

Ultra-fast ICP-OES determination of trace elements in water, conforming to US EPA 200.7 and using next generation sample introduction technology

Application note

Environmental

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Introduction

This work describes an implementation of the US EPA 200.7 guidelines for the analysis of trace elements in water using the Agilent SVS 2, a new and innovative sample introduction system for the Agilent 720/730 Series ICP-OES, to improve sample throughput.

A typical sample analysis cycle using an ICP-OES involves sample uptake at high pump rates from the autosampler to the plasma, followed by a stabilization delay to allow the plasma to return to equilibrium. The sample is then measured and rinsed from the system. A high-throughput contract laboratory using a conventional sample introduction system would typically measure a solution in approximately 2 min 30 s.

The SVS 2 improves sample introduction efficiency by greatly reducing sample uptake and washout times. This can more than double sample throughput, and significantly reduce operating costs. In addition, as there is a constant flow of solution to the plasma, plasma stability is improved and stabilization times are reduced.



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Instrumentation

An Agilent 720 Series simultaneous ICP-OES with axially viewed plasma and SPS 3 Sample Preparation System was used for this work.

The Agilent 720 features a custom designed CCD detector, which provides true simultaneous measurement and full wavelength coverage from 167 to 785 nm. The CCD detector contains continuous angled arrays that are matched exactly to the two-dimensional image from the echelle optics. The thermally stabilized optical system contains no moving parts, ensuring excellent long-term stability.

The SVS 2 has two software triggered valve positions. The first position allows the sample to be quickly loaded into a sample loop using a positive displacement pump operating at up to 500 rpm. The sample is loaded and ready to be aspirated into the plasma for measurement. The controlling software triggers the valves to switch and inject the sample into the ICP-OES. In a typical ICP-OES analysis without the SVS 2, sample is fast-pumped into the plasma, and the pump speed is then reduced to normal speed for the duration of the measurement. The change from high to low sample flow destabilizes the plasma and may result in an unstable signal. To allow the plasma to re-equilibrate at the normal pump speed, a stabilization time of 10–15 s is required to enable the signal to stabilize prior to measurement. Using the SVS 2, the flow of solution into the plasma remains constant. High pump speeds are used to fill the sample loop, but the sample loop is disconnected from the plasma during this step. The continuous flow of solution through the nebulizer ensures better plasma stability and allows much shorter stabilization delays to be used. In addition, an uptake delay is not required and a stabilization of <10 s is sufficient to load the sample loop and inject the sample into the plasma to attain a stable signal. Conventional ICP-OES systems operating without the SVS 2 would typically require an additional 25 seconds to perform the same function.

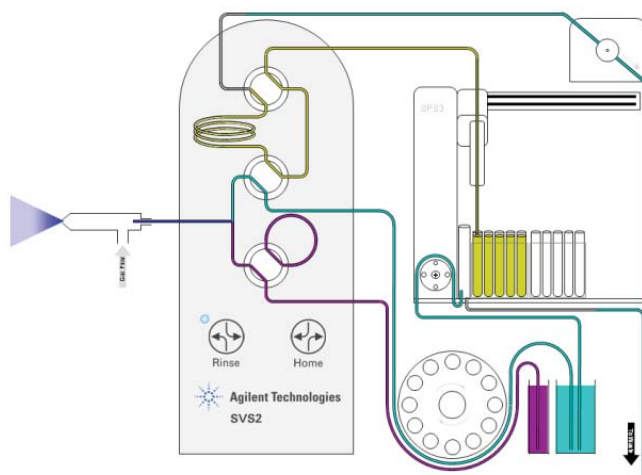


Figure 1. Agilent SVS 2 in sample load position

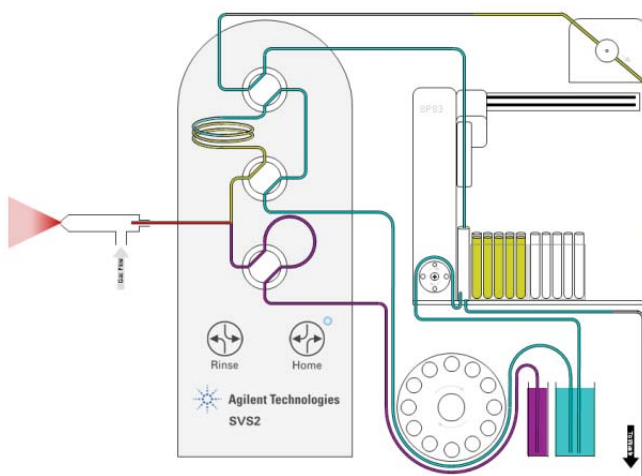


Figure 2. Agilent SVS 2 in sample inject position

For a complete description of the SVS 2 throughput advantages, hardware, and modes of operation see Reference 1.

