Challenge

Highly precise high-throughput analysis of 21 elements (+4 internal standards) in drinking water according to U.S. EPA 200.8.

Solution

The unmatched sensitivity of the PlasmaQuant MS Q enables fastest and most precise analyses resulting in lowest cost per sample.

Speed Up Your Work – High-throughput Analysis of Drinking Water with ICP-MS

Introduction

Drinking water is the world's most important resource and most consumed food. Quality control for drinking water is regulated by international and national regulations and norms. For example, the U.S. Environmental Protection Agency (EPA) has released the Method 200.8 which specifies criteria for the determination of trace elements in waters and wastes by ICP-MS. In Europe, the Council Directive 98/83/EC of 3 November 1998 specifies quality criteria for water intended for human consumption. The analyses are carried out internally by producers and water suppliers or externally by contract labs in order to guarantee safe products free from toxic contaminations. Almost all analyses offered by contract labs follow regulations and standards in order to harmonize the measurement procedures. For those labs requiring high sample throughput each day, not only accuracy, precision and robustness of the method chosen are important but especially the speed of analysis matters. The more samples that can be analyzed per hour, the lower the cost per sample.

Fast sampling systems were developed for ICP mass spectrometers, dramatically decreasing sample uptake time and thus total analysis time per sample[1]. The limiting factor is no longer the supply and rinsing time of the sample, but the measuring time that depends on the number of elements to be analyzed. However, reducing the data acquisition time will directly affect the precision of the results as less averaging is possible due to the time constraint. Therefore, precision is the key parameter for the evaluation of high-throughput methods.

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Using Analytik Jena's patented iCRC technology for interference removal, we demonstrate the measurement of 82 drinking water samples per hour with 21 elements (+4 internal standards). Even with this high sample throughput, highly precise results were achieved (average RSD <2.2 %) according to the U.S. EPA 200.8 regulation. Due to the robustness of the method and the unmatched sensitivity of the PlasmaQuant MS Q, an even higher precision with an average RSD of 1.5 % is demonstrated at a very competitive throughput of 60 samples per hour. In combination with the lowest argon consumption on the market, this translates into lowest cost per sample.

Materials and Methods

A PlasmaQuant MS Q equipped with Micro Mist (0.4 ml/min) nebulizer, Scott double-pass spray chamber and Fassel torch with 2.4 mm injector was used for the analyses. A fast sample introduction system (oneFAST, ESI) was combined with an ASPQ3300 autosampler to improve the throughput. Featuring the patented ReflexION technology and the self-cleaning pre-quadrupole, the PlasmaQuant MS Q reduces contaminations of the ion optics and quadrupole to an absolute minimum avoiding unnecessary cleaning steps and maintenance.

To reduce the costs per sample it is necessary to minimize the time per sample. The sample analysis cycle can be divided into measurement time and non-productive steps such as sample uptake or washout, read delays and autosampler movements (see Figure 1). Those non-productive steps are minimized using the ESI oneFAST system, significantly boosting sample throughput[1]. The measurement time and thus sample throughput is then defined by the requested precision that needs to be achieved.

