

Challenge
Sensitive analysis of trace elements and precise determination of mineral levels in drinking water with a standard ICP-OES setup.

Solution
High-resolution ICP-OES with high sensitivity to comply with concentration limits of drinking water regulations without the requirement of further accessories.

Intended audience
Environmental laboratories, municipal water authorities, water treatment facilities.

Monitoring drinking water quality with high-resolution ICP-OES

Introduction

Drinking water is the most basic and yet the most important food for human beings. The World Health Organization (WHO) states that "Access to safe drinking-water is essential to health, a basic human right and a component of effective policy for health protection".[1] In this regard authorities have implemented laws to ensure the quality of drinking water. Prominent examples are the european directives of drinking, natural and mineral water [2, 3] enforced by the European Union or the Safe Drinking Water Act passed by the United States of America.

Here, purity requirements, cleanup and disinfection methods, sampling and measurement intervals and minimum requirements regarding microbiological, chemical and physical indicator parameters are established. The European Drinking Water Directive sets limits for harmful elements such as antimony, arsenic, boron, cadmium, chromium, copper, lead, mercury, nickel and selenium in the low µg/L range whereas indicator elements like aluminum, iron and sodium are accepted in a mg/L range.[2] Elevated concentrations of harmful elements may originate from environmental pollution of sources such as surface fresh waters, ground water, precipitation and seawater and from the different pre-treatment processes that are required to produce drinking water. Corrosion of plumbing material can also be a source of toxic metal contamination that can have adverse effects on human health.

Based on these laws, individual countries and regions derived drinking water standards and regulations which may add parameters due to local peculiarities. For instance, the German drinking water ordinance added uranium with a limit of 10 µg/L as a parameter to be monitored for drinking water quality due to local uranium deposits in geological formations.

Methodologies to assess element concentrations as water purity parameters are described in regulations such as US EPA 200.7 and 200.8 or ISO 11885. Here, optical emission and mass spectrometry with inductively coupled plasma (ICP-OES/ ICP-MS) have become the standard instrumentation to monitor trace elements as well as mineral contents in all sorts of water samples.

Nevertheless, atomic absorption spectrometry (AAS) techniques such as graphite furnace (GF-AAS) or flame instruments (FI-AAS) are still being heavily used in quality

assessment of drinking, surface and waste waters. Fulfilling the analytical task of a highly sensitive analysis of toxic trace elements (As, Cd, Hg, Pb) in the sub-µg/L range alongside a highly precise analysis of mineral contents (Ca, K, Mg, Na) in the mg/L range with one of the above mentioned techniques, demonstrates a challenge for water laboratories. Whereas ICP-MS provides highly accurate trace detection capabilities, it is not well suited to determine mineral contents up to 200 mg/L with high accuracy and precision. Common ICP-OES instrumentation provides far better performance for the assessment of mineral contents but often lacks the sensitivity to reliably detect toxic trace metals.

Within this study, the performance of the PlasmaQuant 9200 Elite ICP-OES featuring high sensitivity and high spectral resolution was evaluated for the analysis of drinking water. The here presented approach describes the analysis of minerals and trace elements in drinking water with a standard ICP-OES setup in contrast to the use of an ultrasonic nebulizer (USN) accessory or a combination of analysis techniques. The suitability of this methodology was validated by investigating several certified reference materials as well as spike recoveries, precision and long-term stability. As acceptance criteria for trace element detectability the German drinking water ordinance was chosen due to its low limits for toxic trace metals including uranium.

Materials and methods

Sample preparation

All laboratory ware was washed with deionized 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 prepared using single element and multi-element standard solutions (Merck, Sigma-Aldrich). The single and multi-element working standards were prepared by serial volume/volume dilution in polypropylene of the stock solutions using a SimPrep system (Cetac, Omaha, NE, USA). All calibration standards (see table 3) and blank solution were acid matched (1% (v/v) HNO_3, 1% (v/v) HCl) with the sample solutions. The tap water sample was collected from a domestic household supply and was acidified directly after collection. NIST certified drinking-water reference material and high purity standard certified reference materials for drinking water were used for validating the developed method.

Calibration

Calibration levels for each element were chosen based on the legal limit values. At least five calibration standards were used for each element as described in table 1.

