

Environmental

Analysis of drinking water in compliance with EPA Method 200.8, Revision 5.4

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Goal

To demonstrate the performance of the Thermo Scientific™ iCAP™ RQplus ICP-MS for analysis of a variety of water samples, including surface waters, groundwaters, and drinking waters, in accordance with regulatory guidelines of U.S. EPA Method 200.8, Revision 5.4

Introduction

U.S. EPA Method 200.8, Revision 5.4, provides procedures and guidelines for the determination of dissolved and total recoverable elements in a variety of samples, primarily ground waters, surface waters and drinking water, but also wastewater, soils, and sludges using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). Analytical laboratories performing environmental analyses according to EPA approved methods may experience high sample workloads requiring quick turnaround and reporting of results. In addition to these challenges, compliance with comprehensive quality control protocols and detection limits are key requirements to ensure accurate results and data quality.

This application note describes the analytical workflow developed for the iCAP RQplus ICP-MS, enabling laboratories to perform uninterrupted analysis of water samples for extended periods. The iCAP RQplus ICP-MS offers a comprehensive solution for effective handling of samples with variable matrix content, often characterized by the amount of Total Dissolved Solids (TDS). A built-in mass flow controller facilitates the addition of argon gas into the sample aerosol for automatic and reproducible gas dilution of the samples before entering the plasma. This approach of sample dilution using argon gas reduces the amount of dissolved solids that reach the plasma, minimizing deposition of matrix on the interface cones, thereby reducing drift and ensuring consistent readout of QC standards and long-term robustness and reliability.

The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software was used to control the ICP-MS instrument and to generate, process, and report analytical data. The method was set up as a template in the software to allow easy generation of data files for daily analysis where the entire workflow meets the quality control requirements described in EPA Method 200.8.

Experimental

Instrument parameters and experimental conditions

The iCAP RQplus ICP-MS was operated in conjunction with a Thermo Scientific™ iSC-65 autosampler for automated and unattended operation of the instrument. As the use of a collision/reaction cell is not permitted for the analysis of drinking water using EPA Method 200.8, the iCAP RQplus ICP-MS was operated in Standard (STD) mode. To correct for isobaric and polyatomic interferences, appropriate correction equations were used as required in EPA Method 200.8. Additionally, internal standardization was employed to monitor and compensate for physical interferences, instrument drift, and signal suppression or enhancement caused by the sample matrix. Table 1 summarizes the configuration of the sample introduction system and typical instrument parameters used in this study. The optimized instrument conditions were obtained using the autotune routines included in the Qtegra ISDS Software to ensure that analytical robustness and detection sensitivity were achieved during analysis.

Table 1. Instrument configuration and typical operating parameters

Parameter	Value
Nebulizer	MicroMist™ nebulizer (400 µL·min ⁻¹)
Interface cones	Ni – tipped sample and skimmer
Skimmer cone insert	High matrix
Spray chamber	Cyclonic quartz
Injector	Quartz, 2.5 mm i.d.
Torch	Quartz torch
Auxiliary flow (L·min ⁻¹)	0.8
Cool gas flow (L·min ⁻¹)	14
Nebulizer flow (L·min ⁻¹)	0.38
CRC conditions	Not used as per EPA Method 200.8 v5.4 requirements
AGD setting	Low
Additional gas, argon (% of range)	55
RF power (W)	1,550
Sampling depth (mm)	8
Number of replicates	3
Spray chamber temp. (°C)	2.7

As mentioned, equations to correct for polyatomic interferences were applied in this study. Table 2 summarizes the analytes and the equations used for the correction of their concentrations.