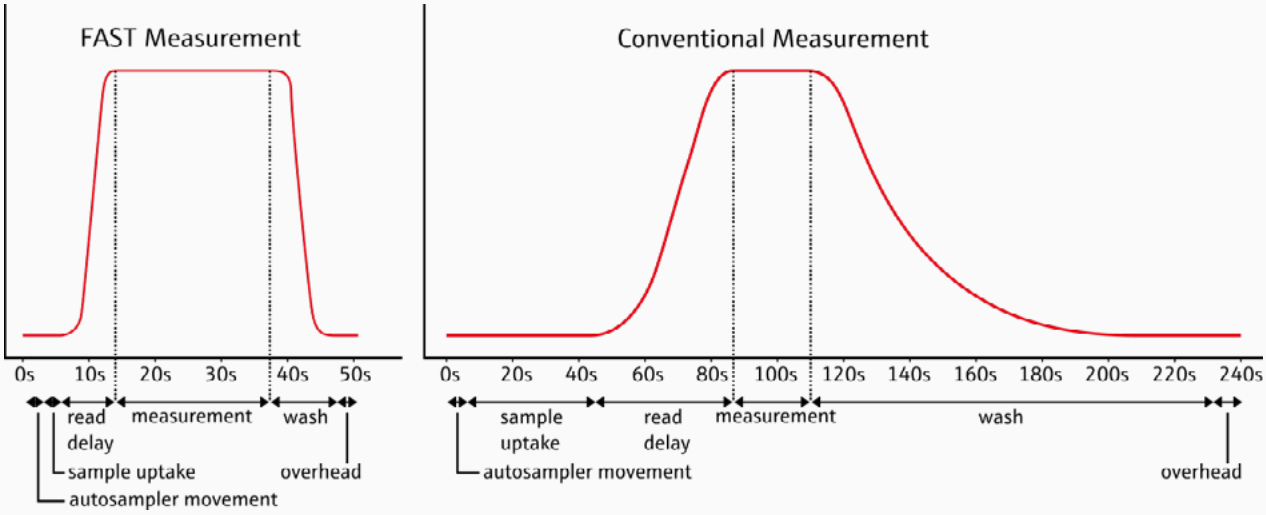

Figure 1: Comparison of different steps during sample uptake, measurement and washout with and without ESI oneFAST.

The Aspect MS software fully controls and monitors all functions and accessories of the instrument. A warm-up routine which can be adapted to the user's needs automatically performs all required steps reducing instrument downtimes to a minimum. The software allows the automatic optimization of all ion optics, nebulizer and plasma parameters and guides the user through the method development process. It contains built-in quality controls for monitoring the results as required by regulations. Out-of-specification results trigger predefined actions thereby minimizing user actions. The Aspect MS software provides intuitive data analysis, export and report functions for optimal integration in modern laboratory environments and LIMS systems.

Samples and Reagents

- All samples and standards were prepared using high-purity reagents. Samples were diluted by a factor of 2 with deionized water (<0.055 mS, ELGA Lab). Standards and samples contained 1 % nitric acid (Ultrapure, Merck).
- Calibration solutions were prepared from a stock solution using the multi-element standard Calibration Mix 2 (Analytik Jena) and single-element standards (ICP grade) for Ag, Sb, Hg, and Mo. The concentrations used for calibration are shown in Table 1.

Table 1: Concentration of the standards used for calibration.

Element	Concentration of standards [ppb]				
Be	0.5	5	50	100	500
Al	0.5	5	50	100	
V	0.5	5	50	100	
Cr	0.5	5	50		
Mn	0.5	5	50		
Co	0.5	5	50		
Ni	0.5	5	50	100	
Cu	0.5	5	50	100	
Zn	0.5	5	50	100	500
As	0.5	5	50	100	500
Se	0.5	5	50	100	500
Mo	0.5	5	50	100	
Ag	0.5	5	50		
Cd	0.5	5	50	100	
Sb	0.5	5	50	100	
Ba	0.5	5	50	100	500
Hg	0.5	5	50		
Tl	0.5	5	50	100	
Pb	0.5	5	50	100	
Th	0.5	5			
U	0.5	5			

Out of the 21 analytes, 6 representative calibration curves (Be, Al, Mn, Mo, Ba and Tl) are shown in Figure 2. Correlation coefficients >0.99996 were achieved for all elements. The obtained very high correlation coefficients, low RSDs and minor deviations of the individual standards from the regression curve show the excellent quality of the calibration even at high sample throughput.

