Rapid, interference-free analysis of water according to US EPA Method 200.7

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Goal

To develop a complete solution for the fast analysis of various water samples using the Thermo Scientific™ iCAP™ PRO Series ICP-OES Duo system according to the requirements of United States Environmental Protection Agency Method 200.7, including a demonstration of accuracy, robustness, and sensitivity, with application of interference corrections and quality control protocols.

Introduction

Monitoring natural and drinking waters is essential to ensure the well-being of an entire eco-system and consumer health. Levels of permissible organic and inorganic contaminants are regulated by local, national, and international legislation. In the United States of America, the Environmental Protection Agency (EPA) is responsible for setting and regulating national standards for the quality of drinking water and drinking water sources. In order to assess the quality of drinking, ground, and surface waters for the presence of inorganic contaminants (e.g., trace metals), laboratories follow EPA Method 200.7: Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma–Atomic Emission Spectrometry (also known as Inductively Coupled Plasma—Optical Emission Spectrometry).[1] This method details the preparation and analysis of various types of water samples using ICP-OES.

ICP-OES is widely used for the analysis of major and trace elements in various types of samples (e.g., food, environmental) due to its ability to detect low elemental concentrations, robustness, and wide linear dynamic range. Contract testing laboratories following regulatory methods, such as EPA Method 200.7, need robust analytical instrumentation to analyze a variety of samples (e.g., drinking water, wastewater, soil, sludges) daily. For these busy laboratories, it is important to meet the workload demand without compromising the quality of data.

The correction of spectral interferences is a requirement of EPA-approved analytical methods, such as Method 200.7, to obtain accurate results. In ICP-OES, spectral interference correction is accomplished by applying Interelement Correction (IEC) factors to correct false positive or false negative results due to partial or direct spectral overlaps caused by interfering elements. Within advanced instrumentation software, an IEC feature automatically determines and applies IEC factors to the analytical results, which may be perceived concentrations due to direct or partial spectral overlaps. The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software, which controls the iCAP PRO Series ICP-OES instruments, includes a feature to automatically calculate IEC factors by concentration. The IEC feature is a simple workflow using limits to apply corrections and flags to identify data that has been corrected.

In this application note, a comprehensive analytical method for water analysis according to EPA Method 200.7 was developed and tested using the iCAP PRO XP ICP-OES Duo system operated by the Qtegra ISDS Software.[2] This application note compliments the existing application note AN44422, 'US EPA Method 200.7 using Thermo Scientific iCAP PRO XPS Duo ICP-OES',[3] which describes the EPA Method 200.7 workflow and validation. This work focuses on improvements in the speed of analysis, concentration-based interelement correction, and the robustness of the method for an extended analytical run.

Experimental

Instrument parameters and experimental conditions

The iCAP PRO XP ICP-OES Duo instrument, operated in Axial iFR and Radial iFR modes, was used in this study to measure the 32 analytes required by EPA Method 200.7. Details of the sample introduction system components and instrument parameters are given in Table 1. Automated sample introduction was carried out using a Teledyne™ CETAC™ ASX-560 autosampler. Furthermore, to enhance the speed of analysis and improve sample throughput, the autosampler was coupled with the *ASXPRESS® PLUS* rapid sample introduction accessory. The parameters for both are shown in Table 2. This configuration dramatically reduces the sample uptake and rinse time between samples. An analysis time of 57 seconds per sample, including uptake, data acquisition, and rinse, was achieved. A 5 ppm yttrium internal standard solution, prepared in a matrix of 1% nitric acid and 1% hydrochloric acid, was added online to correct for drift and physical interferences.