Tables 1 and 2 list the operating conditions used for the ICP OES and the SVS 2 during this analysis.

Table 1. ICP OES instrument operating parameters

Note: All Glass sample introduction system (part number 9910117800) used.

Condition	Setting
Power	1.4 kW
Plasma gas flow	15 L/min
Auxiliary gas flow	1.5 L/min
Spray chamber type	Glass cyclonic (single-pass)
Torch	Standard one piece quartz axial
Nebulizer type	SeaSpray
Nebulizer flow	0.7 L/min
Pump tubing	Rinse/Instrument pump: white-white tabs (1.02 mm id) Waste: blue-blue tabs (1.65 mm id) Ionization buffer/Internal standard: black-black tabs (0.76 mm id)
Pump speed	12 rpm
Total sample usage	1 mL
Replicate read time	20 s
Number of replicates	2
Sample uptake delay time	12 s
Stabilization time	0 s
Rinse time	0 s
Fast pump	Off
Background correction	Fitted

Table 2. Agilent SVS 2 operating parameters

Condition	Setting
Sample uptake delay time	12 s
Stabilization time	0 s
Rinse time	0 s
Fast pump	Off
Background correction	Fitted
Nebulizer type	SeaSpray

Preparation of calibration solutions

Calibration and quality control solutions were prepared from Inorganic Ventures, Inc multi-element solutions designed for US EPA 200.7 methodology.

Method 200.7 standards — prepared 1:100 from:

- WW-Cal-1 A : Ag, As, B, Ba, Ca, Cd, Mn, Se, Sr
- WW-Cal-1 B : Sb
- WW-Cal- 2 : K, Li, Mo, Na, Ti
- WW-Cal-3 : Ce, Co, P, V
- WW-Cal-4 A : Al, Cr, Hg, Zn
- WW-Cal-4B : SiO₂, Sn
- WW-Cal-5 : Be, Fe, Mg, Ni, Pb, Ti

200.7 Quality Control Solutions — prepared 1:100 from:

- QCP-QCS-1 : Ag, Al, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, P, Pb, Se, Sr, Ti, V, Zn
- QCP-QCS-2 : Mo, Sb, SiO₂, Sn, Ti

200.7 Interference Check Solutions — prepared 1:100 from:

- 2007ICS-1 : B, Mo, Si, Ti
- 2007ICS-2 : Sb
- 2007ICS-3 : Ag, As, Ba, Be, Cd, Co, Cr, Cu, K, Mn, Ni, Pb, Se, Ti, V, Zn
- 2007ICS-4 : Al, Ca, Fe, Mg, Na

Laboratory Fortified Blanks — prepared 1:100 from:

- WW-LFS-1 : Ag, Al, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, P, Pb, Se, Sr, Ti, V, Zn
- WW-LFS-2 : Mo, Sb, SiO₂, Sn, Ti

Laboratory Fortified Matrix Spikes also prepared from WW-LFS-1 and 2.

The calibration and QC solutions were diluted with >18 MW/cm³ deionized water and stabilized in 5% v/v HNO₃ (Merck Ultrapur). The calibration blank was prepared from >18 MW/cm³ deionized water in 5% v/v HNO₃. An ionization buffer/internal standard solution of composition 1% CsNO₃/10 ppm Scandium was prepared from Merck Tracepur CsNO₃ and 1000 ppm Scandium stock.