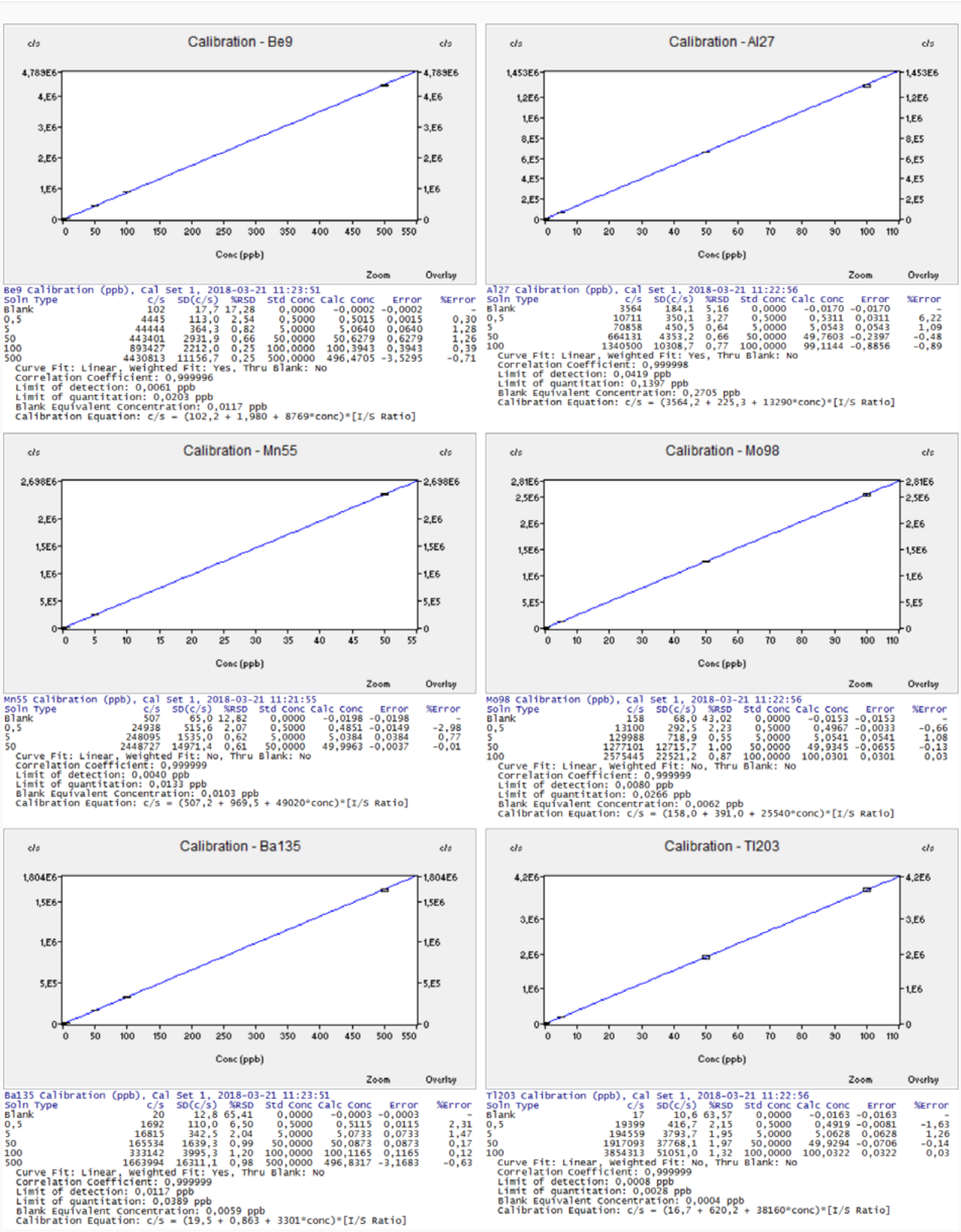

Figure 2: Representative calibration curves.

Instrument settings and method parameters

A robust method utilizing helium as a collision gas for effective interference removal by kinetic energy discrimination (KED) was developed to achieve high accuracy and robustness at minimum analysis time per sample. Internal standards (^{6}Li, Y, Rh and Ir) were added on-line to the sample via a T-piece at 20 ppb concentration. The method parameters used are listed in Table 2.

Table 2: Method parameters.

Parameter	Specification
Plasma Gas Flow	9 l/min
Auxiliary Gas Flow	1.45 l/min
Nebulizer Gas Flow	1.01 l/min
Spray Chamber Temperature	3 °C
RF Power	1450 W
Sampling Depth	5.0 mm
Dwell Time	20 ms (50 ms for Be, As, Se)
Scans per Replicate	7 (peak hopping, 1 pt/peak)
No. of Replicates	6
Pump Rate, Tubings	15 rpm, black/black PVC pump tubing for sample; orange/green PCV tubing for internal standards
Stabilization Delay	19 s
Sample Loading Time	7 s
iCRC Gas Flow	120 ml He/min
Detector Attenuation	none

Results and Discussion

Table 3 lists the elemental concentrations measured in tap water (Jena, Germany) and in certified reference materials (NIST 1640a and NIST 1643f).

Table 3: Determined concentrations of Jena tap water and certified reference materials.

[ppb]	Be9	Al27	V51	Cr52	Mn55	Co59	Ni60	Cu65	Zn66	As75	Se82
tap water	0.0	2.7	0.5	0.2	1.1	0.0	0.9	63.7	47.7	0.9	1.5
NIST 1640a	2.9	52.8	14.2	38.5	38.7	19.7	23.5	81.2	52.0	7.8	19.3
NIST 1643f	13.1	131.9	35.9	17.5	34.9	24.1	54.6	19.8	70.2	54.0	11.7

