Challenge
The precise determination of trace elements while analyzing bulk elements.

Solution
The PlasmaQuant 9200 series with its DualView Plus option provides an extended linear dynamic range from sub-ppb level to percentage range.

Intended audience
Environmental scientists, analytical chemists, wastewater treatment professionals, regulators, and technical decision-makers involved in sewage sludge management, nutrient recovery, and elemental analysis.

Determination of phosphorus and other critical elements in sewage sludge

Introduction

Phosphorus and phosphorus compounds are essential for all living things. Without phosphorus, organisms cannot be built up and function. In humans and animals, for example, this applies to DNA but also to bones and teeth. Plants stunt if they cannot absorb enough phosphates. Phosphorus is irreplaceable for the production of fertilizers and helps to secure food supplies worldwide.

Phosphorus was classified as a critical raw material by the European Commission in the "List of Critical Raw Materials for the European Union"[1]. In 2012, the German government also emphasized the need for sustainable management of this material flow that is relevant to resource conservation. In addition, the German sewage sludge ordinance (GSSO, AbfKlärV)[2] includes the obligation to recover phosphorus from 2029. To meet GSSO requirements, phosphorus must be recovered if a sewage sludge contains 20 grams or more per kilogram of dry matter.

Sewage sludges originate from municipal wastewater treatment plants (WWTP), in which wastewater from private households and comparable facilities in particular are treated. They are considered as waste, but because of their relatively high content of valuable nutrients (e.g., Ca, K, N) they have considerable resource potential. Depending on its levels of pollutants, sewage sludge can be used as fertilizer on agricultural soils or in landscaping measures.

The European Union has passed several directives to be adopted by the member states to regulate the application of sewage sludge to land (e.g., „Sewage Sludge Directive 86/278/EEC"[3]). They prohibit the use of sludge from treatment plants unless the specified requirements (see Table 1) are fulfilled. The GSSO regulates in particular the pollutant requirements for the utilization of sewage sludge for fertilizer purposes on agriculturally used soils. In order to ensure the unrestricted usability of the soils intended for sewage sludge application, the ordinance provides for regular pollutant tests of these soils and standardizes pollutant limit values (see Table 1) in this respect, which may not be exceeded. As an overall consequence, levels of nutrients (e.g., P) and pollutants (e.g., Cd, Hg, Pb) in sludges from urban and industrial wastewater treatment need to be controlled on a regular base.

Due to its multi-element determination capability, high dynamic linear range, and sensitivity, inductively coupled plasma-optical emission spectrometry (ICP-OES) is widely used for the analysis of soil and sludge. The application is described in standard procedures such as EPA methods 3050B and 6010C, DIN EN 16174:2012-11, and the ISO standard ISO 11885:2007.

In this study, a high-resolution ICP-OES, the PlasmaQuant 9200 Elite, was used for the analysis of major, minor, and trace elements in different sludge samples. The exceptionally high resolution in combination with the DualView Plus option allows for interference-free analysis of all investigated analytes ranging from sub-ppb to percentage range. The sample preparation was performed according to EN 16174:2012. The accuracy of the method was investigated using the standard reference material NIST 2781 and a sewage sludge sample, which was part of a national round robin test. Additionally, analyte recovery and long-term stability tests were performed to verify the suitability of the analytical method and instrument performance.

Table 1: Limits of European and German sewage sludge directives

Element	86/278/EEC [mg/kg]	German Sewage Sludge Ordinance [mg/kg]
As	-	40
Cd	20-40	1.5
Cr	-	-*
Cu	1000-1750	900
Hg	16-25	1.0
Ni	300-400	80
Pb	750-1200	150
Tl	-	1.0
Zn	2500-4000	4000

* Labeling is required for concentrations exceeding 300 mg/kg of dry matter in accordance with the German Fertilizer Ordinance