Table 3. Calibration scheme

Elt	(nm)	Std 1A	Std 1B	Std 2	Std 3	Std 4A	Std 4B	Std 5
Ag	328.068	0.5						
Al	308.215					10		
As	188.98	10						
B	249.772	1						
Ba	493.408	1						
Be	313.042							1
Ca	315.887	10						
Cd	226.502	2						
Ce	418.659			2				
Co	228.615			2				
Cr	205.56					5		
Cu	324.754	2						
Fe	259.94							10
K	766.491		20					
Li	610.365		5					
Mg	279.078							10
Mn	261.02	2						
Mo	203.846			10				
Na	589.592			10				
Ni	231.604							2
P	214.914				10			
Pb	220.353							10
Sb	206.834		5					
Se	196.026	5						
Si	251.611						10	
Sn	189.925						4	
Sr	421.552	1						
Ti	334.941			10				
Tl	190.794							5
V	292.401				2			
Zn	213.857					5		

US EPA 200.7 guidelines summary

This method is a performance based set of guidelines for the analysis of 32 elements in drinking waters and waste waters. Preferred wavelengths, quality control and calibration procedures are defined. Method performance criteria such as method detection limits, spectral interference check procedures and linear range determination are also outlined. The Minimum QC requirements as described in section 9.0 Quality Assurance/Quality Control of Method 200.7 Rev 5.0 are as follows:

Demonstration of laboratory capability

Periodic analysis of:

- Laboratory reagent blanks
- Fortified blanks
- Other laboratory solutions as a continuing check of performance
- Maintain performance records of data quality

Initial demonstration of performance

- Establish Linear Dynamic Range (LDR)
- Measure Quality Control Solution to +5% Recovery
- Determine Method Detection Limits
- Spectral Interference Check

Monitor laboratory performance

Periodic analysis of:

- Laboratory Reagent Blank (LRB)
- Laboratory Fortified Blank (LFB)
- Instrument Performance Check Solution (IPC)
- Interference Check Solutions (ICS)

Assess analyte recovery and data quality

- Laboratory Fortified Matrix Spikes (LFM)
- Standard Reference Materials (if available)

The mnemonics used in the description of the 200.7 quality control scheme are shown in Table 4.

Table 4. Mnemonics used in the description of the 200.7 quality control scheme

Mnemonic	Description	Sample rate	Limit or %R
QCS	Quality Control Solution: Second source calibration check.	After initial calibration	95–105%
ICS	Interference Check Solution: Verifies effectiveness of correction processes.	3 months	-
IPC	Instrument Performance Check: Continuing drift and accuracy verification.	1 in 10 and end of run	90–110%
Blank	Measure blank as sample.	1 in 10	< IDL

For a full description of the US EPA 200.7 Guidelines including the appropriate standard and sample sequence, see Reference 2.

Initial demonstration of performance

Linear range analysis (LRA)

The LRA represents the upper concentration limit for each analyte of the ICP-OES linear range beyond which results cannot be reported without dilution of the sample. The maximum error for each calibration standard within the linear range cannot exceed 10%.

Table 5. Linear dynamic range

Element	LDR (ppm)	Element	LDR (ppm)	Element	LDR (ppm)
Ag 328.068	50	Cu 324.754	100	Sb 206.834	500
Al 308.215	1000	Fe 259.940	100	Se 196.026	500
As 188.980	200	K 766.491	50	Si 251.611	200
B 249.772	100	Li 670.784	100	Sn 189.925	70
Ba 493.409	10	Mg 279.079	1000	Sr 421.552	10
Be 313.042	2	Mn 261.020	200	Ti 334.941	20
Ca 315.887	100	Mo 203.846	100	Tl 190.794	100
Cd 226.502	20	Na 259.592	100	V 292.401	30
Ce 413.765	100	Ni 231.604	50	Zn 213.857	20
Co 228.616	100	P 214.914	1000		
Cr 205.552	40	Pb 220.353	100		

Method detection limits (MDL)

The MDL of each element was determined following the procedure defined in 40 CFR, part 136 Appendix B, as specified in Section 9.2.1 Method 200.7 revision 5. A standard solution containing analytes at a concentration of 3–5 times the instrument manufacturer’s suggested IDL was measured on three non-consecutive days.

