

Drinking Water Compliance Monitoring using US EPA Method 200.8 with the Thermo Scientific iCAP Q ICP-MS

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Key Words

iCAP Q, US EPA Method 200.8, Natural Waters, ICP-MS

Introduction

The United States Environmental Protection Agency (US EPA) first developed and published Method 200.8: “Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)” in 1994. This method is now widely used for the determination of twenty-two elements in ground, surface and drinking waters in both the United States and elsewhere. Large numbers of samples are often determined with this method as part of local and national regulatory compliance monitoring as well as by private contract laboratories.

ICP-MS instruments based on collision and reaction cell technologies are the technique of choice for accurate multi-elemental ICP-MS analysis in a wide variety of applications due to their ability to suppress polyatomic interferences in a wide range of sample types. The US Federal Register currently mandates that measurements made using EPA Method 200.8 for drinking water analysis must however rely on mathematical interference correction equations rather than collision and reaction cell technologies in order to achieve accurate results.

The Thermo Scientific iCAP Q ICP-MS was validated for use against Revision 5.4 of the US EPA Method 200.8 with the goal of completing a single measurement – consisting of uptake, data acquisition and washout – within 60s in order to maximize sample throughput in the routine, environmental laboratories performing these analyses.



Instrument configuration

A Thermo Scientific iCAP Qa ICP-MS was used for all measurements since it is not equipped with collision cell technology. The instrument was therefore operated in standard (non collision cell) mode. In this mode, the QCell in the iCAP Q is not pressurized with a gas and acts as an ion guide. The sample introduction system used consisted of a Peltier cooled (3 °C), baffled quartz cyclonic spray chamber, PFA-ST nebulizer and quartz torch with a 2.5 mm i.d. removable quartz injector. All samples were presented for analysis using a SC-4DX autosampler with integrated 7-port FAST valve from Elemental Scientific (Omaha, NE, USA).



Figure 1:
The Thermo Scientific iCAP Q

General Analytical Conditions

Table 1. Instrument operating parameters.

| Parameter | Value |
|--|---|
| Peristaltic pump speed | 40 rpm |
| Pump tubing | orange/green tubing for both carrier (sample) and internal standard |
| Nebulizer | PFA-ST |
| Interface cones | Nickel |
| RF Power | 1550 W |
| Cool gas flow | 14 L/min |
| Auxiliary gas flow | 0.8 L/min |
| Nebulizer gas flow | 0.97 L/min |
| Number of sweeps | 20 |
| Dwell Times | 0.001 - 0.02 ms |
| Data points per isotope | 1 |
| Replicates per analysis | 3 |
| Signal stabilization time | 15 s |
| FAST sample loop | 0.5 mL |
| FAST uptake time | 3 s |
| FAST rinse time (dual stations) | 1+3 s |
| Total analysis time (sample to sample) | 56 s |

Analysis Times

In order to achieve the high throughput required by monitoring bodies and private contract laboratories, per sample analysis times have to be to highly efficient and as short as possible. With the improved sensitivity of the iCAP Qa, integration times per isotope can be significantly reduced for EPA Method 200.8 analyses, leading to the shortest data acquisition times possible. The ESI FAST sample introduction system uses a series of technologies to reduce uptake of and washout between samples, minimizing these potentially significant analysis overheads.

Through the combination of the iCAP Q and the FAST sample introduction system, sample to sample analysis times (including uptake, data acquisition and washout) of < 60 s were achieved for the routine analysis of samples to US EPA Method 200.8 (Figure 2).