Materials and methods

Sample preparation

All laboratory equipment was washed with deionized (DI) water from a PURELAB system (18.2 MΩ-cm, ELGA LabWater, High Wycombe, England). Chemicals were of analytical reagent grade. All multi-element stock solutions were made up using single element and multi-element standard solutions (Merck, Sigma-Aldrich, CPAchem, Inorganic Ventures). The working standards were prepared by serial volume/volume dilution in polypropylene tubes of the stock solutions using 1% (v/v) HNO_3. Yttrium (Y) was added on-line to all blanks, standards, and samples as internal standard. The artificial sewage sludge solution for determining the long-term stability was prepared from single and multi-element standard solutions and contained the following analyte concentrations: 0.1 mg/L (Hg , Tl), 0.5 mg/L (Ag, As, Cd, Cr, Cu, Mn, Ni, Pb, Se, Zn), 50 mg/L (Mg), 150 mg/L (Al, Fe, P, S), 300 mg/L (Ca).
The sample list consisted of one standard reference material (SRM), Domestic Sludge NIST 2781, and a sewage sludge sample, which was part of a national round robin test (RRT) (“Phosphorus determination in sewage sludge” (2021) by the Federal Institute for Materials Research and Testing (Bundesanstalt für Materialforschung und -prüfung, BAM).

The sample preparation was performed in accordance with EN 16174:2012 (Method B), which requires a microwave-assisted acid digestion step. Before taking each triplicate to be analyzed, the contents of the sample bottles were homogenized by shaking the bottle upside down. Afterwards, approximately 0.5 g of homogenized sample were accurately weighed (0.0001 g) and added to a digestion vessel (DAP60). Successively, 0.5 mL of DI water, 6 (± 0.1) mL HCl, and 2 (± 0.1) mL HNO_3 were added. The mixture was swirled carefully and left standing for at least 15 minutes before the vessel was closed.
Subsequent heating (175 °C, 10 min) was performed in a speedwave XPERT microwave digestion system. Afterwards the vessels were allowed to cool to room temperature (RT) to avoid foaming and splashing. The solutions were transferred to a graduated polypropylene tube, diluted to 50 mL with DI water, and centrifuged (1125xg, 10 min). The supernatants were immediately submitted to the analysis. The analysis results were not related to the dry mass, but to the initial weight of the sample.

Calibration

Calibration levels for each element were chosen based on the expected concentration ranges. At least three calibration points were used for each element, as described in Table 2. Selected calibration curves are shown in Figure 1.

Table 2: Concentration of calibration standards

Element	Unit	Cal. 0	Std. 1	Std. 2	Std. 3	Std. 4	Std. 5	Std. 6	Std. 7
As, Hg , Tl	mg/L	0	0.01	0.1	-	-	-	-	-
Cd	mg/L	0	0.01	0.1	1.0	-	-	-	-
Ag, Ni, Se	mg/L	0	-	0.1	1.0	-	-	-	-
Cr, Pb	mg/L	0	-	0.1	1	10	-	-	-
Cu	mg/L	0	-	-	1	10	-	-	-
Mg	mg/L	0	-	-	-	-	10	50	200
Ca	mg/L	0	-	-	-	-	40	200	1000
K	mg/L	0	-	-	-	-	4	20	100
Fe, P, S	mg/L	0	-	-	-	-	20	100	500
Mn, Na, Zn	mg/L	0	-	-	-	-	1	5	25