[ppb]	Mo98	Ag107	Cd112	Sb121	Ba135	Hg202	Tl203	Pb207	Th232	U238
tap water	0.7	0.2	0.0	0.2	200.0	0.4	0.0	2.4	0.1	5.4
NIST 1640a	45.3	7.4	3.8	5.1	145.7	0.2	1.5	11.7	0.1	24.1
NIST 1643f	118.9	1.0	5.8	56.7	503.2	0.3	6.5	17.1	0.1	0.0

Accuracy

Certified reference materials were measured in order to verify the accuracy of the method. The concentration results were found within 91 and 103 % of the specified value and therewith within the ±10 % range as specified by U.S. EPA 200.8. Additionally, two lab-fortified matrices (LFM, +1 ppb and +10 ppb) were measured to verify the method's accuracy. The recovery rates of the LFMs were between 91 and 104 % and therefore within the specified range of 70 to 130 %.

It is important to note that good recovery rates for small spikes on high sample concentrations can only be achieved with a precise measurement. For this reason the EPA 200.8 regulation states that the spiked concentration is dependent on the instrument's sensitivity and that it should be equal to the concentration in the sample. Due to the outstanding sensitivity of the PlasmaQuant MS Q and the thereby enhanced precision, it was possible to correctly analyze lab-fortified matrix samples adding only 10 % to the actual sample concentration.

Precision

The relative standard deviation (RSD) was used as a parameter to assess the precision of the measurements. On average, a RSD of 1.5 % was achieved. The results for selenium were less precise due to its inherent low ionization efficiency resulting in only a low count rate. Precision and accuracy of the certified reference materials and lab-fortified matrices are shown in Figure 3. It can be seen that all recovery rates are within 90 to 110 % while the RSD is <2 % for low concentrations (LFM +1 ppb, NIST 1640a) and ≈1 % for higher concentrations (LFM +10 ppb, NIST 1643f). The required RSD <5 % for a 10/100 ppb tuning solution standard (depending on sensitivity) to verify instrument stability was achieved for all elements.

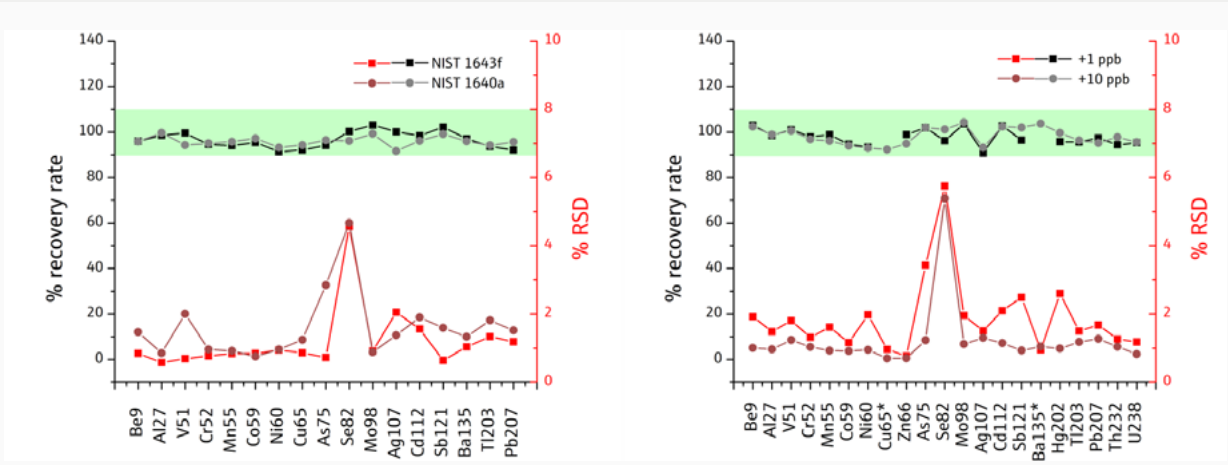

Figure 3: Recovery rate and precision of certified reference materials and lab-fortified blanks. All measurements are within the range specified. The spike concentration of +1 ppb was <5 % of the sample concentration for Cu and Ba and was excluded.

Speed of analysis

With the PlasmaQuant MS Q, 60 samples per hour can be measured with very high precision (mean RSD <1.5 %) allowing to precisely determine LFMs adding only 1 ppb. These results surpass requirements of the U.S. EPA method 200.8 and the European drinking water directive by far, meeting even much stricter requirements and more demanding regulations. However, for many applications not only precision and accuracy but also the speed of analysis are important parameters. A higher sample throughput significantly reduces the cost per sample. If the requirements for the precision of the analysis are not the main priority, the spectrometer's unmatched sensitivity allows to further boost sample throughput to >80 samples per hour still delivering competitive precision (mean RSD 2.2 %) as shown in Figure 4.