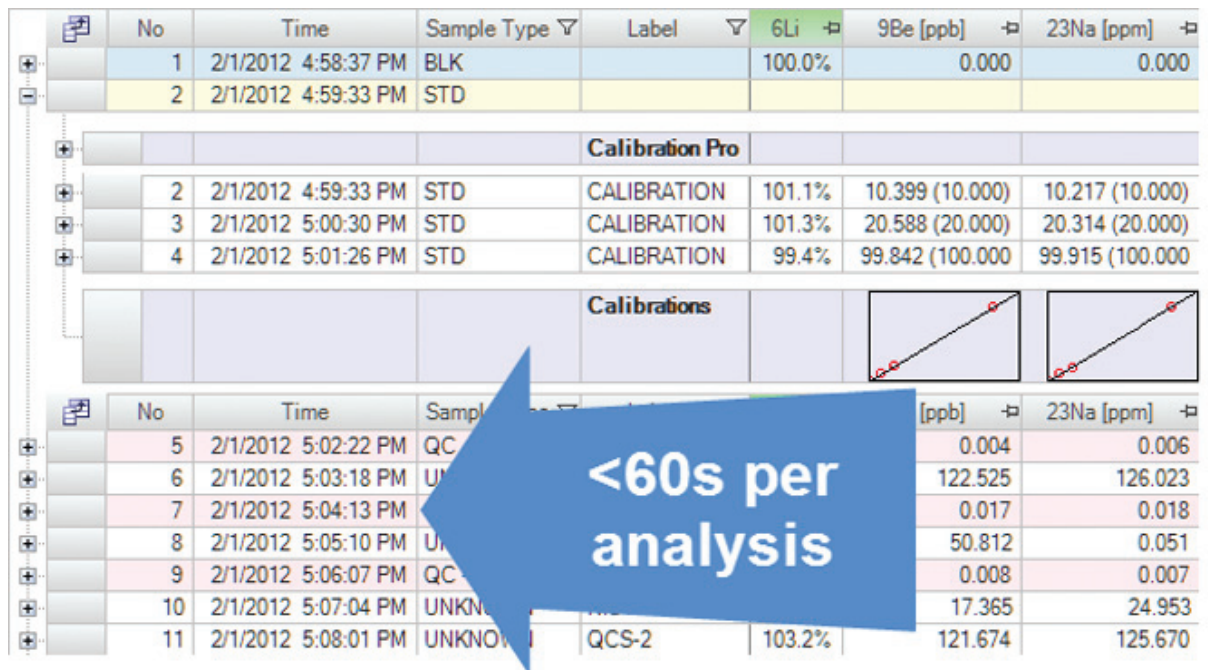


Figure 2. iCAP Qa total analysis times of <60s for US EPA Method 200.8

US EPA ICP-MS Method 200.8

Method 200.8 provides guidelines on general laboratory practices such as sample preparation, standard concentrations and correction equations. It also provides specific rules on various analytical practices that must be followed, including elements and their required isotopes, quality control practices and instrument validation.

Method 200.8 was designed to generate accurate data for regulatory compliance monitoring of drinking waters and natural water sources for inorganic contaminants under the Federal Regulation 40 CFR parts 141 & 143. This regulation states that all supplied waters must comply with the Maximum Contaminant Levels (MCLs) for the contaminants specified in the National Primary Drinking Water Regulations (NPDWRs). Further contaminants are given suggested maximum values in the National Secondary Drinking Water Regulations (NSDWRs) as these elements will affect water properties such as taste and color. The Unregulated Contaminant Monitoring Rule 3 (UCMR-3) requires that measurements are taken and recorded for 2 areas at every water treatment plant, the metals to be tested and their maximum reporting limits (MRL) are shown in table 2.

When Method 200.8 was originally defined ICP-MS instrumentation was at an early stage of development and, as a result, the major elements typically found in potable waters (sodium, magnesium, potassium and calcium) were not included in the list of analytes. With the iCAP Qa however, these matrix elements can be included in a single data acquisition.

Table 2 lists the MCLs and Maximum Contaminant Level Goals (MCLGs) that the EPA defines as the maximum level of an element in drinking water at which no known or anticipated adverse effect on the health of persons would occur. The Method Detection Limits (MDLs) achievable using the iCAP Qa in this work are listed for comparison and in all cases are significantly below the MCL requirements, as well as the minimum reporting levels (MRL) required by UCMR3.

Table 2. US EPA National Drinking Water MCLs, MCLGs and iCAP Qa method detection limits (MDLs) in this study

National Primary Drinking Water Regulations

| Contaminant | MCGL mg/L | MCL mg/L | iCAP Qa MDL mg/L |
|------------------|-----------|----------|------------------|
| Barium | 2 | 2 | 0.000027 |
| Copper | 1.3 | 1.3 | 0.000119 |
| Chromium (total) | 0.1 | 0.1 | 0.000022 |
| Selenium | 0.05 | 0.05 | 0.000084 |
| Uranium | 0 | 0.03 | 0.000006 |
| Lead | 0 | 0.015 | 0.000007 |
| Arsenic | 0 | 0.01 | 0.000011 |
| Antimony | 0.006 | 0.006 | 0.000010 |
| Cadium | 0.005 | 0.005 | 0.000017 |
| Beryllium | 0.004 | 0.004 | 0.000013 |
| Thallium | 0.0005 | 0.002 | 0.000007 |
| Mercury | 0.002 | 0.002 | 0.000011 |

