

ICP-OES detection limits versus speed of analysis

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ABSTRACT

Purpose: This poster shows a comparison of detection limits achieved with different acquisition times and gives an outlook on ways to improve detection limits without compromising speed. As an example, optimum parameters for a key application of ICP-OES analysis are presented.

Methods: Detection limits were established with different acquisition times in ultrapure water. The optimal acquisition times were used for analysis of drinking water according to EU Directive (98/83/EC) in combination with a Sprint Valve for fast sample uptake.

Results: By increasing acquisition times from 1 to 60 seconds, an improvement of detection limits of a factor of 5 to 30 was observed, depending on the element wavelength. Further significant improvements are only reached by applying special sample introduction techniques like hydride generation, ultrasonic nebulization and desolvation. A typical analysis time for the key application with optimally adapted sample introduction parameters was 75 seconds per sample.

INTRODUCTION

Limit of detection is a key characteristic of any ICP method as it defines the “minimum concentration of an analyte (substance) that can be measured and reported with a 99% confidence that the analyte concentration is greater than zero” (EPA, 40 CFR Part 136¹). It is calculated as three times the standard deviation of a repeated analysis when the concentration reaches zero. Detection limits depend on multiple factors in the process of sample preparation and analysis. An important factor that can enhance or decrease detection limits is the time of acquisition of the signal. With longer acquisition times, short term variations in signal intensities are smoothed out which leads to improved detection limits. However, in this case the improvement of detection limits comes along with an increase in analysis time, often unacceptable for routine applications. The user has to find a compromise between detection limits of the method and speed of analysis.

MATERIALS AND METHODS

Instrumentation

A dual view ICP-OES equipped with a switching valve rapid sample introduction system was used in conjunction with an autosampler. Detection limits were established with a standard sample introduction, consisting of a concentric nebulizer, cyclonic spray chamber and 2 mm center tube for different acquisition times (Table 1). For sped up analysis with the Sprint Valve the sample loop size and uptake time were adapted according to the amount of sample being used for the analysis.

Table 1. Analysis parameters.

Parameter	Setting
Pump tubing	Sample Tygon® white/white Drain Tygon® blue/yellow
Analysis pump speed	50 rpm
Spray chamber	Glass cyclonic
Nebulizer	Glass concentric
Nebulizer gas flow	0.5 L min ⁻¹
Coolant gas flow	12 L min ⁻¹
Auxiliary gas flow	0.5 L min ⁻¹
Center tube	2 mm
RF Power	1150 W

Figure 1. Dual view ICP-OES.



Sample Preparation

Calibration and spiked detection limit solutions were prepared from 1000 mg·kg⁻¹ single element solutions provided by SPEX CertiPrep (SPEX CertiPrep Group, Metuchen, US). The individual solutions were made up with 18 MΩ ultra-pure water and trace metal grade HNO₃ (Fisher Chemical, Loughborough, UK) to a final concentration of 1% HNO₃ according to the concentrations shown in Table 2.

RESULTS

Detection Limits

Detection limits were calculated by analyzing a spiked blank with seven replicates and multiplying the standard deviation by 3.14, this was repeated three times and an average taken. For comparison, different acquisition times of 1, 2, 5, 15, 30 and 60 s were used (Figure 2). No significant improvement of detection limits above 60 s acquisition time were achieved. Each step of increase in acquisition times with a factor of two to three lead to an average improvement of the detection limits of factor 1.4 to 1.9 (see Table 3).

Table 3. Average improvement factors for detection limits when increasing acquisition time.

Acquisition time 1	1	2	5	15	30
Acquisition time 2	2	5	15	30	60
Improvement factor for DL	1.7	1.8	1.9	1.5	1.4

An improvement of detection limits of up to a factor of 27 was observed when increasing the acquisition time for Al 167.079 nm from 1 s to 60 s (Table 4). The average improvement factor between acquisition times of 1 s and 60 s was 10.8.