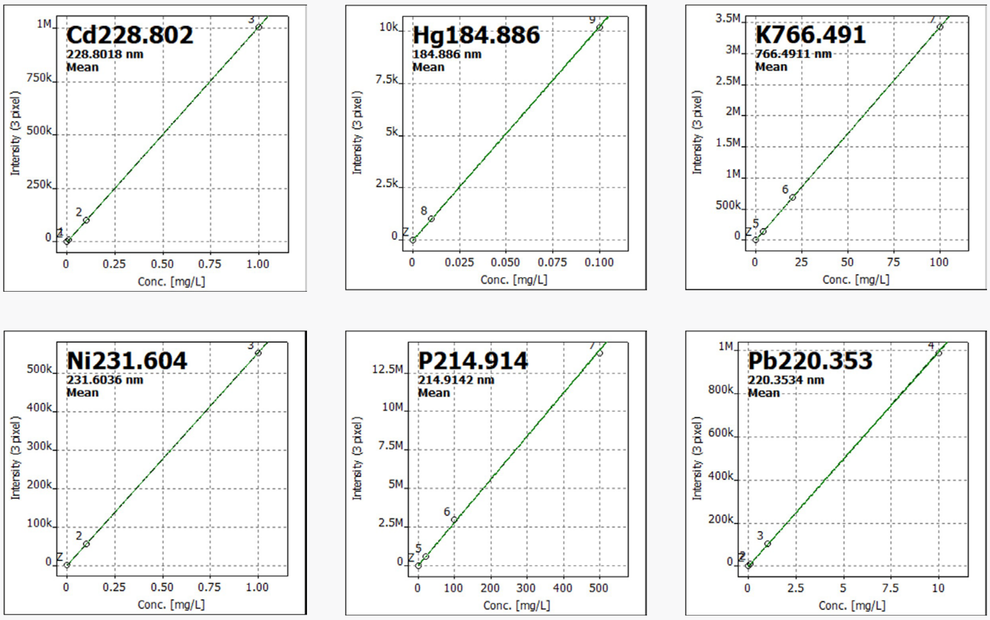


Figure 1: Selected calibration functions

Instrument settings

The analysis was performed on a PlasmaQuant 9200 Elite ICP-OES. The sample introduction components as well as the instrumental settings were selected to achieve a high level of sensitivity for trace elements in possibly high-salt containing matrices. In conjunction with this instrument, a Teledyne CETAC ASX-560 Autosampler was used. An internal standard mixing kit was also used to introduce a 10 mg/L yttrium internal standard solution on-line, resulting in approximately 1mg/L final concentration. A summary of individual settings and components is given in Table 3.

Table 3: Instrument settings

Parameter	Setting
Plasma power	1300 W
Plasma gas flow	8,5 L/min
Auxiliary gas flow	0.6 L/min
Nebulizer gas flow	0.6 L/min
Nebulizer	Concentric, SeaSpray, 2.0 mL/min, Borosilicate
Spray chamber	Cyclonic spray chamber, 50 mL, Borosilicate
Outer tube / Inner tube	Quartz / Quartz
Injector	Quartz, ID: 2 mm
Sample tubing	PVC (red/red)
Internal standard tubing	PVC (green/orange)
Pump rate	1.00 mL/min
Measuring delay / Rinse time	45 s / 15 s
Torch position	-1 mm

Method and evaluation parameters

Method parameters are shown in Table 4.

Table 4: Method parameters

Element	Line [nm]	Plasma View	Integration	Read Time [s]	Evaluation		
					Pixel	Baseline Fit	Poly. Deg.
Y	371.030	axial/radial	Peak	1/1	3	ABC[1]	auto
Ag	328.068	axial	Peak	1	3	ABC	auto
As	188.979	axial	Peak	10	3	ABC	auto
Ca	315.887	att. radial[2]	Peak	1	3	ABC	auto
Cd	228.802	axial	Peak	3	3	ABC	auto
Cr	267.716	axial	Peak	3	3	ABC	auto
Cu	327.396	axial	Peak	1	3	ABC	auto
Fe	259.940	att. radial	Peak	1	3	ABC	auto
Hg	184.886	axial	Peak	10	3	ABC	auto
K	766.491	radial	Peak	1	3	ABC	auto
Mg	285.213	radial	Peak	1	3	ABC	auto
Mn	257.610	att. radial	Peak	1	3	ABC	auto
Na	589.592	radial	Peak	1	3	ABC	auto

Table 4 (continued): Method parameters

Element	Line [nm]	Plasma view	Integration	Read time [s]	Evaluation		
					Pixel	Baseline fit	Poly. Deg.
Ni	231.604	axial	Peak	3	3	ABC	auto
P	214.914	axial	Peak	1	3	ABC	auto
Pb	220.353	axial	Peak	3	3	ABC	auto
S	182.565	axial	Peak	1	3	ABC	auto
Se	196.028	axial	Peak	3	3	ABC	auto
Tl	190.796	axial	Peak	10	3	ABC	auto
Zn	206.200	axial	Peak	1	3	ABC	auto

[1] **A**utomated **B**aseline **C**orrection

[2] Attenuated radial observational view extends linear dynamic range into the percentage range

Results and discussion

Analyte recovery and accuracy

The accuracy of the developed method was investigated by analyzing the standard reference material NIST 2781. Table 5 shows certified values and recovery rates for the tested reference material. All recoveries were within ± 9% of the certified value.