National Secondary Drinking Water Regulations

| Contaminant | MCL mg/L | iCAP Qa MDL mg/L |
|-------------|---------------|------------------|
| Zinc | 5 | 0.000175 |
| Copper | 1 | 0.000119 |
| Iron | 0.3 | 0.004242 |
| Aluminum | 0.050 - 0.200 | 0.000048 |
| Silver | 0.1 | 0.000013 |
| Manganese | 0.05 | 0.000009 |

Unregulated Contaminant Monitoring Rule 3

| Contaminant | MRL mg/L | iCAP Qa MDL mg/L |
|------------------|----------|------------------|
| Strontium | 0.0003 | 0.000008 |
| Cobalt | 0.001 | 0.000006 |
| Molybdenum | 0.001 | 0.000018 |
| Vanadium | 0.0002 | 0.000018 |
| Chromium (total) | 0.0002 | 0.000022 |

Implementation of US EPA Method 200.8

Prior to calibration and analysis the iCAP Qa must be validated for use. The defined protocol requires a 30 minute instrument warm-up time followed by a check of mass calibration, peak resolution and stability using a method specific tuning solution containing beryllium, magnesium, cobalt, indium & lead such that:

1. The mass calibration and the peak width, at 5% peak height, at low and high mass is verified by a mass scan of $^{24, 25, 26}\text{Mg}$ and $^{206, 207, 208}\text{Pb}$. The position of each measured peak maximum **must be <0.1 amu** from the true isotope mass.
2. The resolution of each of the Mg and Pb isotopes **must be 0.65 – 0.85 amu peak width at 5% peak height** to provide optimum sensitivity and freedom from neighbouring isotopes. For example ^{55}Mn and ^{56}Fe could interfere with each other at high ion count rates due to spectral overlap (abundance sensitivity).
3. The required sensitivity and stability across the mass range is verified by running an acquisition with 5 replicates under the optimised tuning conditions and **RSDs must be <5%** for all analytes. Originally the tuning solution was specified at 100 or 10 µg/L but due to the very high sensitivity of the iCAP Qa only a 1 µg/L is required.

In order to improve performance, 1 µg/L of Ba and Ce were added to the iCAP Qa performance report to allow for monitoring and (if necessary) optimization of the levels of potential interferences. The levels of $^{137}\text{Ba}^{++}/^{137}\text{Ba}$ (doubly charged) and $^{140}\text{Ce}^{16}\text{O}/^{140}\text{Ce}$ (oxides) are excellent indicators of the levels of interferences to be expected when analyzing actual samples.

According to Method 200.8, interference corrections are required to minimize false positives recorded for elements suffering from spectral interferences in the ICP-MS mass spectrum. As interference corrections are calculated under a specific auto-tuning regime, any element(s) suffering from interferences analyzed under the same tuning conditions will be accurately corrected. Both isobaric (where isotopes of different elements are coincident at the same nominal mass) and polyatomic (where more than one isotope combines to form an interference at the same nominal mass) interference corrections are required. Isobaric correction will depend on the mass bias of the ICP-MS used and tuning; for example if ^6Li is used as an Internal Standard it must be corrected for any natural lithium in the sample. The magnitude of any polyatomic corrections will be related to the observed level of $^{140}\text{Ce}^{16}\text{O}/^{140}\text{Ce}$ as well as mass bias over the mass difference between the matrix element and its oxide. Doubly charged interferences (M^{++}) are not usually an issue for drinking water samples unless they contain high levels of rare earth elements (REE) that may, for example, interfere with ^{75}As ($^{150}\text{Sm}^{++}$, $^{150}\text{Nd}^{++}$) and ^{82}Se ($^{164}\text{Dy}^{++}$, $^{164}\text{Er}^{++}$).

The 200.8 Performance Report available in the Thermo Scientific Qtegra control software of the iCAP Qa automatically checks the detector cross calibration, mass accuracy and peak width, sensitivity, instrument background (instrument detection limit) and signal stability for all isotopes as required by the Method. The Performance Report also monitors the levels of $^{137}\text{Ba}^{++}/^{137}\text{Ba}$ and $^{140}\text{Ce}^{16}\text{O}/^{140}\text{Ce}$ to ensure that the instrument is within acceptable limits for accurate analysis of any isotopes suffering from (potential) interferences. If any of the method defined instrumental performance requirements fail to meet the required criteria, the Qtegra software will automatically perform a Method 200.8 specific AutoTune of all necessary parameters. Due to the high robustness and stability of the iCAP Qa sample introduction system, interface and ion lenses, regular re-tunings are not required.

