Challenge
U.S. EPA compliant analysis of trace metals in high matrix samples with a broad concentration range of element content.

Solution
PlasmaQuant MS Series with high sensitivity, ultimate precision, and 11 orders of magnitude for detection, provides good results for trace metals in wastewater.

Wastewater Analysis following U.S. EPA 200.8 using ICP-MS

Introduction

Water is one of the most controlled media and essential for all existing life on earth. Waterbodies such as lakes, rivers, oceans, and wetlands are not only the source of human life. They also serve as a life base for plants, animals, and insects and must be protected and preserved. Due to the increasing water scarcity worldwide, it is necessary to change and rethink the way we handle water.

To ensure the high quality of water worldwide, federal institutions like the United States Environmental Protection Agency (U.S. EPA) or the European Committee for Standardization (CEN) are responsible for providing and regularly revising methods of water monitoring to be implemented in laboratories that are certified for a standard conformity of water analysis.

The analysis of trace metals in water is one of the most used applications. Several techniques can be used to measure the elemental composition of wastewaters, including atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectroscopy (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS). Depending upon the number of elements and samples, laboratories must select appropriate techniques and validate analytical methods constantly, to reach the specified limits of quantification (LOQ) and react flexibly to new regulations or changing requirements.

Up to now, ICP-OES is the most common elemental analysis techniques for wastewater. The ICP-MS technique provides highly accurate trace detection capabilities and is used to cover a wide variety of water samples with up to 3.5% of TDS (total dissolved solids).

Using the example of real wastewater samples, this application note will demonstrate the complete analyzing process including quality program steps according to the U.S. EPA Method 200.8[1], sample pre-treatment by microwave-assisted digestion, sample preparation, method validation, and results. Besides U.S. EPA 200.8, other regulations such as DIN EN ISO 17294[2] give comparable advice and recommendation related to the analysis of water. Therefore the described method and data is also valid for regions outside the EPA regulated countries.

Materials and Methods

Samples preparation

The laboratory ware was washed with deionized (DI) water from a PURELAB system (18.2 MΩ cm, ELGA LabWater, High Wycombe, England). All single and multi-element working standards were prepared by serial volume/volume dilution in polypropylene tubes from the stock solutions (Merck, Sigma-Aldrich, CPAChem, Inorganic Ventures) using 1% (v/v) sub-boiled nitric acid (HNO_3). All samples (if not already stabilized) and blank solutions were acidified with HNO_3 to give a final acid concentration of 1% (v/v).

This study includes three wastewater samples that were part of a national German inter-laboratory testing (ILT). Different reference materials were used for method validation and summarized in Table 1. Inter-laboratory testing (ILT) (also called Round Robin Test (RRT) or proficiency testing) is usually done on a regular base, so that laboratories have the opportunity for external validation and certification. The described analysis took place within the “59th National Round Robin Test - Elements in Wastewater - 03/21”, organized by the Staatliche Betriebsgesellschaft für Umwelt und Landwirtschaft Sachsen (BfUL), Germany.
The sample preparation for the ILT samples was performed in accordance to EPA Method 3015A (SW-846)[3] and DIN EN ISO 15587-2[4], which require a microwave-assisted acid digestion step. Therefore, a 25.0 (± 0.1) mL aliquot of the sample and 6.25 (± 0.10) mL sub-boiled HNO_3 were added to a digestion vessel (PM60). The mixture was swirled carefully and leave for at least 15 minutes before the vessel was closed. Subsequent heating (20 min, 200 °C) 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 into graduated polypropylene tubes and diluted to a final volume of 50 mL with DI water. For the analysis by ICP-MS, all samples were diluted 1:10. To correct long-term signal drifts and matrix effects, 10 µg/L of ^{89}Y, ^{103}Rh, ^{185}Re, and ^{193}Ir were added as internal standards online via a Y-piece. For sample introduction via the peristaltic pump, black/black tubings (PVC, 0.030 mm ID) for samples and orange/green tubings (PVC, 0.015 mm ID) for the internal standard solution were used. For the direct analysis of mercury, an aliquot of each RRT sample was taken and stabilized by adding 200 µg/L Au (Merck, 1 g/L).