Table 1: Concentration of calibration standards

Element	Unit	Cal 0	Std. 1	Std. 2	Std. 3	Std. 4	Std. 5	Std. 6	Std. 7	Std. 8	Std. 9	Std. 10	Std. 11	Std. 12
Ag	µg/L	0	0.125	0.25	0.50	1.0	2.5	5.0	10	-	-	-	-	-
Al	µg/L	0	-	-	-	-	2.5	5.0	10	20	50	100	250	500
As	µg/L	0	-	-	-	1.0	2.5	5.0	10	20	50	100	-	-
B	µg/L	0	-	-	-	1.0	2.5	5.0	10	20	50	100	250	500
Ba	mg/L	0	0.050	0.100	0.250	0.500	1.00	2.50	5.00	-	-	-	-	-
Be	µg/L	0	0.125	0.25	0.50	1.0	2.5	5.0	10	20	-	-	-	-
Ca	mg/L	0	0.050	0.100	0.250	0.500	1.00	2.50	5.00	10.0	25.0	100	-	-
Cd	µg/L	0	0.125	0.25	0.50	1.0	2.5	5.0	10	20	-	-	-	-
Co	µg/L	0	-	-	-	1.0	2.5	5.0	10	20	50	-	-	-
Cr	µg/L	0	-	0.25	0.50	1.0	2.5	5.0	10	20	50	-	-	-
Cu	µg/L	0	-	-	0.5	1.0	2.5	5.0	10	20	50	100	250	-
Fe	µg/L	0	-	-	0.5	1.0	2.5	5.0	10	20	50	100	-	-

Element	Unit	Cal 0	Std. 1	Std. 2	Std. 3	Std. 4	Std. 5	Std. 6	Std. 7	Std. 8	Std. 9	Std. 10	Std. 11	Std. 12
Hg	µg/L	0	-	-	0.5	1.0	2.5	5.0	10	-	-	-	-	-
K	mg/L	0	-	0.100	0.250	0.500	1.00	2.50	5.00	-	-	-	-	-
Li	µg/L	0	-	-	0.5	1.0	2.5	5.0	10	20	50	100	-	-
Mg	mg/L	0	0.050	0.100	0.250	0.500	1.00	2.50	5.00	10.0	25.0	100	-	-
Mn	µg/L	0	0.125	0.25	0.5	1.0	2.5	5.0	10	20	50	100	-	-
Mo	µg/L	0	-	-	-	1.0	2.5	5.0	10	20	50	100	250	-
Na	mg/L	0	-	0.100	0.250	0.500	1.00	2.50	5.00	10.0	25.0	-		
Ni	µg/L	0	-	-	-	1.0	2.5	5.0	10	20	50	100	-	-
P	µg/L	0	-	-	-	-	2.5	5.0	10	20	50	100	250	-
Pb	µg/L	0	-	-	-	1.0	2.5	5.0	10	20	50	-	-	-
Sb	µg/L	0	-	-	-	1.0	2.5	5.0	10	20	50	100	-	-
Se	µg/L	0	-	-	-	-	2.5	5.0	10	20	50	-	-	-