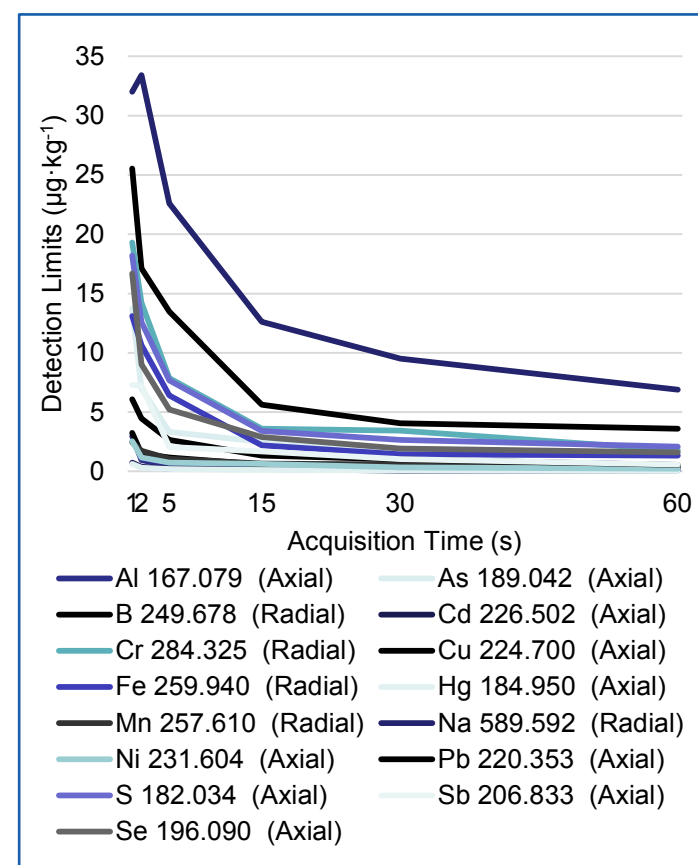
Table 4. Improvement factors for different analytes when increasing the acquisition time.

Element and wavelength (nm)	View	1-60	1-5	15-60	5-15
Increase factor of acquisition time					
Al 167.079	Axial	26.7	6.4	1.8	2.3
As 189.042	Axial	10.3	4.1	1.9	1.3
B 249.678	Radial	7.1	1.9	1.6	2.4
Cd 226.502	Axial	8.8	3.1	2.3	1.2
Cr 284.325	Radial	10.7	2.5	2.0	2.2
Cu 224.700	Axial	11.0	2.8	2.0	2
Fe 259.940	Radial	9.8	2	1.6	2.9
Hg 184.950	Axial	11.8	3.4	2.2	1.6
Mn 257.610	Radial	6.3	2.3	1.7	1.6
Na 589.592	Radial	4.7	1.4	1.8	1.8
Ni 231.604	Axial	11.3	3.4	2.8	1.2
Pb 220.353	Axial	11.0	2.3	2.4	2
S 182.034	Axial	8.7	2.4	1.6	2.2
Sb 206.833	Axial	12.8	3.6	2.9	1.2
Se 196.090	Axial	10.4	3.2	1.8	1.8
Average improvement of DL		10.8	3.0	2.0	1.9

Table 2. Concentration of elements in calibration and spiked detection limit (DL) solution.

Element	Calibration solution (mg·kg ⁻¹)	Spiked DL solution (µg·kg ⁻¹)
Hg	0.01	0.5
Cd	0.15	1.5
Mn	0.3	3
Ni	0.4	4
Cu	0.5	5
Al	0.75	7.5
As, Pb, Sb	1	15
Fe	1.5	15
S, Se	2	20
B, Cr	2.5	25
Na	6.5	65

Figure 2. Detection limits of various analytes in dependence of different acquisition times.

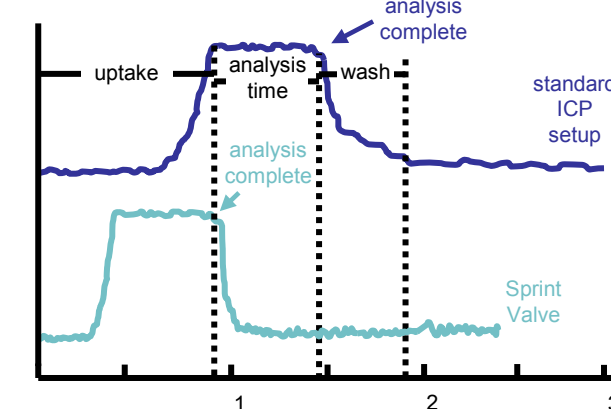


All collected detection limit improvement factors were compared to the increase factor of the according acquisition times used. Figure 3 shows that there is no significant improvement of detection limits above acquisition time increase factors of 60.