Internal Standards: Method 200.8 specifies the use of at least three Internal Standards for the correction of matrix effects, including matrix suppression / enhancement and sensitivity drift. Nine possible isotopes can be used as Internal Standards: ^6Li , ^{45}Sc , ^{89}Y , ^{103}Rh , ^{115}In , ^{159}Tb , ^{165}Ho , ^{175}Lu , and ^{209}Bi . They span the complete mass range and are generally used to correct analytes of similar mass, e.g. ^{208}Pb is usually corrected by ^{209}Bi . The recoveries for all the Internal Standards, relative to the original response in the initial calibration blank (automatically set by Qtegra software to 100%) must be within 60% - 125% for all blanks, standards, QC samples and unknowns. Any analysis falling outside of this range requires additional dilution and/or re-analysis of the failed sample(s) after additional rinsing of the sample introduction system or recalibration. These additional processes take time and reduce sample throughput. The iCAP Qa interface was specifically designed to minimize such effects and provides excellent long-term stability during the analysis of the high and varying matrix levels found in samples such as natural waters.

Internal Standard failure is automatically detected by the Qtegra software (Figure 3), flagging failures by predefined color coding in the online results display. In the example shown here, the NIST sample already contains one or more Internal Standard elements at a significant level.

| Label | %Li | %Sc | %Y | %Rh | %In | %Tb | %Ho | %Bi |
|----------------|--------|--------|--------|--------|--------|-----|-----|-----|
| QCS | 112.1% | 111.7% | 108.6% | 108.8% | 107.7% | | | |
| URS | 113.7% | 112.3% | 111.6% | 108.7% | 108.4% | | | |
| W8 | 114.0% | 114.8% | 112.2% | 108.4% | 107.1% | | | |
| W8Q | 113.1% | 112.8% | 112.8% | 108.4% | 108.3% | | | |
| NIST | 104.0% | 114.7% | 111.1% | 112.3% | 100.2% | | | |
| TAP-WATER | 111.3% | 112.4% | 108.7% | 108.4% | 102.8% | | | |
| TAP-WATER SPK1 | 112.0% | 112.8% | 111.1% | 108.7% | 108.4% | | | |

Figure 3. Automatic internal standard monitoring without $^6\text{Li}/^7\text{Li}$ correction

In this case, provided suitable additional Internal Standards are being monitored, it is permissible to recalculate the data using an alternate Internal Standard isotope. The NIST 1643e sample in Figure 3 contains 14.09 µg/L ^{209}Bi so all the elements usually corrected by ^{209}Bi can be corrected using ^{159}Tb without having to re-run the samples. NIST 1643e also contains 17.4 µg/L natural lithium, of which ~1.4 µg/L is ^6Li , resulting in a potential error in internal standard correction for elements close to lithium. This problem is corrected by implementing an interference correction factor (Figure 4).

| Label | Y | 100.0% | 100.0% | 100.0% | 100.0% | 100.0% |
|-------|---|--------|--------|--------|--------|--------|
| Sc | | 91.0% | 91.7% | 93.0% | 93.8% | 87.7% |
| Y | | 91.7% | 92.3% | 91.8% | 93.7% | 93.4% |
| Yb | | 91.0% | 91.8% | 93.2% | 93.4% | 92.7% |
| Pr | | 91.7% | 92.8% | 92.0% | 93.4% | 93.8% |
| Bi | | 91.0% | 91.7% | 91.7% | 91.0% | 93.0% |
| Tb | | 92.0% | 92.4% | 93.7% | 93.8% | 93.8% |
| Tb+Yb | | 91.0% | 92.0% | 91.7% | 93.7% | 93.4% |

Figure 4. Automatic internal standard monitoring with $^6\text{Li}/^7\text{Li}$ correction activated

The Internal Standard solution may be manually added by pipetting from a multi-element mix into each blank, standard and sample or may be automatically added “on-line” using a mixing ‘Y’ connector before the nebulizer. The concentration of each element in the Internal Standard mixture should take into account the sensitivity of the ICP-MS at each mass. Internal Standard stability is very important since all the data generated for the target analytes are corrected after each replicate, therefore an Internal Standard with a high RSD will compromise the precision of the analyte it is correcting. With the iCAP Qa configuration used in this work an Internal Standard mixture of 20 µg/L ^6Li , and Sc, 4 µg/L Ga, Y, In, Tb and Bi was added on-line using the 7 port FAST valve that generated a stable signal for each of the elements (Table 3).