Table 6. Method detection limits

Element	MDL (ppb)	Element	MDL (ppb)	Element	MDL (ppb)
Ag 328.068	0.1	Cu 324.754	2	Sb 206.834	2.7
Al 308.215	2.6	Fe 259.940	3	Se 196.026	4
As 188.980	3.3	K 766.491	15.8	Si 251.611	13
B 249.772	1.2	Li 670.784	1.5	Sn 189.925	1.3
Ba 493.409	2	Mg 279.079	2.8	Sr 421.552	0.2
Be 313.042	0.3	Mn 261.020	0.2	Ti 334.941	0.4
Ca 315.887	8.4	Mo 203.846	1.6	Tl 190.794	1.9
Cd 226.502	0.2	Na 259.592	5.4	V 292.401	2.1
Ce 413.765	1.3	Ni 231.604	1.4	Zn 213.857	0.6
Co 228.616	0.4	P 214.914	16.1		
Cr 205.552	1.1	Pb 220.353	1.8		

Initial QCS performance

As part of the initial demonstration of lab performance, it is necessary to analyze a quality control solution and achieve a recovery of $\pm 5\%$ of the true values for each element.

Table 7.

Element	%R	Pass/fail	Element	%R	Pass/fail
Ag 328.068	99.2	Pass	Mn 261.020	103.2	Pass
Al 308.215	99.2	Pass	Mo 203.846	99.6	Pass
As 188.980	101	Pass	Na 259.592	98.1	Pass
B 249.772	101	Pass	Ni 231.604	101.2	Pass
Ba 493.409	99.4	Pass	P 214.914	98.6	Pass
Be 313.042	102	Pass	Pb 220.353	101.5	Pass
Ca 315.887	102	Pass	Sb 206.834	92.7	Pass
Cd 226.502	101	Pass	Se 196.026	100.3	Pass
Ce 413.765	99	Pass	Si 251.611	99	Pass
Co 228.616	99.8	Pass	Sn 189.925	100.6	Pass
Cr 205.552	104	Pass	Sr 421.552	100.6	Pass
Cu 324.754	101.5	Pass	Ti 334.941	99.8	Pass
Fe 259.940	99.3	Pass	Tl 190.794	99.6	Pass
K 766.491	97.2	Pass	V 292.401	100.7	Pass
Li 670.784	97.5	Pass	Zn 213.857	98.5	Pass
Mg 279.079	96.9	Pass			

Spectral interference check

From METHOD 200.7 Revision 4.4 Section 7.15:

SIC solutions (containing similar concentrations of the major components in the samples, for example, ≥ 10 mg/L) can serve to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the SIC solution confirms an operative interference that is $\geq 10\%$ of the analyte concentration, the analyte must be determined using a wavelength and background correction location free of the interference or by another approved test procedure. The analysis of solutions 2007ICS-1 through 4 at the utilized wavelengths shows no significant spectral interferences when using the default ICP 720 background correction technique.

Analytical results

Reference materials were analyzed using the instrument and accessory conditions as defined in Tables 1 and 2. Their results are reported in Tables 8 to 10.

Instrument stability

The Instrument Performance Check (IPC) solution was analyzed every 10 samples over a period of six hours. The measured concentration of each element in the IPC must be within $\pm 10\%$ of the true value, the IPC results trends are a measure of the stability of the instrument. Figure 3 shows that conditions remain stable over the duration of the six hour period. The precision for all 32 elements was better than 2%.

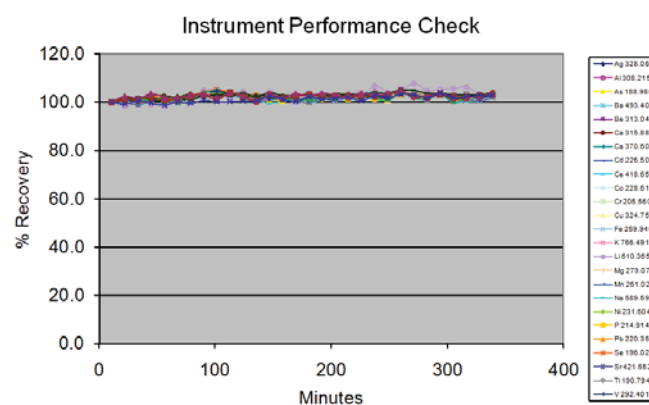


Figure 3. Long-term stability of instrument performance check (IPC) was better than 2% over 6 hours

Speed of analysis

An analysis sequence that conforms to US EPA protocols can be time-consuming since there are a large number of QC solutions required for conformance to the protocol. In this study, the use of the SVS 2 sample introduction system dramatically reduced analysis time, with a resulting tube to tube analysis time of 68 s.