Table 1: List of samples and reference materials being analyzed

Sample	Supplier
NIST 1643f – Certified	National Institute of Standards and Technology
NIST 1640a – Certified	National Institute of Standards and Technology
Certified wastewater-Trace metals solution A (CWW-TM-A)	High Purity Standards
Certified wastewater-Trace metals solution B (CWW-TM-B)	High Purity Standards
Certified wastewater-Trace metals solution C (CWW-TM-C)	High Purity Standards
Certified wastewater-Trace metals solution D(CWW-TM-D)	High Purity Standards
ERM-CA713 Wastewater (trace elements)	Sigma-Aldrich
RRT wastewater sample A	BfUL
RRT wastewater sample B	BfUL
RRT wastewater sample C	BfUL

Calibration

All calibration solutions were prepared in a 1% HNO_3 solution using multi-element standards (TraceCERT® Periodic Table Mix 1 for ICP, 10 mg/L; 4-Element Standard Sb, Mo, Sn, Ti, Bruker Daltonics,100 mg/L) and a single element standard (Hg: CPAchem, 1000 mg/L). Calibration levels for each element were chosen based on the expected concentration range (Table 2).

Instrument settings

A PlasmaQuant MS Q was equipped with an autosampler (ASX-560, CETAC) with enclosure and HEPA filter, 4-channel peristaltic pump, MicroMist™ (0.4 mL/min) nebulizer, Scott double-pass spray chamber, 2.4 mm injector torch, nickel sampler and skimmer cone. Sample preparation and measurements were carried out in a routine analytical laboratory and not under clean room conditions.

Table 2: Concentration of calibration standards

Standard	Concentration [µg/L]	
	Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Tl, Th, U, V, Zn, Mo, Sb, Sn	**Hg**
Blank	0	0
Standard 1	0.1	0.01
Standard 2	0.5	0.5
Standard 3	1.0	2
Standard 4	10	-
Standard 5	20	-
Standard 6	50	-
Standard 7	100	-

Table 3: Instrument configuration and settings - PlasmaQuant MS Q

Parameter	Specification
Nebulizer	MicroMistTM (0.4 mL/min)
Spray chamber	Peltier cooled quartz glass Scott double-pass
Torch	Fassel torch with 2.4 mm injector
Sampling depth	5.0 mm
Cones	Nickel sampler and skimmer cone
iCRC gases, flow	H_2 – 80 mL/min; He – 120 mL/min
Autosampler	ASX-560 (CETAC), enclosure with HEPA filter
Pump tubing	PVC (black/black)
Internal standard tubing	PVC (green/orange)
Pump rate	23 rpm
Plasma gas flow	9.0 L/min
Sheath gas flow	0.0 L/min
Nebulizer gas flow	1.00 L/min
RF power	1.35 kW
Auxiliary gas flow	1.2 L/min
Stabilization delay (condition set)	20 s (H_2), 12 s (nG), 15 s (He)*
Spray chamber temperature	3 °C

* Shorter stabilization times can be achieved, but for better RSD values in this application note longer times were used

Table 4: EPA 200.8 Elements

Element	**Isotope**	**Gas mode**	**Elemental Correction Equation***
	[m/z]		
As	75	Hydrogen	- 3.127 * (Se77 - 0.815 * Se82)
Se	78	Hydrogen	- 0.03043 * Kr83
Be	9	no Gas	
Mo	98	no Gas	- 0.1111 * Ru101
Ag	107	no Gas	
Cd	114**	no Gas	- 0.0268 * Sn118 - 1.6285 * Pd108
Sn	118	no Gas	
Sb	123	no Gas	- 0.1286 * Te125
Ba	137	no Gas	- 0.0009008 * La139 - 0.003394 * Ce140
Hg	202	no Gas	
Tl	205	no Gas	
Pb	206, 207, 208	no Gas	206+207+208
Th	232	no Gas	
U	238	no Gas	
Al	27	Helium	
V	51	Helium	- 3.1081 * Cl37O16 + 0.3524 * Cr52
Cr	52	Helium	
Mn	55	Helium	
Co	59	Helium	
Ni	60	Helium	
Cu	63	Helium	