Table 5: Comparison of the reference values with the determined mass fractions for NIST SRM 2781 (Domestic sludge)

Element	NIST SRM 2781 (Domestic Sludge)					
	Reference value [mg/kg]		Uncertainty [mg/kg]	Measured mass fraction [mg/kg]	RSD[1] [%]	Recovery [%]
Ag	86.3	±	1.7	83.9	1.5	97.2
As	7.81	±	0.67	7.98	0.6	102.2
Ca	36 440	±	1 830	36 190	0.8	99.3
Cd	11	±	2	10.8	0.9	98.2
Cr	143	±	14	134	1.5	93.7
Cu	601	±	16	576	0.9	95.8
Fe	24 300	±	2 100	24 973	1.8	102.8
Hg	3.68	±	0.14	3.46	1.4	94.0
Mg	4 850	±	290	4 780	2.0	98.6
Mn	745	±	33	751	0.6	100.8
Ni	72.3	±	6.3	67.1	0.3	92.8
P	24 300	±	400	22 580	0.4	92.9
Pb	183	±	15	167	0.3	91.3
Se	16.0	±	1.5	15.1	0.6	94.4
Tl[2]	-		-	0.787	2.0	-
Zn	1 120	±	34	1 140	1.6	101.8

[1] Relative standard deviation based on the measurement of three independent replicates

[2] Not certified

Additionally, spiking experiments were carried out to illustrate the applicability of the analytical method. ISO 11885 requires that the recovery of the spiked analyte concentration must be within ± 20% of the concentration equivalent added to the sample for matrix effects to be considered negligible. To evaluate that, the RRT sample was spiked after the digestion step with the desired elements. Table 6 shows the analyte recoveries which all were within a ± 14% range illustrating the applicability of the analytical method.

Table 6: Quantitative results and analyte spike recoveries for different sewage sludge samples

Element	**Sewage Sludge**			**SRM NIST 2781**		
	Measured conc. [mg/L]	**Spiked conc. [mg/L]**	**Recovery [%]**	**Measured conc. [mg/L]**	**Spiked conc. [mg/L]**	**Recovery [%]**
Ag	0.017	0.5	93	0.858	0.5	97
As	0.050	0.5	93	0.075	0.05	91
Ca	869	200	97	366	200	103
Cd	0.010	0.5	98	0.104	0.5	89
Cr	0.309	0.5	90	1.33	0.5	96
Cu	4.88	0.5	96	5.84	0.5	97
Fe	312	100	99	257	100	100
Hg	0.003	0.05	111	0.035	0.05	111
K	25.9	20	103	28.7	20	102
Mg	89.5	50	101	49.3	50	105
Mn	3.94	5	100	7.39	5	107
Na	5.69	5	103	9.93	5	103
Ni	0.248	0.5	86	0.600	0.5	92
P	251	100	99	221	100	100
Pb	0.396	0.5	87	1.67	0.5	95
S	106	100	108	137	100	102
Se	0.031	0.5	93	0.151	0.5	88
Tl	0.015	0.05	94	0.008	0.05	92
Zn	7.70	5	106	10.8	5	104

Long-term stability

Long term stability was investigated by monitoring the results of an artificial sewage sludge sample for ten hours resulting in recoveries in the range of ± 7% (see Figure 2). Relative standard deviations below 1.65% (for analytes) and 1.05% (for internal standards, Figure 3) indicate a highly stable performance of the instrumentation throughout the 10 hours of measurement.