Table 8. NIST SRM 1643e results.

Trace elements in water: sample source NIST US Dept of Commerce.

Element	Spec µg/L	Found	Dup	QC spike	Spike level	% rec LCS	RPD dup %	% spike rec
Ag 328.068	1.062	1.123	1.042	0.061	0.075	105.7	7.5	79.8
Al 308.215	141.8	151.936	150.101	2.172	2	107.1	1.2	101
As 188.980	60.45	57.051	59.461	0.862	0.8	94.4	4.1	100.6
B 249.772	157.9	159.72	161.242	0.473	0.3	101.2	0.9	104.4
Ba 493.408	544.2	534.966	537.325	0.728	0.2	98.3	0.4	96.5
Be 313.042	13.98	13.843	13.867	0.212	0.2	99	0.2	99.1
Ca 315.887	32300	30995.4	30966.2	31.982	1	96	0.1	98.7
Cd 226.502	6.568	6.565	6.586	0.209	0.2	100	0.3	101.2
Co 228.615	27.06	26.775	27.176	0.227	0.2	98.9	1.5	100.1
Cr 205.560	20.4	20.271	20.423	0.423	0.4	99.4	0.7	100.7
Cu 324.754	22.76	23.729	23.126	0.334	0.3	104.3	2.6	103.4
Fe 259.940	98.1	98.036	99.205	3.076	3	99.9	1.2	99.3
K 766.491	2034	2017.45	2026.59	12.149	10	99.2	0.5	101.3
Mg 279.078	8037	7901.66	7913.59	9.792	2	98.3	0.2	94.5
Mn 257.610	38.97	39.725	39.569	0.244	0.2	101.9	0.4	102.1
Mo 203.846	121.4	119.736	120.517			98.6	0.7	
Na 589.592	20740	19061.6	19007.1	21.896	3	91.9	0.3	94.5
Ni 231.604	62.41	61.763	60.219	0.557	0.5	99	2.5	99
P 214.914		41.893	56.332	6.178	6		29.4	102.3
Pb 220.353	19.63	21.138	20.422	1.028	1	107.7	3.4	100.7
Sb 206.834	58.3	55.64	54.15			95.4	2.7	
Se 196.026	11.97	14.118	13.377	1.973	2	117.9	5.4	97.9
Si 251.611		27.676	26.563	0.193			4.1	
Sr 421.552	323.1	320.029	324.499	0.517	0.2	99	1.4	98.5
Tl 190.794	7.445	8.162	7.773	2.008	2	109.6	4.9	100
V 292.401	37.86	36.671	36.843	0.339	0.3	96.9	0.5	100.8
Zn 213.857	78.5	79.832	79.133	0.284	0.2	101.7	0.9	102.1

Table 9. NIST SRM 1640a results.

Trace elements in natural water: sample source NIST US Dept of Commerce.