Table 3. Internal standard sensitivity and stability from 5 one minute analyses. Intensities here are shown for the 1:1 diluted internal standard solution as measured.

| | ^6Li | ^{45}Sc | ^{71}Ga | ^{89}Y | ^{115}In | ^{159}Tb | ^{209}Bi |
|----------|---------------|------------------|------------------|-----------------|-------------------|-------------------|-------------------|
| Mean | 827687 | 1703271 | 209059 | 609781 | 743238 | 1048099 | 778287 |
| %RSD (%) | 0.4 | 1.3 | 1.6 | 2.3 | 1.1 | 3.0 | 2.2 |
| Mean | 847136 | 1705478 | 209404 | 608630 | 741727 | 1040486 | 789913 |
| %RSD (%) | 0.9 | 1.9 | 1.7 | 2.1 | 1.7 | 3.4 | 0.2 |
| Mean | 829906 | 1688674 | 209889 | 609846 | 744484 | 1026919 | 789655 |
| %RSD (%) | 0.4 | 2.7 | 3.0 | 0.7 | 1.4 | 2.6 | 0.5 |
| Mean | 839016 | 1666942 | 208506 | 607796 | 727153 | 1041726 | 778287 |
| %RSD (%) | 2.6 | 1.2 | 0.6 | 1.0 | 1.9 | 2.2 | 2.2 |
| Mean | 835335 | 1675004 | 208222 | 607010 | 745382 | 1022570 | 786512 |
| %RSD (%) | 0.2 | 0.9 | 1.6 | 2.6 | 0.2 | 0.8 | 3.5 |

Method Detection Limit: Method 200.8 defines a specific protocol for determining the Method Detection Limit (MDL). The analysis method, complete with data acquisition parameters, interference and internal standard correction is used to calibrate the instrument over the required reporting ranges and seven reagent blank solutions spiked at 2-5 times the estimated instrument detection limit (IDL) are analyzed over three non-consecutive days. The Standard Deviation (SD) of the spiked blank data sets over these three days is multiplied by 3.14 (Student’s T Test) to calculate the MDL. MDLs are therefore a function of each element’s sensitivity, day to day reproducibility, instrumental background signal as well as blank contamination and are often significantly higher than instrumental detection limits (IDLs). In practice, the iCAP Qa produces MDLs that are significantly beneath the required MCLs for all elements required in Method 200.8 (Table 2).

Interference Correction: Arsenic and selenium have relatively high ionization potentials that result in low elemental sensitivities. In addition these elements are often compromised by both background and matrix induced spectral interferences in a typical drinking water matrix; ^{75}As by $^{40}\text{Ar}^{35}\text{Cl}$ in a chloride containing matrix and ^{82}Se by $^1\text{H}^{81}\text{Br}$ (and ^{82}Kr) when bromine is present (and when significant krypton is found in the argon gas supply). All potential sources of spectral interferences must therefore be monitored and, in the case of Method 200.8 where collision cell technology to suppress interferences is not supported, to employ accurate interference equations (Table 4) to mathematically correct for these interferences. The use of interference equations also affects the MDL since the correction applied from the monitoring of potential interference source will propagate any errors.

In the iCAP Qa ICP-MS method described here, direct correction for $^{35}\text{Cl}^{16}\text{O}$ (on ^{51}V) and $^{40}\text{Ar}^{35}\text{Cl}$ (on ^{75}As) was achieved by monitoring ^{35}Cl in high resolution and applying the appropriate correction factor. The $^{95}\text{Mo}^{16}\text{O}$ interference on ^{111}Cd was also corrected by measuring ^{95}Mo and applying a direct oxide correction. This approach uses only one equation for each element instead of the more complicated ones described in the original method.