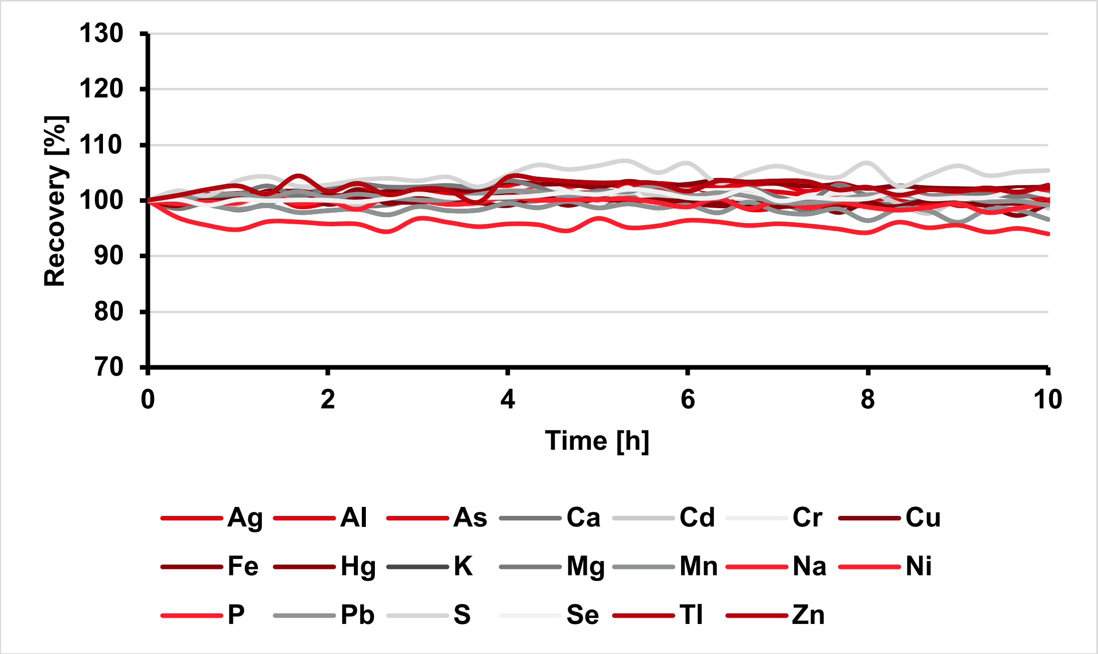


Figure 2: Percentage recoveries of the analytes throughout a 10-hour sequence. RSD values were below 1.65% for all elements.

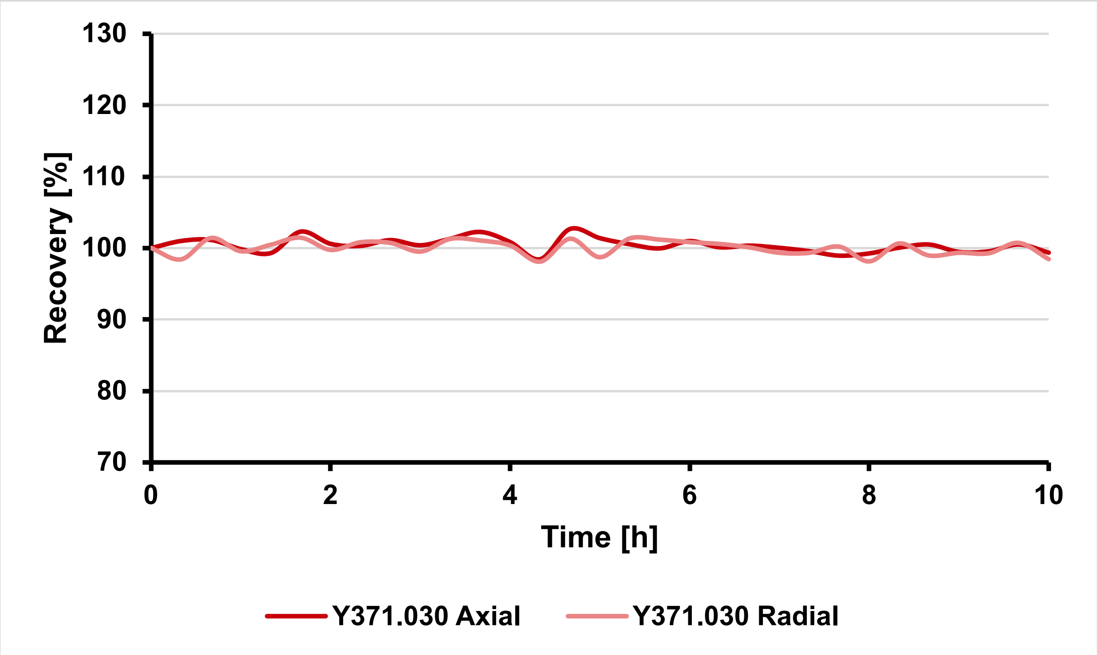


Figure 3: Percentage recoveries of the internal standard (yttrium) throughout a 10-hour sequence. RSD values were below 1.05% for both observational views.

External quality control – Round robin test (RRT)

The overall aim of the RRT organizers was to evaluate the equivalence of different methods for phosphorus determination permissible according to German "sewage sludge ordinance" (GSSO, AbfKlärV). To demonstrate the PlasmaQuant 9200 Elite's performance and the applicability of the analytical method for phosphorus analysis, the application lab of Analytik Jena's headquarters took part in this test. The organizer of the RRT specified the approved analytical methods and the corresponding regulations for sample preparation. Nineteen laboratories submitted results obtained by ICP-OES measurements and sample preparation using a closed microwave digestion system. The results of the RRT are displayed in Table 7.