* EPA 200.8 is recommending mathematical correction equations [1, 4]. For drinking water this is mandatory, for other types of water such as wastewater, interference correction with collision/reaction systems may be considered, if the analyst can proof the correct usage.

** EPA 200.8 recommends m/z 111 but due to higher abundancy, m/z 114 was preferred in this work.

Results and Discussion

Quality control

The EPA method 200.8[1] demands a formal quality control (QC) program. The minimum program requires an initial demonstration of laboratory capability, the periodic analysis of laboratory reagent blanks, fortified blanks, and other laboratory solutions as a continuous check on performance.
The initial demonstration of laboratory capability requires the determination of method detection limits (MDLs) and linear dynamic range (LDR), checks of blank solutions and instrument performance (IPC). Additionally, the accuracy and long-term stability of the method need to be tested.

Linear calibration range and method detection limits

According to Part 9.2.2. of EPA Method 200.8[1], the LDR is defined as the upper limit which recovers within 10% of the actual value when determined against the calibration curve used for the analysis. MDLs should be determined from seven measurements of a fortified blank solution with a concentration of two to five times the instrument detection limit. The resulting standard deviation of the seven measurements is then multiplied by 3.14 (at 99% confidence level) to give the MDL. The method specific LDRs and MDLs are shown in Table 5.

Table 5: LDR and MDL regarding EPA 200.8[1]

Element	**Isotope**	**Gas mode**	**MDL**	**LDR**
	[m/z]		**[µg/L]**	**[µg/L]**
As	75	Hydrogen	0.0150	150*
Se	78	Hydrogen	0.0252	150*
Be	9	no Gas	0.00147	150*
Mo	98	no Gas	0.000592	150*
Ag	107	no Gas	0.00193	150*
Cd	114	no Gas	0.000366	150*
Sn	118	no Gas	0.000726	150*
Sb	123	no Gas	0.00219	150*
Ba	137	no Gas	0.00126	150*
Hg	202	no Gas	0.0132	5*
Tl	205	no Gas	0.000220	150*
Pb	206, 207, 208	no Gas	0.000440	150*
Th	232	no Gas	0.000567	150*
U	238	no Gas	0.000229	150*
Al	27	Helium	0.295	150*
V	51	Helium	0.0239	150*
Cr	52	Helium	0.00913	150*
Mn	55	Helium	0.00441	150*
Co	59	Helium	0.00199	150*
Ni	60	Helium	0.00600	150*
Cu	63	Helium	0.0115	150*
Zn	66	Helium	0.0496	150*

* upper limit of test according to the selected calibration, even higher concentrations are possible by fulfilling the 90% recovery criteria, but not recommended to avoid detector damages and cross contamination

Laboratory reagent blank (LRB) and laboratory fortified blank (LFB)

Different blank solutions must be measured within Method 200.8[1], e.g., the laboratory reagent blank (LRB) which is processed in the same way as samples containing all reagents in the same volumes. LRB should be analyzed with each batch of 20 or fewer samples to address possible contamination from the laboratory environment and should not exceed 10% of the analyte levels determined or should be smaller than 2.2 times of the MDL. Another blank to be measured, is the laboratory fortified blank (LFB) which is prepared by spiking an aliquot of LRB and carried through the whole sample preparation. The accuracy, calculated as percent recovery [%], must be within a ±15% control limit. Table 6 shows the LFB, spiked with two levels of selected elements with a multielement standard solution other than the calibration solution. The LFB was prepared prior to the microwave digestion procedure and carried through the whole method procedure, from sample preparation to final measurement.[1, Section 9.3.2]