Table 4. Interference Correction Equations used in this work

| Isotope | Interference Correction |
|-------------------|--|
| ^6Li | $- 0.072397 * ^7\text{Li}$ |
| ^{51}V | $- 0.002217 * ^{35}\text{Cl}$ |
| ^{52}Cr | $- 0.299387 * ^{13}\text{C}$ |
| ^{56}Fe | $- 0.0064 * ^{43}\text{Ca}$ |
| ^{59}Co | $- 0.002187 * ^{43}\text{Ca}$ |
| ^{60}Ni | $- 0.0015 * ^{43}\text{Ca}$ |
| ^{63}Cu | $- 0.006974 * ^{47}\text{Ti}$ |
| ^{66}Zn | $- 0.002536 * ^{47}\text{Ti}$ |
| ^{75}As | $- 0.000132 * ^{35}\text{Cl}$ |
| ^{82}Se | $- 1.00087 * ^{83}\text{Kr} - 0.002906 * ^{79}\text{Br}$ |
| ^{111}Cd | $- 0.001574 * ^{95}\text{Mo}$ |
| ^{115}In | $- 0.013873 * ^{118}\text{Sn}$ |
| ^{123}Sb | $- 0.12446 * ^{125}\text{Te}$ |
| ^{208}Pb | $+ 1 * ^{206}\text{Pb} + 1 * ^{207}\text{Pb}$ |

The iCAP Qa exhibits low and stable polyatomic interference levels that allow for MDLs that easily meet environmental analysis requirements with very short signal integration times (Table 2).

Linear Dynamic Range (LDR) - while low MDL values are important, the higher concentration levels found in everyday samples may also challenge ICP-MS instrumentation. As matrix concentration ranges can vary enormously from sample to sample it is desirable to employ an analytical technique also capable of measuring tens to hundreds of mg/L in environmental samples. Method 200.8 defines the upper LDR to be the concentration above which the reported concentration deviates by > 10% from that extrapolated from the standard calibration.

The iCAP Qa allows for on-the-fly sensitivity attenuation using variable mass resolution to allow calibrations for matrix elements, e.g. Na, Mg, K and Ca, well in excess of 100 mg/L. Tables 5 and 6 show < 10% deviation in concentrations reporting at 300 mg/L of all the major elements and 3 mg/L for the minor elements of which all but zinc and barium were measured in the Analog detector mode .

Table 5. Linear dynamic range test - major & minor elements (pulse counting & analog)

| Isotope | Calibration mg/L | LDR mg/L | LDR x2 mg/L | LDR x3 mg/L |
|-------------------|---------------------|-----------------|-----------------|-----------------|
| ^{23}Na | 99.9 | 102 | 206 | 307 |
| ^{25}Mg | 10.0 | 10.1 | 20.0 | 30.4 |
| ^{39}K | 10.0 | 10.3 | 21.0 | 32.6. |
| ^{43}Ca | 100 | 102 | 211 | 325 |
| | $\mu\text{g/L}$ | $\mu\text{g/L}$ | $\mu\text{g/L}$ | $\mu\text{g/L}$ |
| ^{56}Fe | 993 | 1003 | 2026 | 3069 |
| ^{63}Cu | 1000 | 1000 | 1986 | 2975 |
| ^{66}Zn | 996 | 1022 | 2082 | 3008 |
| ^{135}Ba | 1002 | 1005 | 2032 | 3061 |

Table 6. Linear dynamic range test - trace elements (pulse counting & analog)

| Isotope | Calibration $\mu\text{g/L}$ | LDR $\mu\text{g/L}$ | LDR x2 $\mu\text{g/L}$ | LDR x3 $\mu\text{g/L}$ |
|-------------------|--------------------------------|------------------------|---------------------------|---------------------------|
| ^9Be | 99.9 | 103 | 197 | 292 |
| ^{27}Al | 100 | 103 | 205 | 318 |
| ^{51}V | 101 | 104 | 219 | 327 |
| ^{52}Cr | 100 | 101 | 208 | 324 |
| ^{55}Mn | 100 | 102 | 211 | 327 |
| ^{59}Co | 100 | 101 | 203 | 315 |
| ^{60}Ni | 100 | 102 | 202 | 302 |
| ^{75}As | 100 | 104 | 202 | 300 |
| ^{82}Se | 100 | 109 | 204 | 291 |
| ^{95}Mo | 100 | 97.2 | 196 | 326 |
| ^{107}Ag | 100 | 97.6 | 189 | 274 |
| ^{111}Cd | 100 | 103 | 198 | 284 |
| ^{123}Sb | 100 | 100 | 212 | 314 |
| ^{205}Tl | 100 | 100 | 210 | 319 |
| ^{208}Pb | 100 | 97.8 | 208 | 317 |
| ^{232}Th | 100 | 95.8 | 209 | 321 |
| ^{238}U | 100 | 94.2 | 203 | 309 |

Due to the high instrumental sensitivity afforded by the iCAP Qa, only the trace elements beryllium, nickel, arsenic, selenium and cadmium were measured in the Pulse Counting detector mode over the entire calibration range. Molybdenum and antimony were measured at different concentrations in both Pulse Counting and Analog detector modes and demonstrate excellent detector cross calibration.