Table 7: Quantitative results for round robin test sample

Element	Sewage Sludge Sample				
	RRT Mean [g/kg]	CVr* [%]	Measured [g/kg]	CVr,L* [%]	z-score*
P	26.01	1.5	25.62	1.1	-0.3

* Calculation was performed in accordance to ISO 5725-2

Sensitivity and spectral resolution

According to ISO 11885, the limits of detection (LODs) are calculated following the equation 1:

$$\text{LOD} = 3 \times s_0$$

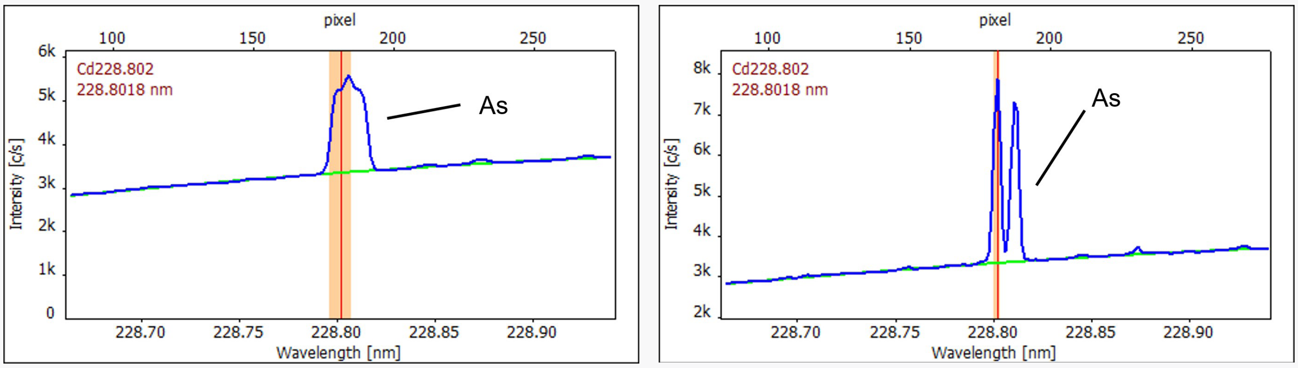
where s_0 is the standard deviation of 10 replicates of the blank. The instrumental and method detection limits, which consider the dilution factor of the digestion step, are shown in Table 8.

Table 8: Instrumental detection limits (IDLs) and method detection limits (MDLs) for analytical lines utilized

Element	Line [nm]	Plasma View	IDL [µg/L]	MDL [mg/kg]
Ag	328.068	axial	0.21	0.02
As	188.979	axial	0.49	0.05
Ca	315.887	att. radial[1]	3.29	0.33
Cd	228.802	axial	0.10	0.01
Cr	267.716	axial	0.20	0.02
Cu	327.396	axial	0.24	0.02
Fe	259.940	att. radial[1]	1.18	0.12
Hg	184.886	axial	0.41	0.04
K	766.491	radial	22.7	2.27
Mg	285.213	radial	0.40	0.04
Mn	257.610	att. radial[1]	0.20	0.02
Na	589.592	radial	4.72	0.47
Ni	231.604	axial	0.18	0.02
P	214.914	axial	3.69	0.37
Pb	220.353	axial	0.59	0.06
S	182.565	axial	9.75	0.97
Se	196.028	axial	1.61	0.16
Tl	190.796	axial	0.42	0.04
Zn	206.200	axial	0.17	0.02

[1] Attenuated radial observational view extends linear dynamic range into the percentage range

Interference-free detection of trace signals is a prerequisite for reliable and accurate monitoring of sewage sludge. Trace signals can easily be interfered by matrix components. In this regard, high spectral resolution provides well separated peaks of high definition and therefore circumvents the risk of spectral interferences in sewage sludge analysis. Figure 4 displays a comparison of spectra on the example of cadmium (Cd). Since sewage sludge often contains high concentrations of iron (Fe), the sensitive quantification of Cd with ICP-OES can be very challenging. The two most sensitive lines of Cd at 226.502 and 214.441 nm are prone to Fe interferences. Using an ICP-OES with medium to low spectral resolution can easily result in overestimation of Cd in such Fe-rich samples. Therefore, the user is forced to switch to Cd at 228.802 nm to enable at least a less sensitive analysis. Since sewage sludge frequently contains relatively high amounts of arsenic, this analytical line is only usable on HR ICP-OES. The spectra of an instrument with average spectral resolution (left) reveals an insufficient separation of the Cd line at 228.802 nm and the surrounding matrix peaks, which makes it impossible to use this line for reliable quantification. In this case, using an alternative, less sensitive line is inevitable with the consequences of an increased MDL as well as inferior precision and accuracy at the limit concentration. In contrast to the average resolution, the high spectral resolution of the PlasmaQuant 9200 Elite provides a baseline-separated signal for Cd at 228.802 nm. Thus, the sensitive quantification of Cd remains accessible resulting in a lowest possible MDL and highest reliability of the obtained results. The high spectral definition also contributes to an improved sensitivity since it results in larger peak heights and increased readings for a basic three-pixel peak evaluation as commonly applied in ICP-OES.