Table 2. Summary of analytes and correction equations used during analysis

Analytes	Correction equation
As	$3.127 [(^{77}\text{Se} - 0.815 * ^{82}\text{Se})]$
Cd	$1.073 [(^{108}\text{Cd} - 0.712 * ^{106}\text{Cd})]$
Pb	$[^{206}\text{Pb} + ^{207}\text{Pb} + ^{208}\text{Pb}]$
Mo	$[0.146 * ^{99}\text{Ru}]$
V	$3.127 [(^{63}\text{Cr} - 0.113 * ^{52}\text{Cr})]$

Calibration standards

To determine analytical figures of merit, such as Instrument Detection Limits (IDLs), linear range and correlation coefficients, calibration curves were generated for 21 analytes using six calibration standards and a calibration blank. Multi-element standards were prepared from single element stock standards of each target analyte (1,000 mg·L⁻¹, SPEX™ CertiPrep, Metuchen, NJ, USA). Two different stock solutions were prepared at concentration level of 10 mg·L⁻¹ to accommodate analytes with different concentrations and chemical compatibility. The stock solutions were then diluted gravimetrically using 1% (v/v) nitric acid as a diluent resulting in the concentrations specified in Table 3. An internal standard solution containing 10 µg·L⁻¹ of ⁶Li, Sc, Y, Tb and Bi was added online continuously during the analysis. All solutions used for analysis consisted of 1% (v/v) HNO₃ in ultrapure water containing 100 µg·L⁻¹ gold as a stabilizer for mercury.

Table 3. List of target analytes and their concentrations in calibration standards (µg·L⁻¹)

Analytes	STD 1	STD 2	STD 3	STD 4	STD 5	STD 6	STD 7
Hg	0	0.01	0.1	0.25	1	2	5
Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Ag, Tl, Th, U, V, Zn	0	1	5	25	100	200	500

Sample preparation

In total, 10 different ground water, surface water and drinking water samples were collected locally and analyzed for the determination of dissolved elements. Samples were filtered using 0.45 µm pore size membrane filters followed by acidification using nitric acid to adjust the nitric acid concentration of the sample to approximately 1%. Multiple aliquots of these samples (equally split between ground water, surface water, and drinking water) were then analyzed to assess accuracy and precision, performance of duplicate measurements, and robustness over an 18-hour analysis. A certified reference material (SLRS-5, natural river water) was included in the analysis as an additional verification of accuracy.

Results and discussion

Linear range and instrument detection limits

The IDLs for all analytes were calculated following the guidance provided in EPA Method 200.8, Revision 5.4, by analyzing ten replicate measurements of the calibration blank and multiplying the standard deviation of these measurements by three. Detection limits must be below the standards for inorganic contaminants in drinking water set by the National Primary Drinking Water Regulations (NPDWR) and the National Secondary Drinking Water Regulations (NSDWR), which are summarized in Table 4 with the Maximum Contaminant Level (MCL) and Secondary Maximum Contaminant Level (SMCL) for each inorganic contaminant or

analyte in this study. The IDLs achieved for all analytes were below the requirement of the regulations, indicating that the developed method enables sensitive determination of all target analytes meeting or exceeding the detection requirements. The correlation coefficients (R^2) obtained for all analytes were greater than 0.999, demonstrating excellent linear response for the established concentration range for each analyte. The analyte masses (m/z), correlation coefficients, and IDLs are summarized in Table 5.

Table 4. List of analytes and their MCLs in drinking waters allowed by NPDWR and NSDWR

MCL		SMCL	
Analyte	MCL (mg·L ⁻¹)	Analyte	MCL (mg·L ⁻¹)
Sb	0.006	Al	0.05 to 0.2
As	0.010	Ag	0.1
Ba	2.0	Cu	1.0
Be	0.004	Mn	0.05
Cd	0.005	Zn	5
Cr	0.1		
Pb	0.015		
Hg	0.002		
Se	0.05		
Tl	0.002		