Table 6: Lab Fortified Blank (LFB) Example*

Isotope	Spike Level I [µg/L]	Recovery [%]	Spike Level II [µg/L]	Recovery [%]
As75	10	98	100	98
Se78	10	98	100	96
Be9	10	108	100	105
Mo98	-	-	-	-
Ag107	-	-	-	-
Cd114	10	97	100	97
Sn118	-	-	-	-
Sb123	-	-	-	-
Ba137	10	94	100	95
Hg	-	-	-	-
Tl205	10	94	100	91
Pb206, 207, 208	10	99	100	94
Th232	-	-	-	-
U238	-	-	-	-
Al27	10	85	100	97
V51	10	99	100	96
Cr52	10	99	100	92
Mn55	10	107	100	100
Co59	10	99	100	92
Ni60	10	102	100	111
Cu63	10	99	100	90
Zn66	10	103	100	96

* for the LFB Spike Solution, a standard stock solution different to the calibration solution was chosen, therefore some elements are not shown

Quality control sample, initial performance check and stability

After the calibration, two QC samples must be run to verify the quality of calibration standards and instrument performance. This includes the quality control sample (QCS) made from a different stock solution and the initial performance check (IPC) originating from the same source as the calibration. The recovery of both standards must be within ±5% of the stated value. For this work, an external Certified Reference Material (NIST 1640a*) was used as QCS.

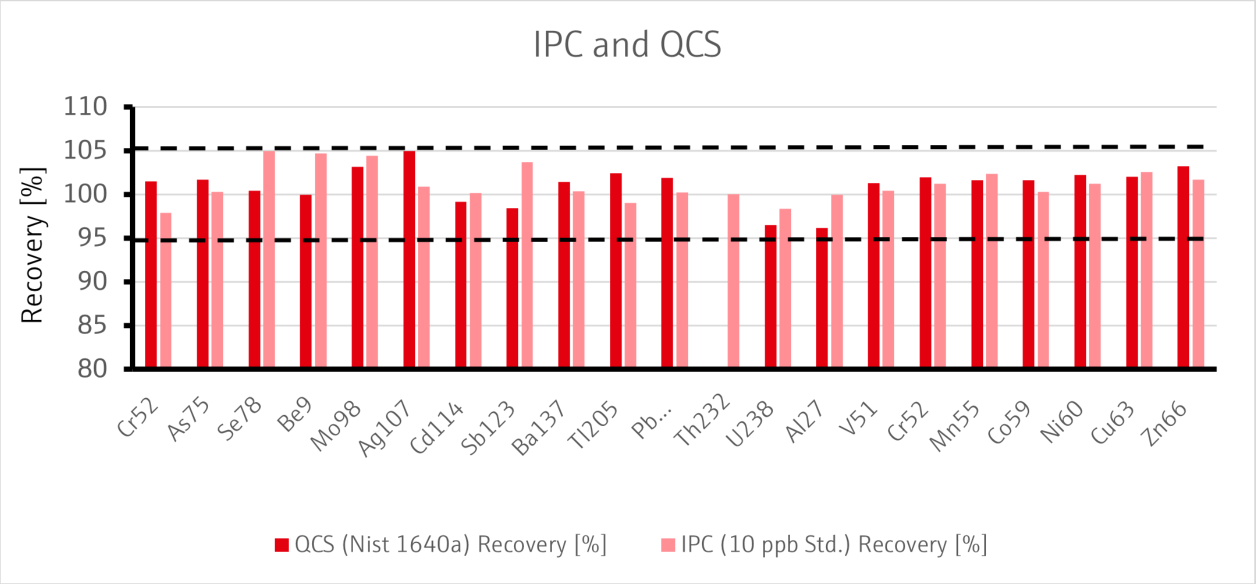

Figure 1: Recovery of Quality Control Sample and Initial Performance Check Standard

* Th232 is not certified in NIST 1640a

The EPA quality program (comparable to European Regulations DIN EN ISO 17294[2]) requires the continuous measurement of the IPC over the entire sequence, usually every tenth analyses and at the end of the run. The IPC results should be within the allowed range of 85-115% of the known value, as shown in Figure 2.