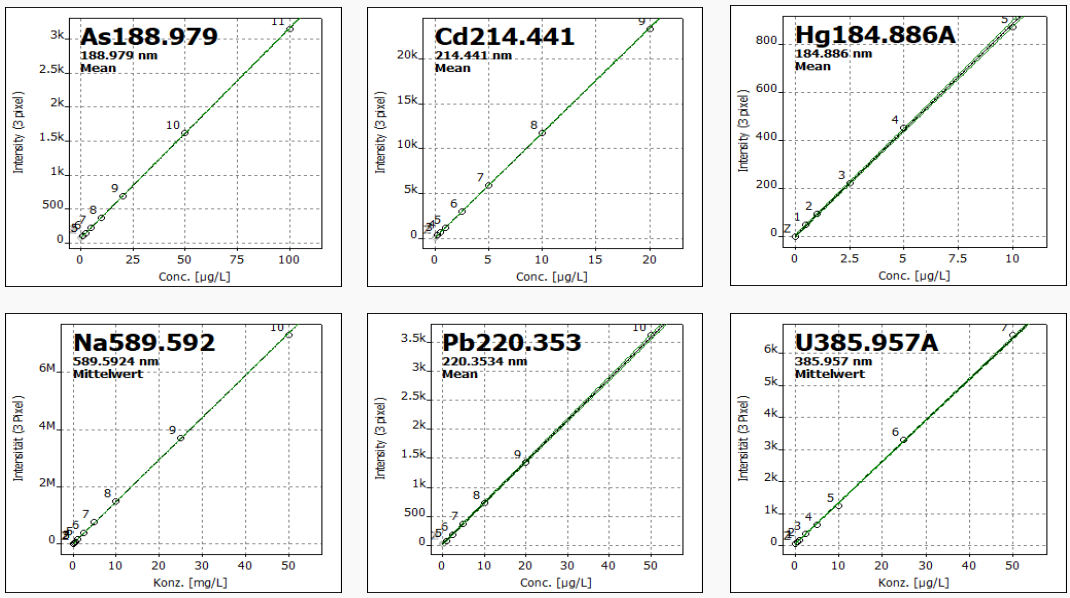


Figure 1: Exemplary calibration functions

Instrument settings

The analysis was performed on a PlasmaQuant 9100 Elite ICP-OES in combination with a SimPrep system, which was used as sample preparation station as well as autosampler for the analysis. The sample introduction components as well as the instrumental settings were selected to achieve a high level of sensitivity. Representative test measurements on a PlasmaQuant 9200 Elite confirmed consistent performance under the adjusted plasma conditions. A summary of individual settings and components is given in table 2.

Table 2: Instrument settings

Parameter	Specification Plasmaquant 9100 Elite	Specification Plasmaquant 9200 Elite
Plasma power	1350 W	1300 W
Plasma gas flow	14 L/min	9 L/min
Auxillary gas flow	0.5 (1.0)[A] L/min	0.8 (1.0)[A] L/min
Nebulizer gas flow	0.6 (0.5)[A] L/min	
Nebulizer	Concentric, Seaspray, 2.0 mL/min, Borosilicate	
Spray chamber	Cyclonic Spray Chamber, 50 mL, Borosilicate	
Outer/Inner tube	Quartz/Quartz	
Injector	Quartz, ID: 2 mm	
Pump tubing	PVC (black, black)	
Sample pump rate	2.0 mL/min	
Delay time	45 s	
Torch position	0 mm	

A ... Setting used for Mercury as part of analytical method with automatic switching of settings within one sample run

Method and evaluation parameters

Table 3: Method parameters

Element	Line [nm]	Plasma view	Integration mode	Read time [s]	Evaluation			
					No. of pixel	Baseline fit, Pixel No.	Polyn. degree	Correction
Ag	328.068	axial	peak	3	3	ABC[1]	auto	-
Al	396.152	axial	peak	3	3	ABC	auto	-
As	188.979	axial	peak	20	3	ABC	auto	-
B	249.773	axial	peak	3	3	ABC	auto	-
Ba	455.403	radial	peak	3	3	ABC	auto	-
Be	323.042	axial	peak	3	3	ABC	auto	-
Ca	315.887	radial	peak	3	3	ABC	auto	-
Cd	214.441	axial	peak	3	3	ABC	auto	-
Co	228.651	axial	peak	3	3	ABC	auto	-
Cr	267.716	axial	peak	3	3	ABC	auto	-
Cu	324.754	axial	peak	3	3	ABC	auto	-
Fe	259.940	axial	peak	3	3	ABC	auto	-
Hg	184.886	axial	Peak	20	3	ABC	auto	-
K	766.491	radial	Peak	3	3	static	auto	-
Li	670.791	axial	Peak	3	3	ABC	auto	-
Mg	285.213	radial	Peak	3	3	ABC	auto	-
Mn	257.610	axial	Peak	3	3	ABC	auto	-

Element	Line [nm]	Plasma view	Integration mode	Read time [s]	Evaluation			
					No. of pixel	Baseline fit, Pixel No.	Polyn. degree	Correction
Mo	202.030	axial	Peak	3	3	ABC	auto	-
Na	589.592	radial	Peak	3	3	ABC	auto	-
Ni	231.604	axial	Peak	3	3	ABC	auto	-
P	213.618	axial	Peak	3	3	ABC	auto	-
Pb	220.353	axial	Peak	10	3	ABC	auto	-
Sb	217.581	axial	Peak	20	3	ABC	auto	-
Se	196.028	axial	Peak	10	3	ABC	auto	-
U	385.957	axial	Peak	10	3	ABC	auto	-