Table 1. Instrument configuration and operating parameters

Instrument parameter	Setting
Spray chamber	Glass cyclonic
Nebulizer	Glass concentric nebulizer
Center tube	2.0 mm (quartz)
Torch	Thermo Scientific™ Enhanced Matrix Tolerance (EMT) Duo Torch
Pump speed	45 rpm
Flush pump speed	100 rpm
Nebulizer gas flow	0.5 L·min^{-1}
Auxiliary gas flow	0.5 L·min^{-1}
Coolant gas flow	12.5 L·min^{-1}
RF power	1,150 W
Replicates	3
Exposure time	Axial iFR—5 s Radial iFR—5 s

Table 2. Teledyne CETAC ASX-560 autosampler and *ASXPRESS PLUS* rapid sampling accessory parameters

CETAC ASX-560 autosampler parameters	
Uptake time	4 s
Wash time	0 s
***ASXPRESS PLUS* parameters**	
Extra loop rinse	False
Loop size	2 mL
Loop rinse delay	1 s
Loop evacuation delay	1 s
Loop load time	3 s
Equalization delay	2 s
Time to evacuate probe	1 s
Probe wash	3 s
Rinse station fill	5 s

Sample preparation

All water samples (drinking water, groundwater, surface water, and hard water) analyzed in the study were prepared (filtered and acidified) per the sample preparation method given in EPA Method 200.7. All calibration standards were prepared using multielement stock standard solutions containing different concentrations of target analytes to comply with the working range suggested in EPA Method 200.7. Four-point calibration curves were generated for 32 analytes using three calibration standards and a calibration blank. Details of the calibration standard solutions are given in Table 3. The linear range of each analyte wavelength was determined as specified in Method 200.7.

Table 3. Target analyte concentrations in calibration standard solutions

Elements	Standard 1 (mg·L⁻¹)	Standard 2 (mg·L⁻¹)	Standard 3 (mg·L⁻¹)
Ag	0.125	0.25	0.5
B, Ba, Be, Sr	0.25	0.5	1
Cd, Co, Cu, Hg, Mn, Ni, V, Ce	0.5	1	2
Sn	1	2	4
Cr, Li, Sb, Se, Tl, Zn	1.25	2.5	5
Al, As, Ca, Fe, Mg, Mo, Na, P, Pb, Si, Ti	2.5	5	10
K	5	10	20

Linearity and method detection limits

Method detection limits (MDLs) of the target analytes were determined for various types of water samples as per the guidelines specified in EPA Method 200.7, and the results are detailed in Table 4. Presented MDL values are the average of values obtained from two different iCAP PRO series ICP-OES instruments. The Linear Dynamic Range (LDR) determined for all analytes is also presented in the Table 4.

Considering the high concentrations expected for analytes, such as Al, Ca, Na, K, Mg, Fe, Li, and Sr, in environmental samples, they were measured using the radial plasma view. This approach helps to extend the LDR for these analytes, enabling analysis of various samples without the need to dilute and reanalyze. This also explains slightly higher MDLs achieved for these analytes, which are still sufficiently low for trace environmental analysis.

Table 4. Wavelength, correlation coefficient (R^2), LDR, and MDL achieved using the parameters in Table 1

Element	Wavelength (nm)	Plasma view	R^2	LDR (mg·L⁻¹)	MDL (µg·L⁻¹)
Ag	328.608	Axial	0.9998	>10	0.55
Al	308.215	Radial	0.9995	>1000	21.6
As	193.759	Axial	0.9996	>100	4.7
B	249.678	Axial	0.9994	>100	0.95
Ba	493.409	Radial	0.9993	>50	0.26
Be	234.861	Radial	0.9998	>50	0.13
Ca	315.887	Radial	0.9999	>100	6.9
Cd	226.502	Axial	0.9995	>10	0.15
Ce	413.765	Axial	0.9996	>50	1.68
Co	228.616	Axial	0.9997	>50	0.58
Cr	284.325	Axial	0.9996	>50	0.5
Cu	224.700	Axial	0.9997	>50	0.81
Fe	258.940	Radial	0.9999	>1000	1.7
Hg	194.227	Axial	0.9997	>100	1.04
K	766.490	Radial	0.9995	>1000	37.7
Li	670.784	Radial	0.9998	>100	2.0
Mg	279.079	Radial	0.9999	>1000	22
Mn	257.610	Axial	0.9997	>50	0.05
Mo	203.844	Axial	0.9994	>50	1.7
Na	589.592	Radial	0.9993	>100	11.9
Ni	231.604	Axial	0.9997	>50	0.9
P	177.495	Axial	0.9996	>100	3.16
Pb	220.353	Axial	0.9999	>100	1.51
Sb	206.833	Axial	0.9995	>100	3.3
Se	196.090	Axial	0.9997	>10	5.8
Si	251.611	Radial	0.9998	>2000	14.5
Sn	189.989	Axial	0.9996	>50	0.9
Sr	421.552	Radial	0.9994	>10	0.03
Ti	334.941	Axial	0.9997	>50	0.18
Tl	190.856	Axial	0.9998	>50	2.7
V	292.402	Axial	0.9993	>50	0.49
Zn	213.856	Axial	0.9997	>2	0.3