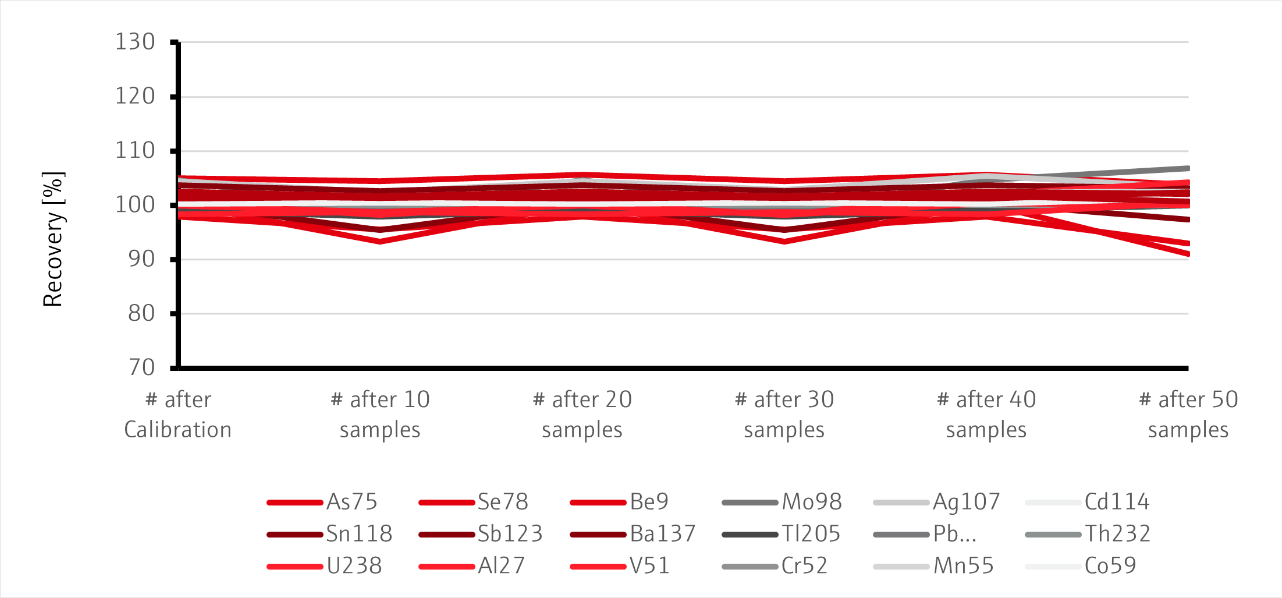

Figure 2: Continuing Calibration Check according to EPA 200.8 part 9.3.4

Certified reference materials similar to the expected sample nature can be analyzed to demonstrate the validity of a method. Therefore, four wastewater reference standards were analyzed. Table 7 shows the certified values and recovery rates for the tested reference materials. All recoveries were within the 85-115% range of the certified value. In addition, a wastewater reference material was analyzed containing low concentrations (close or below the legal limits of important drinking water regulations) of arsenic (As), mercury (Hg), and selenium (Se).