1 ... Automated Baseline Correction

Results and discussion

The here developed method was validated by measuring natural water reference materials with certified contents of trace elements as well as minerals. Recovery values in the range of ±10% (see table 4) for the majority of elements prove the suitability of the employed method. Since the concentration levels in the standard reference materials do not necessarily reflect the limits given in drinking water regulations a tap water sample was investigated for its elemental contents as well as for suitable spike levels, which were selected according to the element specific limits. Table 5 summarizes the results of the measurement of two drinking water samples including spike recoveries ranging from 91% to 106% for low µg/L spike levels (1 to 20 µg/L). Long term stability was investigated by monitoring the results of a spiked water sample for 16 hours, where recoveries in the range of ±4% were achieved (see figure 2).

Table 4: Quantitative results for several standard reference materials (SRMs)

Element	NIST 1640a			NIST 1643f			LGC natural water matrix reference		
	Certified [µg/L]	Measured [µg/L]	Recovery [%]	Certified [µg/L]	Measured [µg/L]	Recovery [%]	Certified [µg/L]	Measured [µg/L]	Recovery [%]
Ag	8.08	7.88	98	0.97	0.95	98	5.00	5.10	102
Al	53.0	55.8	105	134	150	112	250	278	111
As	8.08	8.33	103	57.4	58.6	102	30.0	31.6	105
B	303	310	102	152	175	115	-	-	-
Ba_{radial}	152	158	104	518	527	102	120	121	101
Be	3.03	3.19	106	13.7	14.1	103	10.0	10.4	104
Ca_{radial}	5 615	6 072	108	29 430	30 670	104	18 000	18 800	104
Cd	3.99	4.01	100	5.89	5.70	97	15.0	14.7	98
Co	20.2	20.5	101	25.3	24.4	96	10.0	9.93	99
Cr	40.5	41.4	102	18.5	18.2	98	20.0	20.0	100
Cu	85.8	91.5	107	21.7	21.9	101	60.0	62.2	104
Fe	36.8	39.2	107	93.4	91.8	98	90.0	91.1	101
Hg	Not certified in any of the used SRMs								

Element	NIST 1640a			NIST 1643f			LGC natural water matrix reference		
	Certified [µg/L]	Measured [µg/L]	Recovery [%]	Certified [µg/L]	Measured [µg/L]	Recovery [%]	Certified [µg/L]	Measured [µg/L]	Recovery [%]
K_{radial}	580	589	102	1 932	1932	100	1 880	1 867	99
Li	0.41A	0.35A	87	16.6	15.6	94	-	-	-
Mg_{radial}	1 058	1 110	105	7 454	7 619	102	4 000	4 147	102
Mn	40.1	39.9	99	37.1	35.1	95	30.0	28.6	95
Mo	45.2	46.6	102	115	115	100	50.0	50.5	101
Na_{radial}	3 137	3 299	105	18 830	19 510	104	15 000	15 460	103
Ni	25.3	25.3	100	59.8	56.7	95	30.0	29.0	97
P	Not certified in any of the used SRMs								
Pb	12.1	12.3	102	18.5	17.630	95	15.0	14.4	96
Sb	5.11	4.59	90	55.5	49.1	89	30.0	26.0	87
Se	20.1	19.5	97	11.7	11.5	98	20.0	18.9	95
U	25.4	26.6	105	-	-	-	5.00	4.74	95

A: concentration below method-specific detection limit

Table 5: Analysis of bottle and tap water plus spike recovery studies

Element	MDL[A] [µg/L]	Bottled water	Tap water	Spiked tap water	
		Concentration [µg/L]	Concentration [µg/L]	Spike level [µg/L]	Recovery [%]
Ag	0.22	<MDL	<MDL	1.00	102
Al	0.13	8.23	4.09	5.00	101
As	0.41	1.25	2.37	1.00	96
B	0.18	55.3	23.9	20.0	101
Ba	0.03	2.45	152	*	-
Be	0.01	<MDL	0.07	1.00	106
Ca	1.04	85 570	61 060	*	-
Cd	0.06	<MDL	<MDL	1.00	97
Co	0.20	<MDL	<MDL	5.00	92
Cr	0.07	0.33	<MDL	1.00	94
Cu	0.11	<MDL	20.8	5.00	98
Fe	0.09	<MQL	15.3	5.00	101
Hg	0.13	<MDL	<MDL	1.00	91
K	10.3	2 700	3 663	*	-
Li	0.45	40.1	12.1	20.0	97
Mg	0.38	44 880	23 990	*	-
Mn	0.01	0.63	2.36	5.00	95