Table 5. List of analytes, m/z , correlation coefficients, and IDLs

Analyte	m/z	R^2	IDL (µg·L ⁻¹)	Analyte	m/z	R^2	IDL (µg·L ⁻¹)
Ag	107	0.9999	0.002	Mg	24	>0.9999	1.247
Al	27	0.9998	1.28	Mn	55	>0.9999	1.28
As	75	0.9998	0.071	Mo	95	>0.9999	0.081
Ba	137	>0.9999	0.042	Na	23	0.9998	9.18
Be	9	>0.9999	0.001	Ni	61	0.9998	0.043
Ca	44	0.9999	7.15	Pb	206+207+208	>0.9999	0.008
Cd	111	0.9999	0.009	Sb	121	>0.9999	0.043
Co	59	0.9999	0.003	Se	78	>0.9999	0.08
Cr	52	0.9997	0.034	Ti	48	0.9997	0.097
Cu	63	>0.9999	0.330	Tl	205	0.9999	0.016
Fe	54	>0.9994	0.4123	V	51	0.9996	0.078
Hg	202	0.9994	0.053	Zn	66	>0.9998	0.076
K	39	0.9998	8.113				

Quality control (QC) checks

Laboratory reagent blank (LRB) – LRB sample was prepared from 1% (v/v) HNO_3 in ultrapure water, which was treated similarly to the samples by filtration through a 0.45 μm pore diameter membrane filter. The LRB was analyzed every 15 samples, and resulting concentrations of all analytes were monitored. The concentration of all analytes in subsequent LRB samples were found to be within the acceptable range as specified in EPA Method 200.8.

Laboratory fortified blank (LFB) – An aliquot of LRB was spiked with stock solutions to yield the final concentration of $75 \mu\text{g}\cdot\text{L}^{-1}$ for all analytes, except for Hg (spiked at a concentration level of $0.75 \mu\text{g}\cdot\text{L}^{-1}$). The recovery of each analyte was automatically calculated using the comprehensive QC toolkit available within the Qtegra ISDS Software. The recoveries for all analytes were found to be within the range of 90–105%, meeting method acceptance criteria.

Quality control sample (QCS) – QCS solution was prepared using independent analyte stock solutions (different from the stock solutions used for preparation of calibration standards) to yield analyte concentrations at $50 \mu\text{g}\cdot\text{L}^{-1}$ level (except for Hg, which was spiked at $0.5 \mu\text{g}\cdot\text{L}^{-1}$ concentration level). The QCS was used to confirm the initial validity of calibration standards as well as to confirm the ongoing instrument performance during the measurement of more than 18 hours. The QCS was analyzed every 15 samples, with the percent accuracy for all analytes in each QCS found to be well within the acceptable range of $\pm 10\%$ (equivalent to 90–110%) of the true concentration. Figure 1 summarizes the percent accuracy for aluminum, cadmium, and mercury as representative examples obtained during repeated measurements of the QCS during an analytical run sequence of more than 18 hours involving the analysis of more than 300 various water samples. All other analytes read back well within the acceptable range as well.