Quality Control

Method 200.8 specifies a variety of quality control tests that should be repeatedly analyzed at a defined frequency.

For example, the certified (trace elements in water) reference material, SRM NIST 1643e, was repeatedly measured as a **Laboratory Control Standard (LCS)** throughout the analytical run. All concentration data for the reference material fell within the required +/- 10% concentration window over a wide range of concentrations (Table 7).

Table 7. NIST 1643e laboratory control standard (LCS) recoveries

| Isotope | NIST 1643e | iCAP Qa | Recovery |
|-------------------|------------|---------|----------|
| | µg/L | µg/L | % |
| ⁹ Be | 14.0 | 13.4 | 96 |
| ²⁷ Al | 142 | 153 | 108 |
| ⁵¹ V | 37.9 | 37.2 | 98 |
| ⁵² Cr | 20.4 | 20.9 | 103 |
| ⁵⁵ Mn | 39.0 | 36.2 | 93 |
| ⁵⁶ Fe | 98.1 | 103 | 105 |
| ⁵⁹ Co | 27.1 | 27.6 | 102 |
| ⁶⁰ Ni | 62.4 | 64.7 | 104 |
| ⁶³ Cu | 22.8 | 22.8 | 100 |
| ⁷⁵ As | 60.5 | 57.9 | 96 |
| ⁸² Se | 12.0 | 11.4 | 95 |
| ⁸⁸ Sr | 323 | 304 | 94 |
| ⁹⁵ Mo | 121 | 118 | 97 |
| ¹⁰⁷ Ag | 1.06 | 1.04 | 98 |
| ¹¹¹ Cd | 6.57 | 6.32 | 96 |
| ¹²³ Sb | 58.3 | 56.3 | 97 |
| ¹³⁵ Ba | 544 | 542 | 100 |
| ²⁰⁵ Tl | 7.45 | 7.24 | 97 |
| ²⁰⁸ Pb | 19.6 | 19.1 | 97 |
| | mg/L | mg/L | % |
| ²³ Na | 20.7 | 20.7 | 100 |
| ²⁵ Mg | 8.01 | 8.01 | 100 |
| ³⁹ K | 2.03 | 20.3 | 100 |
| ⁴³ Ca | 32.3 | 30.0 | 93 |

The Quality Control Sample (QCS) is a second source standard that is used to check the accuracy of the calibration and must return values to within 10% of the known concentration for each element; its nominal concentration is defined as 50% of the top calibration standard.

During the analysis run, the QCS was analyzed every 10 samples as the Continuing Calibration Verification (CCV) to assess the accuracy of the calibration. All elements measured were found to be accurate to within ± 10% of the known concentration and were stable (< 2% RSD) over sixty repeat analyses (Table 8). 100 µg/L Au was added to all solutions including the on-line internal standard solution and rinse to ensure optimum performance for mercury. For accurate mercury analysis

sufficient gold should be included in the preservation acid added during sampling to maintain 100 µg/L gold in each solution before eventual analysis.

Table 8. QCS recovery and stability of 60 repeat analyses of the CCV.