Analysis Time

Total analysis time typically consists of the uptake time that the sample needs to reach the plasma, the actual analysis time where data is acquired and a wash time to rinse the system from the former sample analyzed. Shortening acquisition times leads to a decrease of method performance as shown in the previous section. To keep the performance of the analytical method, the uptake and wash time can be reduced by using a fast sample introduction system like the Sprint Valve.

Figure 4. Total analysis time with and without Sprint Valve.



By applying the Sprint Valve the uptake and wash time could be reduced by 30 s and 20 s, respectively. With the chosen sample introduction parameters the sample transport is 1.6 mL·min⁻¹. Optimum load times and possible analysis times were established for different loop sizes.

EU Directive 98/83/EC

As an example for a key application, the EU Directive 98/83/EC for the analysis of drinking water was used (also see Application Note 4317¹²). An analytical method using the Sprint Valve for fast sample introduction was established. Sprint Valve parameters can be found in Figure 5. Yttrium was used as an internal standard at a concentration of 1 mg·kg⁻¹. Drinking water was spiked at two times the method quantification limit (MQL; 3·DL).

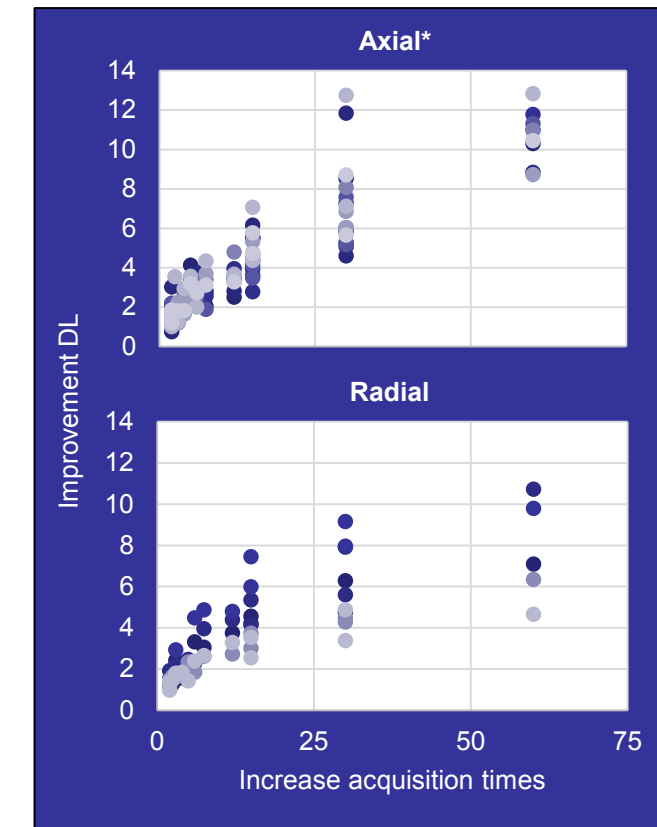
Table 6. Analysis settings for drinking water analysis according to EU directive 98/83/EC.

Parameter	Setting
Loop size	2.5 mL
Repeats	2
Acquisition time	Radial Vis 2 s Axial UV 15 s

The instrument was calibrated and a series of spiked drinking water solutions were run. Internal standard wavelengths were matched to analyte wavelengths by viewing mode (Radial Vis/Axial UV). Table 7 shows that the established MQLs are all better than the maximum contaminant levels (MCL) provided by the EU directive. The spike recoveries are within ± 12% of the spiked concentration.

The average analysis time per sample was 75 s. In comparison to analysis without the Sprint Valve, the speed of the analysis was increased by 50 s.

Figure 3. Detection limit improvement factors in dependence of the increase factor in acquisition time.



*Al167 is excluded for better overview.

Table 5. Sprint Valve load and analysis times for different loop sizes.

Loop (mL)	1	1.5	2	3.5	4.5
Load time (s)	3	4	5	7	9
Possible analysis time (s)	15	35	50	115	150

Figure 5. Sprint Valve parameters.