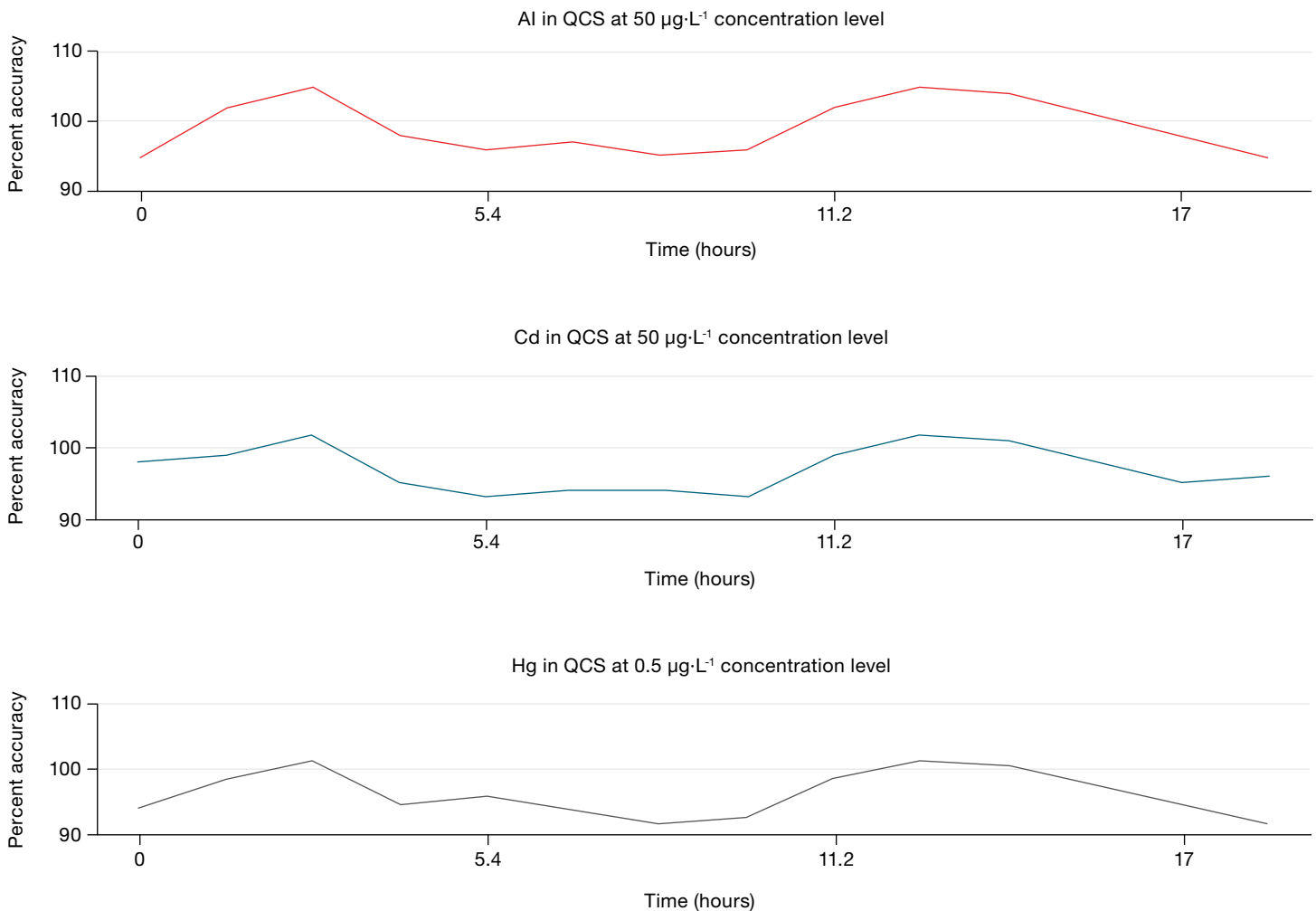


Figure 1. Accuracy of each analyte observed during measurements of the QCS over period of 18 hours

Accuracy

Laboratory fortified matrix (LFM) – To assess and demonstrate method accuracy and precision, one of the surface water samples was spiked in duplicate at a concentration level of 50 µg·L⁻¹ for all analytes (except Hg, which was spiked at a concentration level of 0.5 µg·L⁻¹). The percent recovery of each analyte was calculated automatically within Qtegra ISDS Software based on the measured concentration for the unspiked and spiked replicates of the LFM. The average percent recovery for all analytes was found to be within the range of 85–115%, against the acceptable range of 70–130%, with relative percent difference of less than 5% between duplicate spike measurements. Figure 2 shows the analytes and their average percent recovery calculated from duplicate measurements of a spiked surface water sample.

Analysis of certified reference material (CRM) and observed accuracy – To further demonstrate method accuracy, a CRM (SLRS-5, natural river water) was analyzed three times during a long-term analysis of more than 18 hours. The percent accuracy of each analyte was calculated based on the concentration data obtained during the analysis and the certified values given for each analyte in the SLRS-5 CRM. Table 6 summarizes the list of analytes, their certified concentration values, measured concentrations, and calculated percent accuracy. The percent accuracy values given are the average calculated from three different measurements of SLRS-5 CRM with relative standard deviation (RSD) of less than 5% for each analyte.