Method accuracy

Accuracy and precision of the method were determined by assessing the recovery of spiked analytes in different types of water samples (drinking, tap, ground, river, and hard water). The results of these experiments are presented in Figure 1. Spiked samples were analyzed intermittently over the entire analytical sequence of 14 hours, and recovery values were calculated as the average from the replicate measurements of each category of spiked samples. The data presented in Figure 2 represent the recoveries of target analytes spiked in Hard water-1, Hard water-2, and Hard water-3 with high concentrations of elements such as Na, K, Ca, Mg, Fe, Al, Cl, P, S, and C up to 1,000 mg/L. Recovery values are the average of replicate measurements of spiked samples.

Recovery values obtained for all analytes in both types of spiked samples were in the acceptable range of 85 to 115%, which is in accordance to the requirement mentioned in EPA Method 200.7.

Additionally, Laboratory Reagent Blank (LRB) and Laboratory Fortified Blank (LFB) were also analyzed in duplicate to assess method accuracy where % recovery results were found to be within the acceptance range specified in EPA Method 200.7 for all analytes. For further information on how to assess the accuracy, please refer existing application note AN44422, 'US EPA Method 200.7 using Thermo Scientific iCAP PRO XPS Duo ICP-OES'.

Additionally, a Quality Control sample (QCS) obtained and prepared according to the method protocol was analyzed immediately after the initial calibration and at the end of the analytical sequence (after 14 hours) to ensure the accuracy of the initial calibration throughout the analytical measurement. Table 5 presents the percent recovery of all analytes determined in QCS solution. The accuracy data obtained during the analysis of QCS solutions (initial and final) was observed to be in the range of 95 to 105%, which demonstrates that the accuracy of the calibration standards was within the specified range of ±5% of the stated concentrations of all analytes.

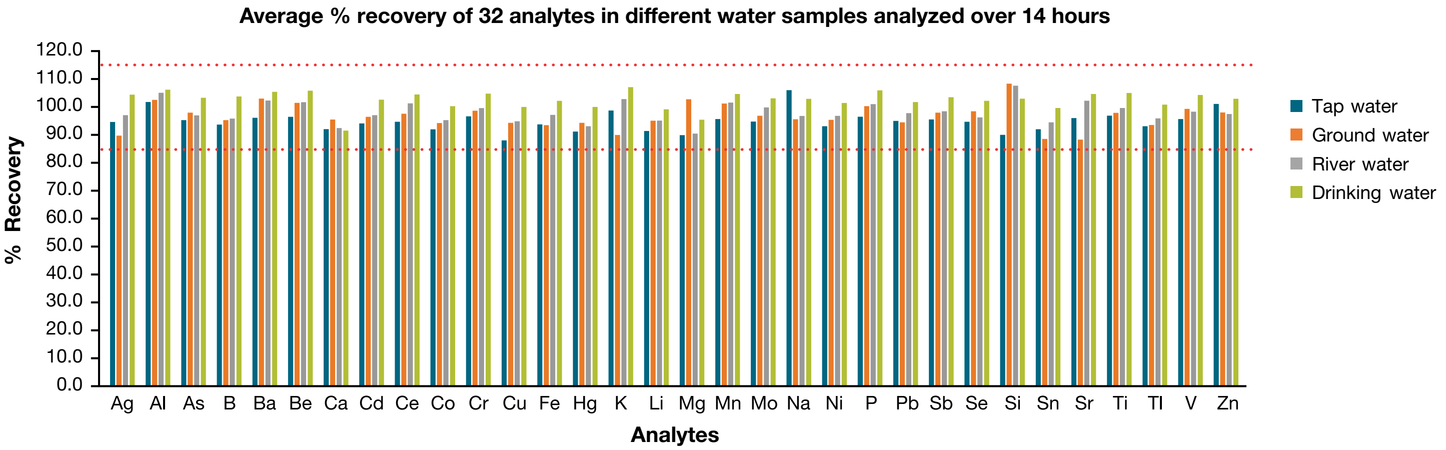


Figure 1. Average % recovery of 32 analytes in tap water, ground water, river and drinking water. Dashed lines indicate the ±15% allowed recovery limits as per EPA Method 200.7 requirements.