Element	MDL[A] [µg/L]	Bottled water	Tap water	Spiked tap water	
		Concentration [µg/L]	Concentration [µg/L]	Spike level [µg/L]	Recovery [%]
Mo	0.17	<MDL	0.96	1.00	104
Na	2.68	23 410	7 488	*	-
Ni	0.09	<MDL	0.82	1.00	101
P	1.27	<MDL	68.7	*	-
Pb	0.36	<MDL	<MQL	5.00	92
Sb	0.42	<MDL	<MDL	5.00	96
Se	0.88	<MDL	<MQL	5.00	103
U	0.55	<MDL	4.77	1.00	99

A: MDL ... method-specific detection limits
MQL ... method-specific quantification limits
*initial concentration to high for spiking

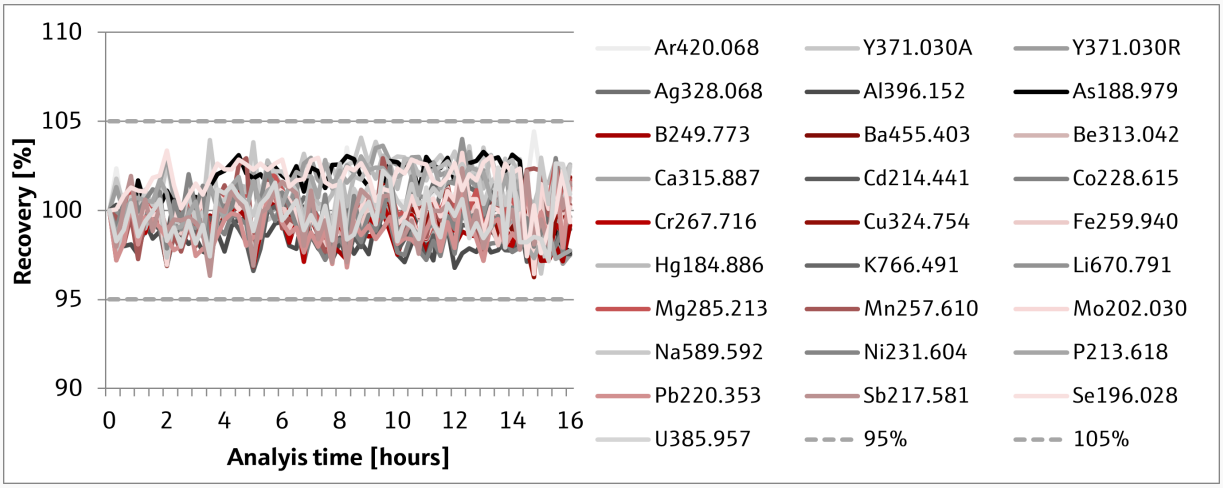


Figure 2: Long-term stability of a 16-hour Measurement of different Elements spiked (50 µg/L) to a Tap Water sample. RSD Values were below 4% for all Elements.

In terms of limit values and required accuracy and precision at the limit concentration, the German drinking water ordinance is amongst the strictest regulations worldwide. Table 6 summarizes the requirements for the most critical trace elements concerning limit concentration (climit), accuracy and precision at the limit concentration and the required MDL, which must be at least ten times below the defined limit. For the example uranium, which is an additional parameter in the German drinking water ordinance, an MDL of 1 µg/L and below must be ensured with precision and accuracy of below 10% at the limit concentration of 10 µg/L.

The precision of the results at the limit concentrations were investigated in further detail. Table 7 shows the results for intraday and interday precision values. Each test was conducted using six individually prepared spiked water samples. The interday precision was performed on three consecutive days. Both tests resulted in precision values far below the regulated limits (table 7). Table 5 compares the achieved MDL, precision and accuracy of the here presented methodology with the requirements and shows the regulation compliance for all critical trace elements.