| Isotope | QCS | Recovery | Mean | RSD |
|-------------------|------|----------|------|-----|
| | µg/L | % | µg/L | % |
| ⁹ Be | 50 | 100 | 50.0 | 0.9 |
| ²⁷ Al | 50 | 104 | 52.2 | 0.7 |
| ⁵¹ V | 50 | 102 | 51.2 | 0.8 |
| ⁵² Cr | 50 | 103 | 51.7 | 0.8 |
| ⁵⁵ Mn | 50 | 99 | 49.4 | 0.7 |
| ⁵⁶ Fe | 500 | 105 | 527 | 1.3 |
| ⁵⁹ Co | 50 | 103 | 51.7 | 0.7 |
| ⁶⁰ Ni | 50 | 105 | 52.7 | 0.8 |
| ⁶³ Cu | 500 | 105 | 524 | 1.2 |
| ⁶⁶ Zn | 500 | 104 | 519 | 0.5 |
| ⁷⁵ As | 50 | 101 | 50.7 | 1.4 |
| ⁸² Se | 50 | 105 | 52.6 | 1.3 |
| ⁹⁵ Mo | 50 | 101 | 50.5 | 1.1 |
| ¹⁰⁷ Ag | 50 | 104 | 52.1 | 1.3 |
| ¹¹¹ Cd | 50 | 105 | 52.7 | 0.9 |
| ¹²³ Sb | 50 | 101 | 50.4 | 1.9 |
| ¹³⁵ Ba | 500 | 102 | 511 | 1.1 |
| ²⁰¹ Hg | 2.5 | 98 | 2.5 | 2 |
| ²⁰⁵ Tl | 50 | 103 | 51.5 | 1.3 |
| ²⁰⁸ Pb | 50 | 102 | 50.8 | 0.5 |
| ²³² Th | 50 | 96 | 48.1 | 0.9 |
| ²³⁸ U | 50 | 96 | 48.1 | 0.9 |
| | mg/L | % | mg/L | % |
| ²³ Na | 50 | 105 | 52.6 | 0.9 |
| ²⁵ Mg | 5 | 104 | 5.19 | 1.3 |
| ³⁹ K | 5 | 105 | 5.25 | 1.0 |
| ⁴³ Ca | 50 | 100 | 49.9 | 0.4 |

The **Laboratory Reagent Blank (LRB)** was run after every QCS to check the laboratory reagents and washout for any contamination. The FAST system was set up to ensure excellent washout between samples such that all LRBs were all > 20x below the MCL for every element.

The **Laboratory Fortified Blank (LFB)** checks the recovery of the analytes after spiking the LRB once per batch of samples (Figure 5).

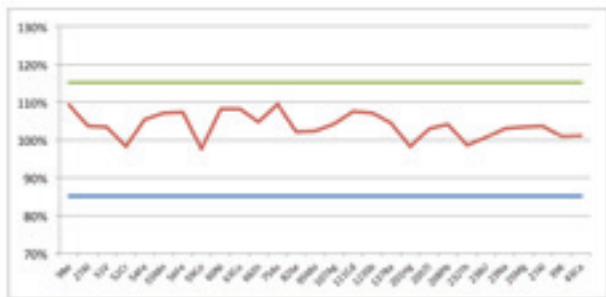


Figure 5. Recoveries for laboratory fortified blank (200.8 Method specified 85% - 115% limits shown)

The **Laboratory Fortified Matrix (LFM)** checks the recovery of analytes in a matrix every 1 in 10 samples (Figure 6).



Figure 6. Laboratory fortified matrix minor & trace element recoveries (Method specified 70 – 130% limits shown)

Stability

Figure 7 shows the signal response for the seven internal standards during a 14 hour analytical run of (>900) natural water samples against EPA Method 200.8, without re-calibration, as displayed in the Qtegra software. The internal standard recoveries are well within the 60 – 125% range defined in Method 200.8.

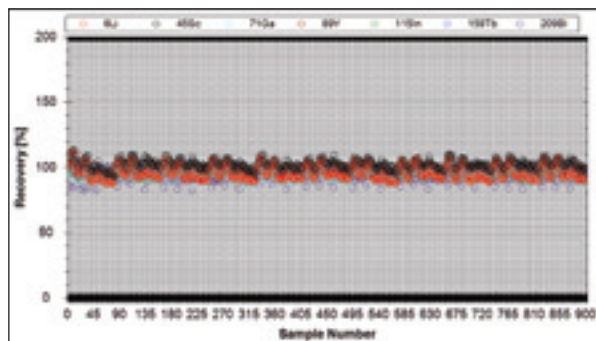


Figure 7. Internal standard recovery (%) over 14 hours

Conclusions

The Thermo Scientific iCAP Qa equipped with an ESI Autosampler and FAST sample introduction system was validated for use with US EPA Method 200.8. After optimising the FAST uptake and washout parameters, the high sensitivity and stability of the iCAP Qa, with its automatic resolution switching and accurate detector cross calibration, achieved the goal of 60 analyses per hour working against US EPA Method 200.8.



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