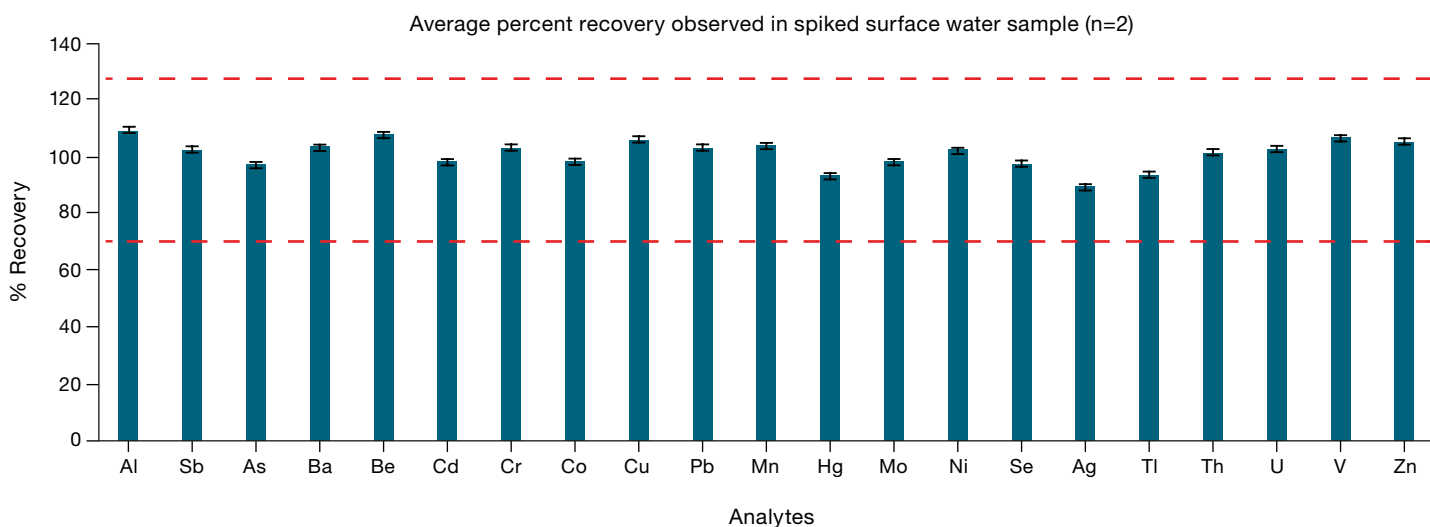


Figure 2. Average percent recovery calculated from the duplicate measurement of spiked surface water sample

Table 6. List of analytes, certified concentrations, observed concentrations, and percent accuracy observed during analysis of SLRS-5 CRM

Analyte	Certified concentration (µg·L ⁻¹)	Observed concentration (µg·L ⁻¹)	% Recovery
Al	49.5	47.1	95.2
V	0.317	0.333	104.9
Cr	0.208	0.195	93.8
Mn	4.33	4.40	101.6
Co	0.05	0.048	96.0
Ni	0.476	0.451	94.7
Cu	17.4	17.6	101.1
Zn	0.845	0.933	110.5
As	0.413	0.393	95.0
Mo	0.27	0.25	92.6
Sb	0.3	0.297	99.2
Ba	14	14.4	102.8
Pb	0.081	0.085	106.2
U	0.093	0.096	103.3

Method robustness

A robust instrument and optimized method are key requirements when analyzing varying sample matrices within an analytical run sequence. Instrument drift and physical interferences, due to the sample matrices, cause signal enhancement or suppression, and must be corrected for. In addition, EPA Method 200.8 includes specific guidelines and requirements such as internal standardization to monitor and correct for instrument drift and physical interferences. An internal standard must be precisely added to all standards and samples in the run sequence and must not deviate outside of the acceptable range of 60–125%, compared to the response observed in the calibration blank.

As previously mentioned, an internal standard solution containing $10 \mu\text{g}\cdot\text{L}^{-1}$ of ${}^6\text{Li}$, Sc, Y, Tb, and Bi was added online during the analysis. Figure 3 shows a plot of the internal standard recovery against the calibration blank throughout the 18-hour analysis. As shown, all internal standard recoveries were within the range of 80–115%, well within the EPA Method 200.8 acceptance criteria. These results demonstrate the robustness of the method and instrument setup that included online sample dilution.