Table 6: Requirements of German drinking water ordinance and according PlasmaQuant 9200 Elite performance parameters.

Element	Requirements by German drinking water ordinance				Performance PlasmaQuant 9200 Elite		
	c_{limit} [µg/L]	Accuracy at c_{limit} [%]	Precicion at c_{limit} [%]	Required MDL [µg/L]	Accuracy at c_{limit} [%]	Precicion at c_{limit} [%]	Achieved MDL [µg/L]
As	10	10	10	1.0	< 4	2.6	0.4
Cd	3.0	10	10	0.3	< 3	0.5	0.1
Hg	1.0	20	10	0.1	< 9	2.3	0.1
Pb	10	10	10	1.0	< 8	2.5	0.4
Sb	5.0	25	25	1.2	< 4	2.4	0.4
Se	10	10	10	1.0	< 3	3.1	0.9
U	10	10	10	1.0	<1	1.9	0.6

Table 7: Intraday and Interday (3 consecutive days) precision determined for critical elements spiked to a tap water sample.

Element	Spiked concentration [µg/L]	Intraday precision (n=6)			Interday precision (n=6/day)		
		Concentration [µg/L]		SD (RSD %) [µg/L]	Concentration [µg/L]		SD (RSD %) [µg/L]
As	3.00	6.38	±	0.17 (2.6)	6.59	±	0.32 (4.8)
Be	0.50	0.55	±	0.002 (0.4)	0.55	±	0.011 (2.1)
Cd	1.50	1.71	±	0.01 (0.5)	1.72	±	0.03 (1.8)
Hg	1.00	0.96	±	0.022 (2.3)	0.98	±	0.052 (5.3)
Pb	3.00	3.36	±	0.08 (2.5)	3.38	±	0.13 (4.0)
Sb	3.00	2.84	±	0.07 (2.4)	2.88	±	0.10 (3.6)
Se	3.00	4.26	±	0.13 (3.1)	4.23	±	0.23 (5.4)
U	3.00	8.16	±	0.15 (1.9)	8.08	±	0.27 (3.4)

SD: standard deviation,
RSD%: relative standard deviation percentage

Interference-free detection of trace signals is a prerequisite for reliable and accurate quality monitoring of drinking water. Trace signals can easily be interfered by unexpected sample compositions or by elevated background readings. In this regard, high spectral resolution provides well separated peaks of high definition and therefore circumvents the risk of spectral interferences in drinking water analysis. Figure 3 displays a comparison of spectra on the example of beryllium. The spectra of an instrument with average spectral resolution (left) reveals an insufficient separation of the most sensitive beryllium line at 313.042 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 the Be line at 313.042 nm. Thus, the most sensitive line 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.