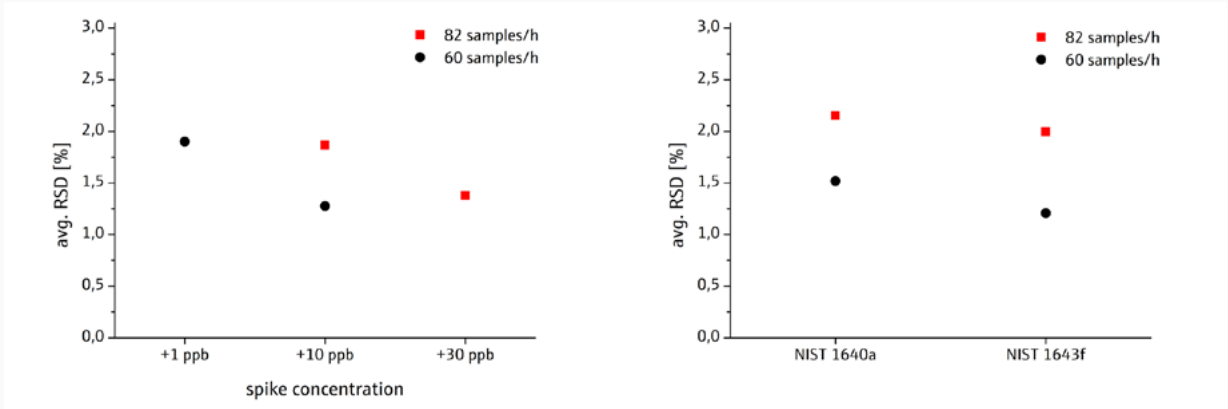

Figure 4: RSD of matrix spikes and certified reference materials measured with two different speeds. The outstanding sensitivity allows to measure 82 water samples per hour with competitive precision.

Robustness

The recovery rate was evaluated as a function of time in order to assess the stability of the instrument and the robustness of the method. The stability of the recovery rates of the certified reference materials, laboratory-fortified matrices and internal standards were excellent during the analyses over the entire mass range. Therefore, the PlasmaQuant MS Q is well suited for routine applications requiring a high sample throughput over a long time (Figure 5).

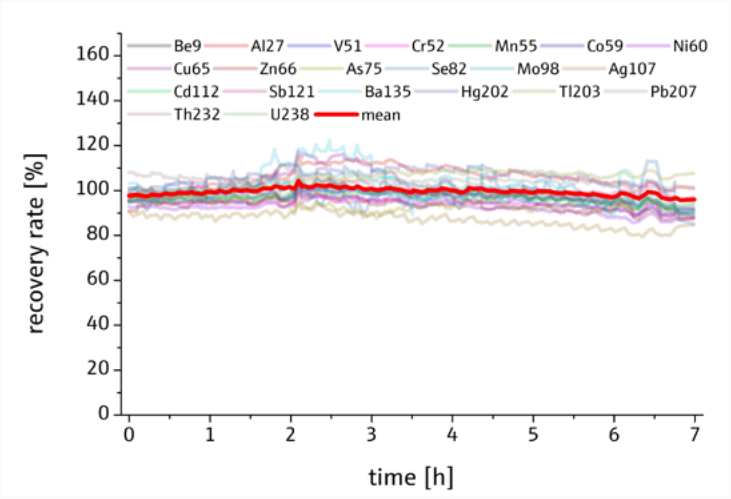

Figure 5: Recovery rate of the certified reference materials and LFMs as a function of time. Stable and accurate results were measured on all masses for 7 hours proving the robustness of instrument and method.

Conclusion

The costs per sample are directly linked to sample throughput and limited by the precision that needs to be achieved. The unmatched sensitivity of the PlasmaQuant MS Q and the resulting precision advantage allows to achieve the highest sample throughputs in the ICP-MS market. The requirements of the U.S. EPA 200.8 regulation are surpassed by far and the performance is maintained for hours proving the method's robustness. By consuming only 50 % argon gas compared to a conventional ICP-MS, the mass spectrometer by Analytik Jena has the lowest running costs on the ICP-MS market.
The combination of minimal running costs and highest sample throughput results in the lowest costs per sample, making the PlasmaQuant MS Q the ideal solution for customers who need to routinely measure a large number of samples.

References

[1] Sample Introduction Accessories for the PlasmaQuant MS Series (TechNote, Analytik Jena)

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Version 1.0
en · 12/2020