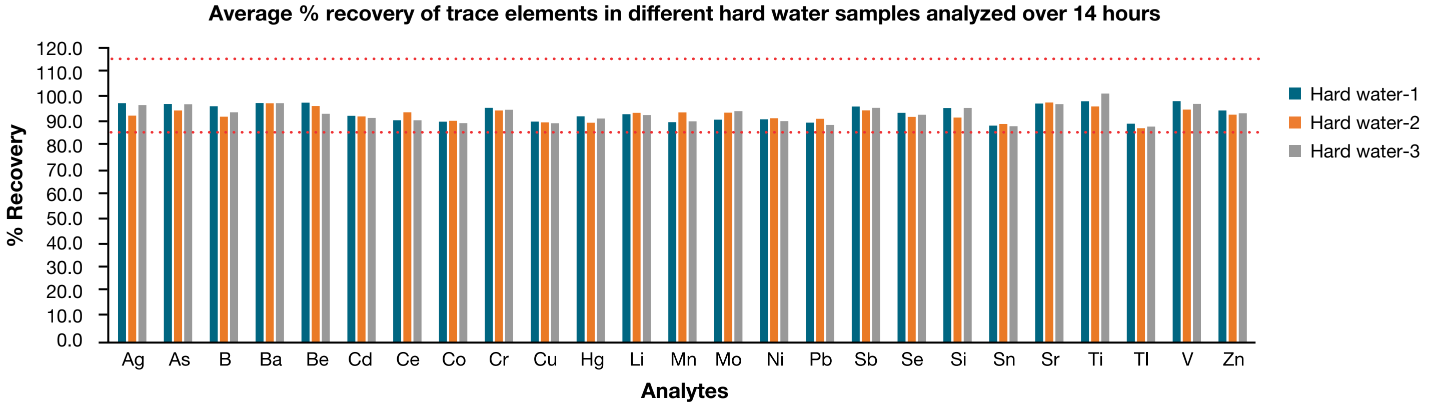


Figure 2. Average % recovery of trace analytes in different hard water samples

Table 5. Recoveries of all analytes observed in QCS solutions analyzed initially and at the end of the analytical sequence

Analyte	% Recovery		Analyte	% Recovery	
	Initial	After 14 hours		Initial	After 14 hours
Ag	103.0	100.3	Mg	102.8	103.1
Al	102.3	104.8	Mn	102.3	104.0
As	101.3	96.8	Mo	98.4	102.1
B	101.0	101.2	Na	104.7	103.9
Ba	96.3	103.5	Ni	100.5	100.4
Be	100.5	104.0	P	100.0	103.6
Ca	97.8	102.1	Pb	101.4	101.1
Cd	100.1	99.2	Sb	99.5	98.2
Ce	97.9	104.5	Se	99.2	96.7
Co	99.9	98.9	Si	98.6	100.3
Cr	104.3	103.5	Sn	99.8	97.4
Cu	99.9	97.2	Sr	101.8	103.9
Fe	95.4	103.7	Ti	101.3	99.6
Hg	98.8	96.2	Tl	103.5	100.3
K	100.2	103.9	V	100.8	100.5
Li	99.4	102.1	Zn	101.6	98.6

Instrument Performance Check (IPC)

As per the requirement of EPA 200.7 Method, IPC is used to evaluate the performance of the instrument with respect to a defined set of method criteria (Sections 7.11 and 9.3.4).[1] The IPC solution needs to be analyzed immediately after the instrument calibration and then after every 10 samples in the analytical sequence. The % recovery of the analytes in subsequent IPC samples analyzed over the entire period of the analytical sequence should fall within ±10% of the true value.