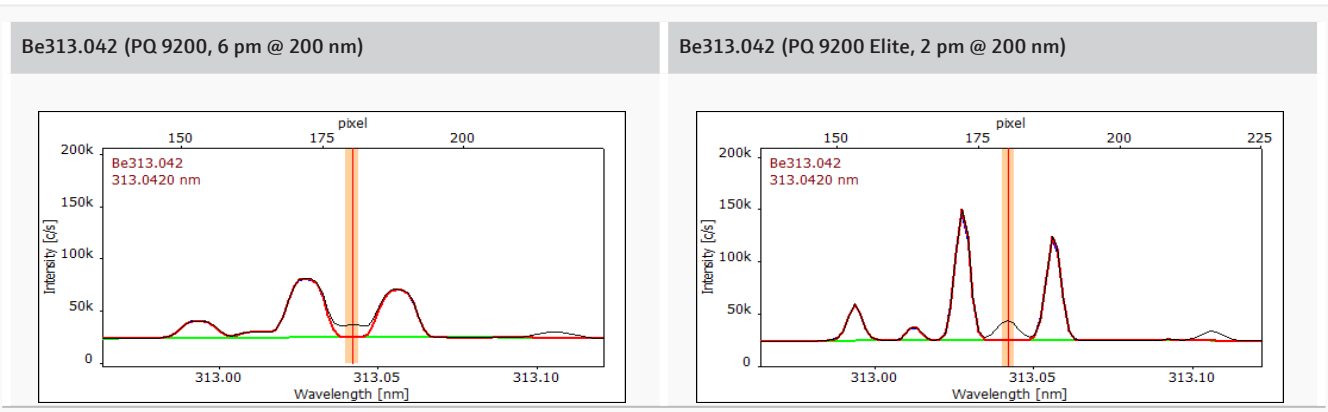


Figure 3: Comparison of PlasmaQuant 9200 (6 pm @ 200 nm) and PlasmaQuant 9200 Elite (2 pm @ 200 nm) illustrating the application advantage of high-resolution spectra (red: sample, black: spike, blue: blank, green: baseline correction (ABC)).

Summary

The here presented method describes the use of a high-resolution ICP-OES in a standard configuration to comply to worldwide drinking water regulations. The comprehensive method validation including the accuracy determination on SRMs and several spiked water samples, precision assessment on low µg/L spikes as well as long-term stability analysis demonstrate the suitability of the PlasmaQuant 9200 Elite ICP-OES system to comply to drinking water directives such as the Safe Drinking Water Act, the European Drinking Water Directive or the German drinking water ordinance.

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. As, Hg, Sb, Se) are to be analyzed together with minerals (e.g. Ca, K, Na, Mg), which is successfully addressed by the DualView Plus feature of the PlasmaQuant 9200 Elite. Besides the common radial and axial plasma observation modes it offers axial plus and radial plus, which attenuate the signal in the respective observation mode. The here described method uses radial plasma observation to measure the high levels of minerals alongside the trace levels of toxic elements in a single measurement run. Running several dilutions to cover the entire concentration range is therefore avoided.

A typical issue of ICP-OES instrumentation is the lack of sensitivity to meet the regulation requirements for trace element detection. In this regard, the PlasmaQuant 9200 Elite offers a high sensitivity which is based on a multitude of technical features. The high frequency generator provides a plasma with superior robustness to deliver a high and constant signal intensity, even for water samples of different mineral contents. The four-winding coil in combination with the counter gas technology provides an elongated analytical zone in axial

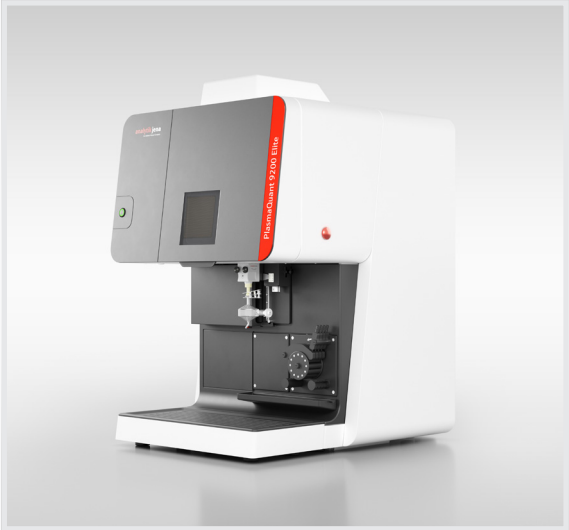


Figure 4: PlasmaQuant 9200 Elite

observation mode to provide as much signal as possible in ICP-OES. On top of this, the spectral resolution of 2 pm @ 200 nm allows for a reliable and interference-free quantification of trace elements by granting access to most sensitive emission lines and high-definition peak shapes with extra sensitivity.

The here proposed setup fulfills all requirements for water quality monitoring, which makes the use of an ultrasonic nebulizer (USN) obsolete. The performance can be even further improved by using a hydride system to push the method detection limits of hydride forming elements into the ng/L range.

The use of the PlasmaQuant 9200 Elite allows water laboratories to perform their entire elemental screening on one instrument to save cost, lab space, time and labor.

Recommended device configuration

Table 8: 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
Teledyne Cetac ASX 560	810-88015-0	Autosampler

References

[1] Guidelines for Drinking-water Quality, 4th Edition, World Health Organization, 2017.

[2] Council directive 98/83/EC (03.11.1998), latest amended by Commission Directive (EU) 2015/1787 of 6 October 2015.

[3] The Safe Drinking Water Act (16.12.1974), latest amended by US government 6th of August 1996.

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