Table 7: Quantitative results for the analyzed certified reference materials (CRMs)

Element	**CWW-TM-A**		**CWW-TM-B**		**CWW-TM-C**		**CWW-TM-D**	
	Certified [µg/L]	**Recovery [%]**	**Certified [µg/L]**	**Recovery [%]**	**Certified [µg/L]**	**Recovery [%]**	**Certified [µg/L]**	**Recovery [%]**
As75	10	99	50	96	150	97	250	97
Se78	10	97	50	97	150	94	250	98
Be9	10	103	50	104	150	105	250	102
As75	10	105	50	102	150	100	250	100
Mo98	50	111	200	101	500	99	1000	100
Ag107	10	98	50	101	150	100	250	100
Cd114	10	96	50	97	150	100	250	97
Sb123	10	96	50	99	150	96	250	100
Ba137	50	98	200	99	500	99	1000	98
Hg	-	-	-	-	-	-	-	-
Tl205	10	96	50	98	150	96	250	96
Pb206, 207, 208	50	99	200	99	500	98	1000	99
Al27	50	113	200	98	500	100	1000	100
V51	50	99	200	99	500	99	1000	98
Cr52	50	97	200	98	500	98	1000	97
Mn55	50	100	200	101	500	101	1000	100
Co59	50	98	200	99	500	99	1000	98
Ni60	50	98	200	99	500	99	1000	98
Cu63	50	99	200	99	500	100	1000	98
Zn66	50	99	200	99	500	99	1000	99

Table 8: Quantitative results for certified reference material WW CA 713

Element	**WW CA 713**	
	Certified [µg/L]	**Recovery [%]**
As	10.8	91
Cd	5.09	96
Cr	20.9	92
Cu	101	90
Hg	1.84	101
Mn	95	102
Ni	50.3	91
Pb206, 207, 208	49.7	94
Se	4.9	90
Zn	78	105

Long-term stability and signal drift

EPA 200.8, Section 9.4.5 recommends monitoring the responses from internal standards throughout the sample set. Figure 3 shows the behavior of the internal standard over an 8-hour measurement to prove stable performance of the hardware. Deviations are not greater than the allowed 60%-125%, proving the applicability and robustness of the method for the routine analysis of wastewater.

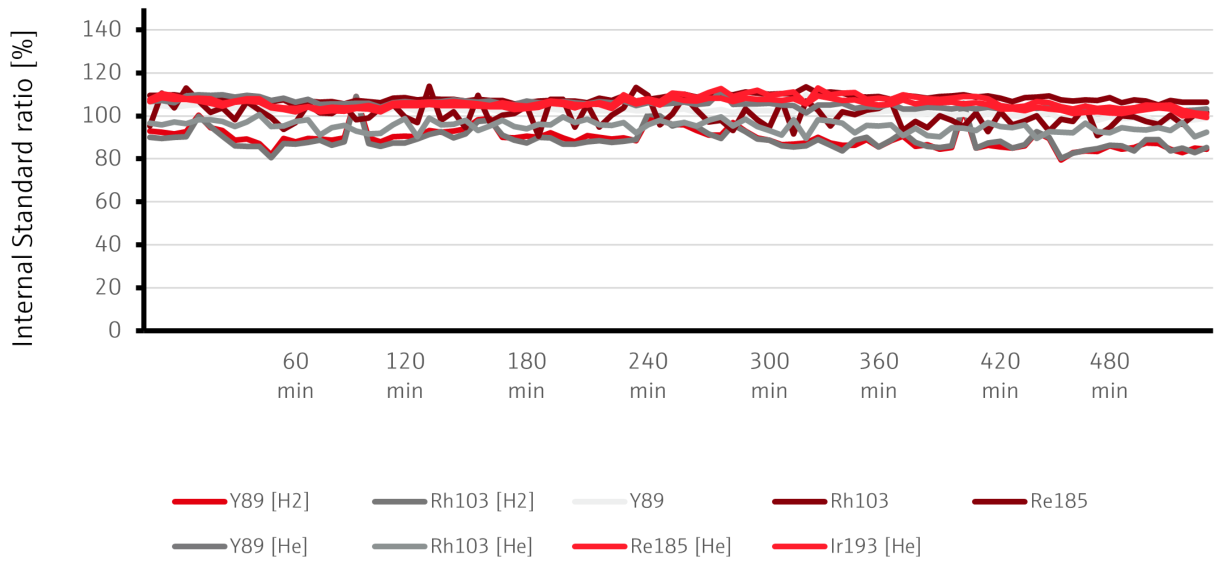

Figure 3: Internal standard ratio determined over a measuring time of in total 8 hours