Element	Spec µg /L	Found	Dup	QC spike	Spike level	% rec LCS	RPD dup %	% spike rec
Ag 328.068	8.081	8.07	8.192	0.071	0.1	99.9	1.5	83.9
Al 308.215	53	53.305	52.266	2.012	2	100.6	2	97.9
As 188.980	8.075	6.677	8.427	0.777	0.8	82.7	23.2	96.3
B 249.772	303.1	321.542	305.727	0.596	0.3	106.1	5	91.5
Ba 493.408	151.8	151.023	147.974	0.337	0.2	99.5	2	93
Be 313.042	3.026	3.038	2.915	0.197	0.2	100.4	4.1	97
Cd 226.502	3.992	3.924	3.789	0.2	0.2	98.3	3.5	98
Co 228.615	20.24	20.064	19.738	0.216	0.2	99.1	1.6	98
Cr 205.560	40.54	39.52	38.749	0.429	0.4	97.5	2	97.4
Cu 324.754	85.75	84.949	83.357	0.378	0.3	99.1	1.9	97.7
Fe 259.940	36.8	37.472	35.993	2.938	3	101.8	4	96.7
K 766.491	579.9	573.916	563.117	10.598	10	99	1.9	100.2
Mg 279.078	1058.6	1042.15	1022.54	2.974	2	98.4	1.9	96.6
Mn 257.610	40.39	40.955	40.316	0.238	0.2	101.4	1.6	98.5
Mo 203.846	45.6	45.991	43.85	0.044		100.9	4.8	
Na 589.592	3137	2911.38	2859.63	5.829	3	92.8	1.8	97.3
Ni 231.604	25.32	24.24	24.058	0.51	0.5	95.7	0.8	97.2
P 214.914		47.423	58.729	5.933	5			117.7
Pb 220.353	12.101	13.404	13.04	1.01	1	110.8	2.8	99.7
Sb 206.834	5.105	5.71	5.237	0.004		111.9	8.6	
Se 196.026	20.13	23.159	20.121	1.912	2	115	14	94.4
Sr 421.552	126.03	127.037	124.371	0.315	0.2	100.8	2.1	94
Tl 190.794	1.619	1.839	1.846	1.977		113.6	0.4	
V 292.401	15.05	15.101	14.542	0.309	0.3	100.3	3.8	98
Zn 213.857	55.64	56.157	55.004	0.256	0.2	100.9	2.1	99.9

Table 10. Trace elements in certified waste water results.

Sample source: High Purity Standards, PO box 41727 Charleston SC. 29423 USA

Cat # CWW-TM-C.

Element	Spec µg /L	Found	Dup	QC spike	Spike level	% rec LCS	RPD dup %	% spike rec
Al	0.5	0.535	0.545	2.553	2	107.0	1.9	100.9
Sb	0.15	0.137	0.141	0.136	0	91.3	2.9	n/a
As	0.15	0.143	0.146	0.914	0.8	95.3	2.1	96.4
Ba	0.5	0.48	0.492	0.673	0.2	96.0	2.5	96.5
Be	0.15	0.14	0.144	0.331	0.2	93.3	2.8	95.5
B	0.5	0.513	0.52	0.84	0.3	102.6	1.4	109.0
Cd	0.15	0.146	0.149	0.341	0.2	97.3	2.0	97.5
Cr	0.5	0.476	0.485	0.86	0.4	95.2	1.9	96.0
Co	0.5	0.478	0.487	0.668	0.2	95.6	1.9	95.0
Cu	0.5	0.494	0.502	0.789	0.3	98.8	1.6	98.3
Fe	0.5	0.486	0.495	3.374	3	97.2	1.8	96.3
Pb	0.5	0.487	0.496	1.443	1	97.4	1.8	95.6
Mn	0.5	0.49	0.492	0.674	0.2	98.0	0.4	92.0
Mo	0.5	0.469	0.481	0.471	0	93.8	2.5	n/a
Ni	0.5	0.477	0.49	0.952	0.5	95.4	2.7	95.0
Se	0.15	0.151	0.149	2.051	2	100.7	1.3	95.0
Ag	0.15	0.144	0.148	0.211	0.075	96.0	2.7	89.3
Sr	0.5	0.481	0.492	0.673	0.2	96.2	2.3	96.0
Tl	0.15	0.145	0.149	2.101	2	96.7	2.7	97.8
V	0.5	0.48	0.49	0.77	0.3	96.0	2.1	96.7
Zn	0.5	0.498	0.509	0.696	0.2	99.6	2.2	99.0

Conclusion

Using the Agilent SVS 2 with an Agilent 720 Series axially viewed ICP-OES resulted in more than a doubling of sample throughput — from approximately 210 seconds² per sample without the SVS 2 to 68 seconds per sample using the SVS 2. Even with the improvement in productivity, analytical performance was maintained. Stability during a six hour period was better than 2% for all elements and detection limits exceeded the requirements of the US EPA.

As the tubing does not make contact with peristaltic pump tubing prior to being aspirated into the plasma, the inert sample path results in reduced sample carry-over.

References

1. D. Hoobin and E. Vanclay, Ultra-fast ICP OES determinations of soil and plant material using next generation sample introduction technology.
2. S. Bridger and M. Knowles, A complete method for environmental samples by simultaneous axially viewed ICP-OES following US EPA guidelines.

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