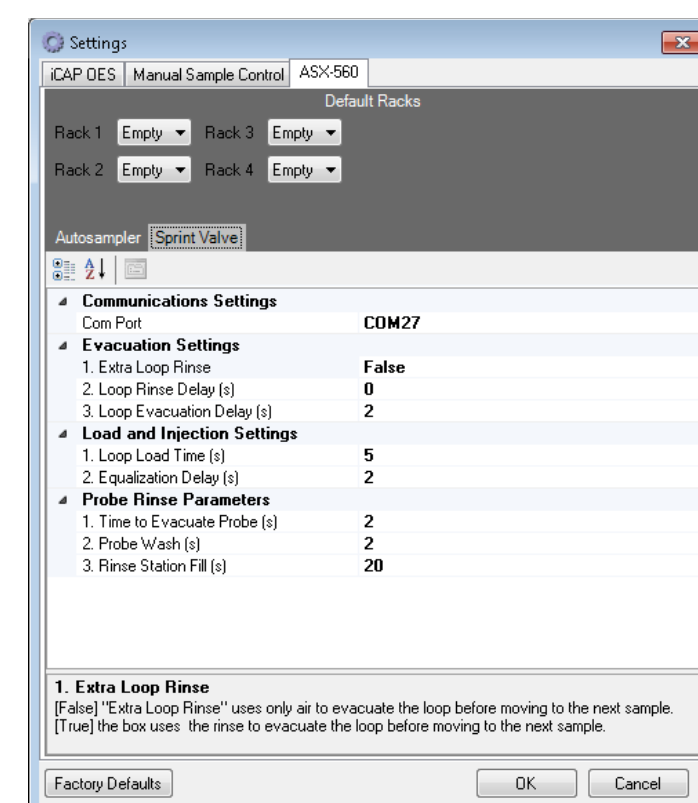


Table 7. Results for analysis of drinking water in mg·kg⁻¹.

Element	Internal standard	Required MCL	MQL	Spike recovery (%)
Al	Y224.306	0.2	0.001	101.6
As	Y224.306	0.01	0.008	99.3
B	Y324.228	1	0.052	99.8
Cd	Y224.306	0.005	0.001	99.5
Cr	Y324.228	0.05	0.043	104.7
Cu	Y224.306	2	0.002	98.0
Fe	Y324.228	0.2	0.032	100.2
Hg	Y224.306	0.001	0.0004	88.7
Mn	Y324.228	0.05	0.005	99.2
Na	Y324.228	250	0.1	87.3
Ni	Y224.306	0.02	0.002	95.5
Pb	Y224.306	0.01	0.004	97.1
SO ₄	Y224.306	250	0.09	107.3
Sb	Y224.306	0.005	0.005	100.1
Se	Y224.306	0.01	0.009	100.2

CONCLUSIONS

In ICP-OES, detection limits may be improved through increasing data acquisition times, however only to a certain extent. Above acquisition times of 60 s only minor improvements of detection limits are possible. Careful evaluation of detection limits in correspondence to the respective application helps to reduce acquisition time and therefore total analysis time, increasing sample throughput. Further improvements in detection capability can only be achieved by applying special sample introduction techniques like hydride generation, desolvation, and ultrasonic nebulization (USN), however compromising analysis times (Table 8).

In the present study it was demonstrated that analysis times can be reduced without compromising detection capability of the method and that the routine application of drinking water analysis is possible with an average throughput of 48 samples per hour.

Table 8. Detection limits for 60 s acquisition time with special techniques (µg·kg⁻¹).

Element	Hydride	Desolvation	USN
Al167.0	-	0.057	-
As189.0	0.029	0.17	0.159
Cd214.4	-	0.011	0.019
Cr205.5	-	0.013	0.022
Cu324.7	-	0.021	-
Fe259.9	-	0.064	0.065
Hg184.9	0.007	-	-
Mn257.6	-	0.0078	-
Pb220.3	-	0.16	0.12
Sb206.8	0.042	0.096	0.18
Se196.0	0.04	0.13	0.19

REFERENCES

- EPA, 40 CFR Part 136. Guidelines Establishing Test Procedures for the Analysis of Pollutants; Whole Effluent Toxicity Test Methods; Final Rule. Appendix B.
- Application Note 43171 – EU Water Analysis Using the Thermo Scientific iCAP 7400 ICP-OES Duo.

TRADEMARKS

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