The IPC solution used in this experiment was prepared per the guidelines of EPA Method 200.7 and contained 2 mg·L^{-1} of most of the analytes, except 0.5 mg·L^{-1} of Ag and 10 mg·L^{-1} of K, P, and SiO$_2$. Figure 3 shows the percent recovery of 32 analytes against the true value in IPC solution analyzed periodically throughout the entire period of the analytical sequence, where all elements can be seen showing accuracy well within the set limit of ±10%.

Instrument robustness

Instrument robustness is critical for laboratories analyzing many different types of samples, from simple to complex matrices, daily. An internal standard is used to monitor drift in the analytical run, due to either signal enhancement or suppression caused by differences between the physical properties of the calibration standards and samples.

Figure 4 shows the behavior of the yttrium internal standard measured in both Axial iFR and Radial iFR plasma viewing modes. The stable and consistent recovery of yttrium throughout the experiment demonstrates the robustness of the entire analytical setup used in the experiment.

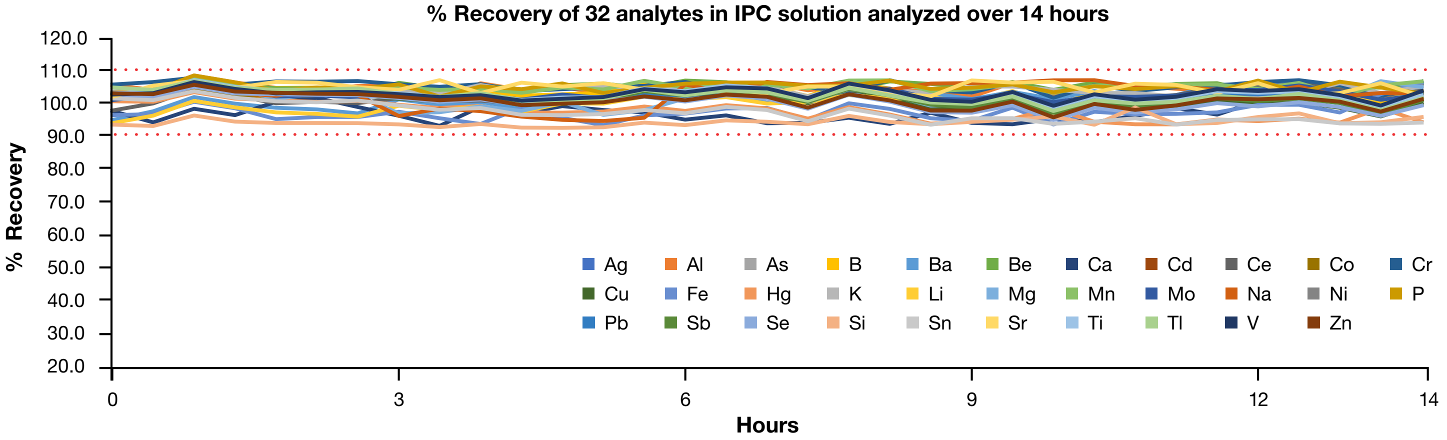


Figure 3. Analyte recoveries in the IPC solutions. Dashed lines indicate the ±10% allowed accuracy limits as per EPA Method 200.7 requirements.