Cd228.802 (PQ 9200, 6 pm @ 200 nm)

Cd228.802 (PQ 9200 Elite, 2 pm @ 200 nm)

Figure 4: Comparison of PlasmaQuant 9200 (6 pm @ 200 nm) and PlasmaQuant 9200 Elite (2 pm @ 200 nm) illustrating the application advantage of high-resolution spectra (red: center wavelength of Cd, blue: Cd and As at maximum legal limits, green: baseline correction (ABC)).

Conclusion

The presented method describes the capabilities of the PlasmaQuant 9200 series (standard configuration) for the analysis of sewage sludge samples. The method validation was performed by analyzing a certified reference material and several spiked sludge samples, as well as long-term stability analysis demonstrating the suitability of the PlasmaQuant 9200 Elite ICP-OES system for the elemental analysis of sewage sludge matrices.

The major challenge of this application includes analyzing elements over a large concentration range (low µg/L to high mg/L) in a single run. Trace elements (e.g., Cd, Hg, Tl) are to be analyzed together with nutrients (e.g., Ca, K, Mg, P), which is successfully demonstrated by the DualView Plus feature of the PlasmaQuant 9200. Besides the common radial and axial plasma observation modes it offers axial plus and radial plus, which attenuates the signal in the respective observation mode. The described method uses radial and attenuated radial plasma observation to measure high levels of minerals alongside trace levels of toxic elements in a single measurement run. Running several dilutions to cover the entire concentration range is therefore avoided.

It could be demonstrated that the requirements in terms of sensitivity, stability, and accuracy to perform the analysis of sludge samples can be met with the here proposed setup. The use of the PlasmaQuant 9200 series allows laboratories to perform the entire elemental screening on one instrument. Both, toxic elements and future critical nutrients, such as phosphorus can be analyzed in parallel side by side without compromising precision.

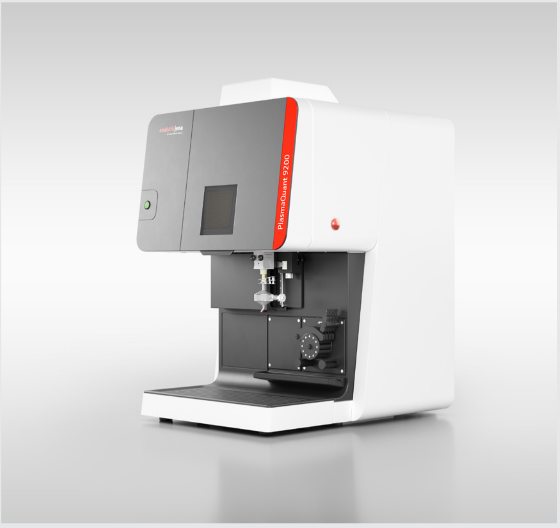


Figure 5: PlasmaQuant 9200 series

Recommended device configuration

Table 9: Overview of devices, accessories, and consumables

Article	Article number	Description
PlasmaQuant 9200 Elite	818-09201-2	High resolution ICP-OES
STANDARD KIT for PlasmaQuant 9x00 series	810-88006-0	Sample introduction kit for aqueous samples
Concentric nebulizer 2mL/min Borosilicate glass, for high salt content	418-13-410-609	Nebulizer for improved robustness and stability
Kit internal Std addition for STANDARD KIT, ORGANIC KIT, SALT KIT	418-13-410-593	Kit for the online addition of an internal standard to the sample
Teledyne Cetac ASX-560	810-88015-0	Autosampler with integrated rinse function

References

[1] Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions, Brussels, 2020

[2] Verordnung über die Verwertung von Klärschlamm, Klärschlammgemisch und Klärschlammkompost (Klärschlammverordnung - AbfKlärV), Revision 2017.

[3] 86/278/EEC Council Directive on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture, 1986

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