Sample run

External quality validation – inter-laboratory testing

Inter-laboratory testing procedures are a popular method for external validation of the laboratories' performance. Identical unknown samples are tested with identical procedures in multiple laboratories. The comparison of the results allows statements to be made about the accuracy and data quality of the participating laboratory.
To demonstrate the PlasmaQuant MS performance and the applicability of the analytical method, the Analytik Jena application lab in Germany took part in a national testing procedure. The sample preparation was carried out for all techniques (ICP-MS and ICP-OES) as described previously. The organizer of the ILT gave specific instructions about the approved analytical methods and sample preparation steps to be used.
All participating laboratories had the choice to either give results measured by AAS, ICP-MS, ICP-OES, or even mixed results. Table 9 shows the analysis results using the PlasmaQuant ICP-MS. For comparison with ICP-OES, please see application note "Wastewater Analysis following U.S. EPA 200.7 using HR ICP-OES"[5].

Table 9: Quantitative results for round robin test samples

Element	Wastewater Sample A			Wastewater Sample B			Wastewater Sample C		
	Assigned	Measured	z-score*	Assigned	Measured	z-score*	Assigned	Measured	z-score*
	µg/L	µg/L		µg/L	µg/L		µg/L	µg/L	
Al	1664.029	1692	0.2	296.473	310.070	0.9	1256.799	1288.059	0,0
As	34.785	33.36	0.0	86.134	79.752	-1.0	175.277	162.553	-1.2
Cd	2.741	2.81	0.3	0.824	0.807	-0.2	6.011	5.986	-0.0
Cr	385.734	386	0.0	96.992	95.577	-0.3	174.162	175.019	0.1
Cu	258.785	257	-0.1	375.709	366.970	-0.4	86.059	85.576	-0.1
Fe	180.552	186	0.4	362.468	358.186	0.0	850.259	842.886	0.0
Hg	0.371	0.357	-0.2	1.017	1.041	0.1	1.522	1.4006	-0.3
Ni	397.862	396	-0.1	120.354	117.967	-0.4	199.558	198.503	-0.1
Pb	54.707	54.8	0.0	131.381	130.410	-0.1	76.425	77.844	0.3
Zn	96.561	92.4	-0.4	167.401	166.506	-0.1	361.720	360.507	-0.0

* calculation of z-score was performed in accordance to DIN 38402-45:2014-06. *The z-score is a numerical measurement that describes a value's relationship to the mean of a group of values. It is measured in terms of standard deviations from the mean. If a z-score is 0, it indicates that the data point's score is identical to the mean score. A z-score of 1.0 indicates a value that is one standard deviation from the mean. Z-scores can be positive or negative, with a positive value indicating the score is above the mean and a negative score indicating it is below the mean.* [10]

Mercury (Hg) plays a special role in the analysis of environmental samples. EPA 200.8 and 200.7 specify Hg to be measured with either ICP-MS or ICP-OES. European regulations such as DIN-EN ISO 17294-2 for determination of water using ICP-MS give recommendations and detailed descriptions about testing Hg with ICP-MS, but DIN EN ISO 11885:1998-04[6] for ICP-OES does not include Hg at all. Additional local regulations sometimes restrict the determination of Hg to the historically used atomic absorption spectrometry (AAS) or atomic fluorescence spectrometry (AFS) techniques.

In this testing procedure, Hg was determined by several different techniques to compare, e.g., cold vapor ICP-OES with the PQ 9100 Elite equipped with the hydride generation system HS PQ Pro[5] as well as direct analysis of the fresh samples with PlasmaQuant ICP-MS with the addition of gold (~ 200 µg/L). Although both techniques give outstanding results, for the inter-laboratory performance check only results determined by AAS and AFS are allowed to be submitted[7,8]. For determination using AAS/AFS, a sample preparation procedure with KBrO3 reagent was accomplished.
Table 10 shows the compared results of all three techniques. The z-scores show the excellent performance of all three techniques. The PlasmaQuant MS provides very good results with minimum effort for the sample preparation procedure. The absence of additional accessories for the analysis of Hg with the PlasmaQuant MS is another advantage.