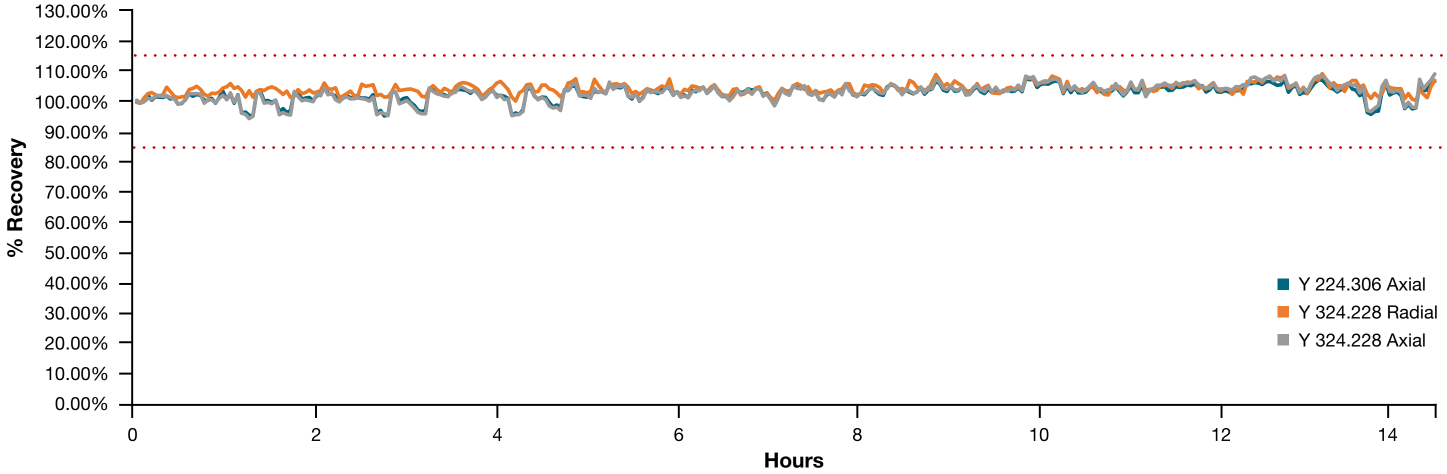


Figure 4. The % recovery of yttrium internal standard throughout the 14-hour analytical run sequence. Dashed lines indicate the ±15% generally allowed recovery limits.

Ensuring accurate analysis with interelement correction (IEC)

Spectral interferences in ICP-OES are due to background emission, emissions from high concentration elements, and overlap of a spectral line on an analyte, all of which must be corrected to obtain accurate results. Sections 3.17, 4.0, 7.13, and 9.3.5 of EPA Method 200.7 discuss these types of interferences and how to compensate for them. For spectral interferences due to direct or partial spectral overlap from an interfering element on an analyte, the concentration-based IEC functionality within the Qtegra ISDS Software simplifies the workflow for determining and applying IEC factors to ensure accurate and reliable results.

From the analyses of the SIC solutions, spectral interferences were observed for the analytes listed in Table 4. The simplified workflow used to determine and apply the IEC factors to resolve the interferents listed in Table 6 will be discussed.

Table 6. List of analytes and interfering elements determined during the analyses of single element SIC solutions

Analytes	Interferents	Analytes	Interferents
Ag	Ce	Mo	Ce
Al	V, Mo, Ce, Mn	P	Cu
As	V, Al	Pb	Al
Ca	Mo	Sb	Cr, Mo, Sn, Ti
Co	Ti	Se	Fe
Cr	Fe	Tl	Ce, Co, Mn, Ti, V
Cu	Fe, Ti, Mo	V	Ti, Ce
Hg	V, Mo	Zn	Ni, Cu, Fe
Mg	Ce		

Figure 5 shows a typical example of interelement interference on As at 193.759 nm due to spectral overlap caused by interfering elements present in mixed SIC solution, resulting in inaccurate measurement of As.

