [5]. One of the conditions is the accreditation with the national accreditation body COFRAC or any other accreditation body within the European Cooperation for Accreditation.

Table 1: Lowest applicable limit values for the discharge of wastewater to water bodies for France, Italy and Germany

Element	Country		
	FRA[4] [mg/L]	GER[6] [mg/L]	ITA[7] [mg/L]
Ag	-	0.1	-
Al	2	2	1
As	0.025	0.05	0.5
Au	-	0.5	-
B	3	3	2
Ba	3	2	20
Cd	0.025	0.005	0.02
Ce	-	0.5	-
Co	-	0.1	-
Cr	0.1	0.025	2
Cu	0.05	0.05	0.1
Fe	2	3	2
Ge	-	0.5	-
Hf	-	0.5	-
Hg	0.02	0.0005	0.005
Mn	1	-	2
Mo	-	0.5	-
Na	-	0.05	-

Element	Country		
	FRA[4] [mg/L]	GER[6] [mg/L]	ITA[7] [mg/L]
Ni	0.05	1	2
P	10	1	1
Pb	0.05	0.02	0.2
Pd	-	0.5	-
Pr	-	0.5	-
Pt	-	0.5	-
Ru	-	0.5	-
Sb	0.5	0.3	-
Se	-	1	0.03
Sn	2	0.2	10
Sr	-	1	-
Ti	-	0.05	-
Tl	-	4	-
V	-	2	-
W	0.25	0.2	0.5
Zn	-	0.5	-
Zr	-	0.5	-

In Germany, the national directive is the wastewater directive [6] which lists specific values for the effluent limit values for the direct discharge of wastewater to water bodies. The monitoring in Germany is mostly organized by federal authorities which issue licenses for the discharge of water and monitor the compliance with these licenses. The wastewater directive lists specific limiting values for different industries to be monitored.

In Italy, the wastewater regulation through the ministerial decree N° 152/2006 [7] differentiates between urban and industrial wastewater and provides limiting values for discharging to surface water, sewer systems and soil.

Table 1 gives on overview of the lowest applicable limit values from the different European legislations across all industries.

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.

This report describes the principal methodology for the analysis of wastewater according to EN ISO 11885. 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 analyzes of a certified reference material.

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 later 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	13.0 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

Calibration Standards

For calibration, commercially available multi-element standards [9],[10] and single element standards [10] were used and acidified with 1% HNO_3 (v/v) [11]. The calibration range is given in table 3.

Table 3: Calibration Standards

Element	Calibration range
As, Au, B, Ba, Be, Cd, Ce, Co, Cr, Ge, Hf, Hg, Li, Mn, Mo, Ni, Pb, Pd, Pr, Pt, Ru, Sb, Se, Si, Sn, Sr, Ti, Tl, V, W, Zr	0 – 2 mg/L
Ag	0 – 0.5 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
Zn	0

Results and Discussion

Table 4 shows the selected wavelengths and the limits of detection (LOD) achieved. The LODs were calculated according to the equation [1]:

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 using 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
Au	242.795	0.9	Ni	231.604	0.5
B	249.773	0.4	P	177.495	1.0
Ba	455.404	0.1	P	178.287	1.5
Be	313.042	0.04	Pb	220.353	2.2
Ca	315.887	2.3	Pd	340.458	4.4
Cd	214.438	0.1	Pr	411.846	5.6
Cd	226.502	0.18	Pt	177.708	1.2
Ce	413.765	6.7	Ru	240.272	1.6
Co	228.616	0.3	Sb	206.833	2.0
Cr	267.716	0.5	Se	196.090	3.2
Cu	324.754	0.8	Si	251.612	0.9
Fe	259.941	0.3	Sn	189.991	0.7
Ge	164.919	0.5	Sr	407.771	0.03
Hf	264.141	1.0	Ti	334.941	0.3
Hg	184.950	0.6	Tl	190.864	1.9
Hg	194.227	0.7	V	311.071	0.7
K	766.491	17	W	207.911	1.1
Li	670.780	0.8	Zn	213.856	0.1
Mg	285.213	0.5	Zr	343.823	0.7

Instrument Performance

Instrument performance must be monitored according to ISO 11885 [8] by regularly analyzing calibration check and instrument performance check solutions. Table 5 displays the recovery of a multi-element standard to check the instrument performance [9].

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 moreover investigated by analyzing a spiked wastewater sample and the reference material ERM-CA713 [13].

Table 6 shows the measured concentrations of the original wastewater sample, the spiked concentrations, which were added to the sample using multi-element standards [9],[10] and single element standards [10], 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
Au 242.795	< LOD	0.100	0.952	95.2
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
Ce 413.765	< LOD	0.100	0.095	95.0
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
Ge 164.919	< LOD	0.100	0.100	99.7
Hf 264.141	< LOD	0.100	0.097	96.6
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
Pd 340.458	< LOD	0.100	0.094	93.5
Pr 411.846	< LOD	0.100	0.094	93.9
Pt 177.708	< LOD	0.100	0.096	96.4
Ru 240.272	< LOD	0.100	0.095	94.6
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
Ti 334.941	< LOD	0.100	0.096	95.7
Tl 190.864	< LOD	0.050	0.046	92.8
V 311.071	< LOD	0.100	0.101	99.0
W 207.911	< LOD	0.100	0.098	98.2
Zn 213.856	0.0291	0.100	0.133	103.9
Zr 343.823	< LOD	0.100	0.095	94.8

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 Interface plasma observation offers a simple, fast, accurate, precise and cost-efficient method for the analysis of wastewater according to DIN EN ISO 11885. 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] Directive 91/271/EEC of 21 May 1991 concerning urban waste-water treatment and the amending directive 98/15/EEC

[2] Directive 2010/75/EC of 24 November 2010 on industrial emissions (integrated pollution and prevention control)

[3] Code de l'environnement – Book II and Book V, Title I ff.

[4] Journal officiel « Lois et Décrets » de la République française Nr. 234 of 6 October 2017, Text Nr.3; Arrêté du 24 août 2017 modifiant dans une série d'arrêtés ministériels les dispositions relatives aux rejets de substances dangereuses dans l'eau en provenance des installations classées pour la protection de l'environnement

[5] Journal officiel « Lois et Décrets » de la République française Nr. 260 of 9 November 2011, Text Nr.6; Arrêté du 27 octobre 2011 portant modalités d'agrément des laboratoires effectuant des analyses dans le domaine de l'eau et des milieux aquatiques au titre du code de l'environnement

[6] Wastewater Ordinance in the version published on June 17, 2004 (BGBl. I p. 1108, 2625), as most recently amended by Article 1 of the Ordinance of January 20, 2022 (BGBl. I p. 87).

[7] Legislative Decree 152/2006 "Norms Concerning the Environment"

[8] EN ISO 11885 – Water quality – determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)

[9] Bernd Kraft GmbH Duisburg, Germany

[10] Inorganic Ventures, Christiansburg, Virginia

[11] HNO_3 Suprapur®, 65%, Merck, Darmstadt, Germany

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

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

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