Table 10: Hg concentrations of wastewater samples from the inter-laboratory test determined by three different analysis techniques

Sample	Technique	Measured [µg/L]	Assigned [µg/L]	z-score
Sample A	ICP-MS	0.3573	0.371	-0.2
	ICP-OES	0.299	0.371	-0.9
	CV-AAS/AFS	0.295	0.371	-0.9
Sample B	ICP-MS	1.0405	1.017	0.1
	ICP-OES	0.852	1.017	-0.7
	CV-AAS/AFS	0.875	1.017	-0.6
Sample C	ICP-MS	1.4006	1.522	-0.3
	ICP-OES	1.28	1.522	-0.7
	CV-AAS/AFS	1.3	1.522	-0.6

Conclusion

This work demonstrates the ability of the PlasmaQuant MS to analyze wastewater samples in accordance with the U.S. EPA Method 200.8. The accuracy was demonstrated by the analysis of reference materials and the successful participation in the external proficiency testing. With an excellent long-term stability performed over 8 hours, covering a typical work day, the PlasmaQuant MS provides robustness in method and device. Due to the high sensitivity and excellent method detection limits, the PlasmaQuant MS allows trace-level determinations. Since U.S. EPA 200.8 gives strict quality control requirements, this application note demonstrates how to integrate the mandatory steps into a routine run. The functionality of the patented interference management system iCRC (integrated Collision Reaction Cell) by use of hydrogen and helium gas was proven to give reliable results by measuring certified reference materials. In addition, the robustness of the sample preparation procedure was monitored and demonstrated within this work. The PlasmaQuant MS provides a comprehensive solution to the challenge of U.S. EPA Method 200.8 for water testing.

Figure 4: PlasmaQuant ICP-MS

References

[1] EPA Method 200.8, "Determination of Metals and Trace Metals in Water and Wastes by Inductively Coupled Plasma Atomic Emission Spectrometry", Rev. 4.4

[2] DIN EN ISO 17294-2:2017-01 Water quality - Application of inductively coupled plasma mass spectrometry (ICP-MS) - Part 2: Determination of selected elements including uranium isotopes (ISO 17294-2:2016)

[3] EPA Method 3015A (SW-846), "Microwave Assisted Acid Digestion of Aqueous Samples and Extracts"

[4] DIN EN ISO 15587-2:2002-07
Wasserbeschaffenheit - Aufschluss für die Bestimmung ausgewählter Elemente in Wasser - Teil 2: Salpetersäure-Aufschluss (ISO 15587-2:2002); Deutsche Fassung EN

[5] Application Note: Wastewater Analysis following U.S. EPA 200.7 using HR ICP-OES

[6] DIN EN ISO 11885:2009-09, Wasserbeschaffenheit - Aufschluss für die Bestimmung ausgewählter Elemente in Wasser - Teil 2: Salpetersäure-Aufschluss; Deutsche Fassung

[7] DIN EN ISO 12846: 2012-08 (E 12) Kaliumbromid-Kaliumbromat-Reagenz

[8] DIN EN ISO 17852: 2008-04 (E 35) Kaliumbromid-Kaliumbromat-Reagenz

[9] U.S. EPA Memorandum, July 14, 2006, accessed on August 21, 2019 at:https://www.waterboards.ca.gov/drinking_water/certlic/labs/documents/ELAPCollisionCellDW200_8.pdf

[10] Adam Hayes,Webarticle Updated September 07, 2021, https://www.investopedia.com/terms/z/zscore.asp

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Version 1.1 · Author: SK
en · 06/2024