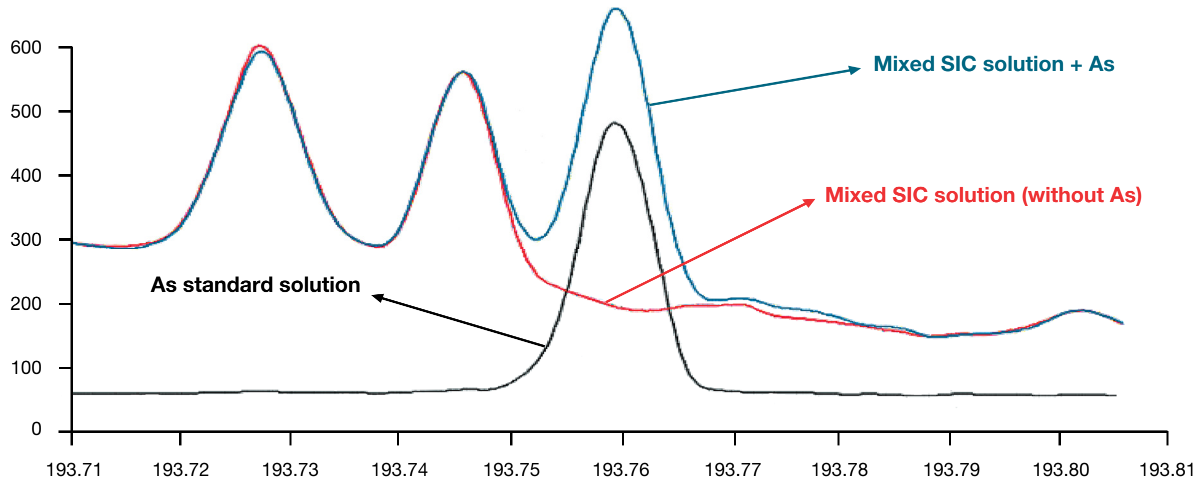
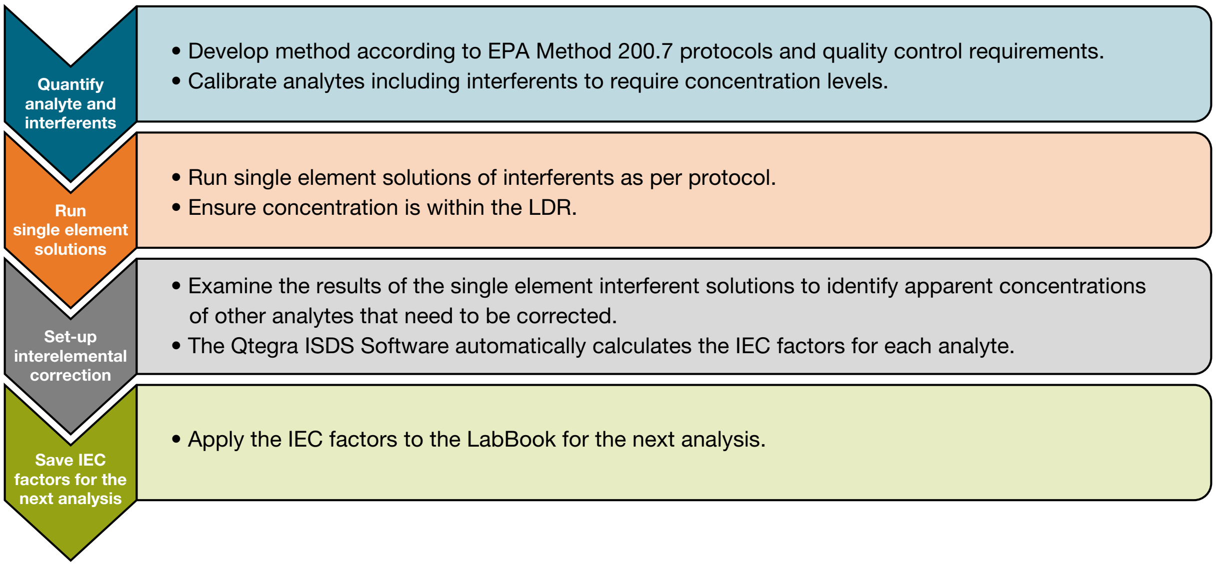


Figure 5. Overlay of emission spectrum obtained with As standard solution, mixed SIC solution, and mixed SIC solution with spiked As

To ensure the accurate measurement of these analytes in the presence of interferents, concentration-based IEC factors for each analyte were determined and applied to the apparent concentrations of the analytes. Figure 6 summarizes the typical IEC workflow that was followed in this study.



- Develop method according to EPA Method 200.7 protocols and quality control requirements.
- Calibrate analytes including interferents to require concentration levels.

- Run single element solutions of interferents as per protocol.
- Ensure concentration is within the LDR.

- Examine the results of the single element interferent solutions to identify apparent concentrations of other analytes that need to be corrected.
- The Qtegra ISDS Software automatically calculates the IEC factors for each analyte.

- Apply the IEC factors to the LabBook for the next analysis.

Figure 6. Typical workflow for determining IEC factors

The IEC factors determined following the protocol in Figure 6 were tested for accuracy by analyzing a mixed SIC solution containing 50 mg·L^{-1} of Cu, Cr, Mo, V, Ca, Ce, 200 mg·L^{-1} of Al, and 300 mg·L^{-1} of Fe. Analytes were spiked in the mix SIC solution to determine % recovery in the presence of interfering elements. Table 7 summarizes the analyte % recoveries obtained in the study.

Table 7. The % recoveries of 23 analytes spiked in the mix SIC solution

Analytes	% Accuracy	Analytes	% Accuracy
Ag	109.6	Na	102.6
As	95.0	Ni	91.6
B	90.8	P	94.3
Ba	94.9	Pb	92.6
Be	96.0	Sb	103.6
Cd	92.4	Se	92.6
Co	91.3	Sn	93.0
Hg	92.9	Sr	100.2
K	107.5	Ti	93.9
Li	105.0	Tl	91.9
Mg	90.4	Zn	98.1
Mn	95.0		

The recoveries obtained for the 23 analytes were within the range of 90 to 110%, indicating that the IEC factors determined and applied worked effectively to correct for interferences due to partial or direct spectral overlap of the interfering elements ensuring accurate measurement of all analytes.

Figure 7 presents a comparison of the percent accuracy obtained for P, As, and Sb spiked in the mixed SIC solution. Use of the IEC function to correct the observed analyte concentrations provides accurate results, where the original apparent concentrations (observed without IEC) suffer significantly and generate either false positive or false negative concentration data, leading to the inaccurate measurement.

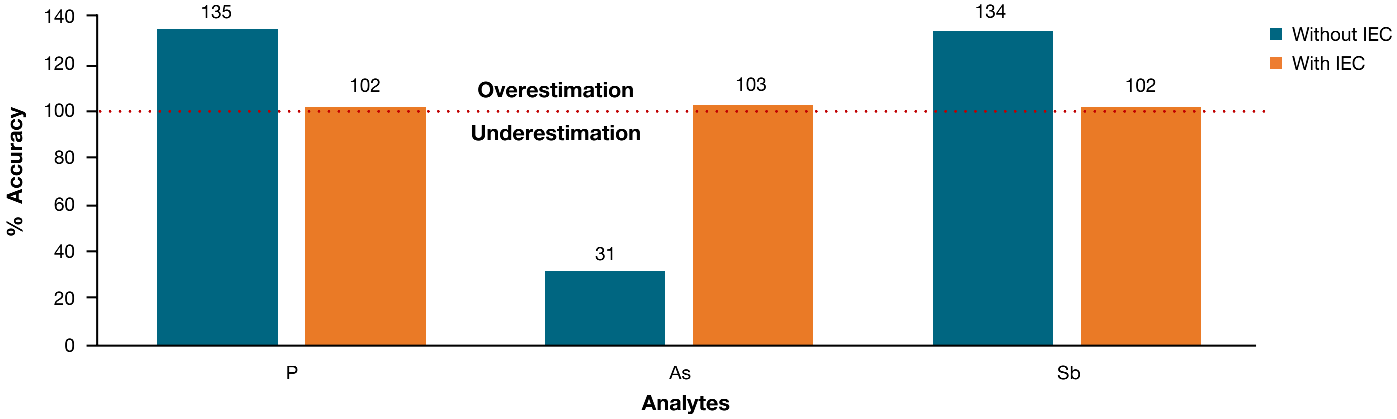


Figure 7. Comparison of percent accuracy data for P, As, and Sb in spiked mixed SIC solution obtained with and without IEC

Conclusion

This application note demonstrates how a method such as EPA 200.7 can be optimized for speed and robustness without compromising key performance criteria. The results obtained demonstrate the following:

- The method detection limits, linear dynamic range, accuracy, instrument performance with IPC and QCS solution, and robustness observed in the study suggest that the iCAP PRO XP ICP-OES Duo instrument can meet the requirements of EPA Method 200.7.
- The stringent quality control requirements of EPA analytical methods can be easily implemented during method development and in the assessment of sample and standard results during analysis using the comprehensive, built-in QC functionality within the Qtegra ISDS Software.
- Use of the iCAP PRO XP ICP-OES Duo instrument with the CETAC ASX-560 autosampler and *ASXPRESS PLUS* rapid sample introduction accessory reduced the sample analysis time to 57 seconds, compared to 132 seconds with the standard configuration, enhancing sample throughput dramatically. This improvement in analysis speed enables busy laboratories to address workload demands successfully, improving overall productivity.
- The concentration-based IEC functionality in the Qtegra ISDS Software ensures accurate sample results.

References

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