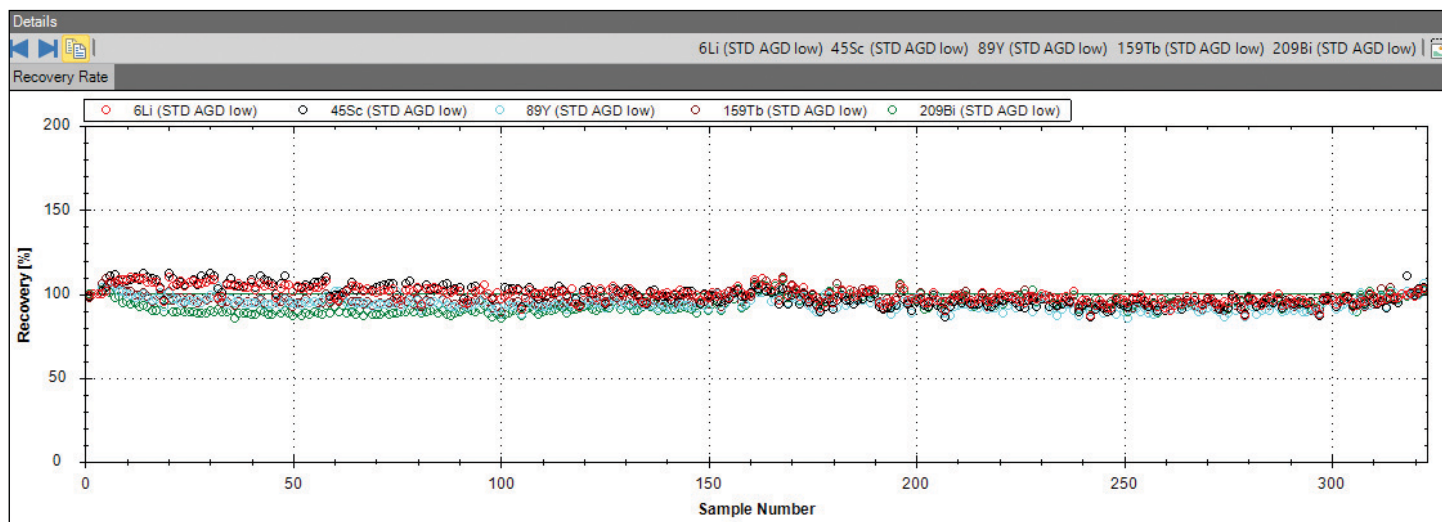


Figure 3. Screen capture taken from Qtegra ISDS Software LabBook highlighting the consistent recovery of internal standard within 80–115% throughout the 18-hour analysis

Conclusion

The quality of analytical data obtained during this study indicates that the iCAP RQplus ICP-MS, equipped with a built-in AGD system for controlled and automatic dilution of the sample aerosol, is a powerful solution for the analysis of varying sample matrices within a single run sequence. Some of the important outcomes of this study are highlighted below.

- The instrument detection limits (IDLs) met the requirements of the method and were below the regulations for inorganic contaminants in drinking water, indicating that the instrument setup, with optimized sample dilution, provides the sensitivity and robustness for the analysis of a variety of water samples in a single, extended analysis.
- The accuracy and precision obtained from the analyses of the fortified matrix samples and SLRS-5 CRM indicate that the developed method and instrument setup were optimized for the variety of samples analyzed. Furthermore, the ease of instrument tuning, operation, and LabBook set up through the Qtegra ISDS Software allows routine analysis of varying environmental samples with minimal effort while improving productivity.

- The accurate results obtained from the analyses of the QCS samples demonstrated on-going instrument performance and calibration over the extended analysis of varying sample matrices.
- The internal standard recoveries of 80–115% observed during the 18-hour analysis demonstrated robustness of the instrument and that the dilution applied to each sample was helpful in minimizing the effects of physical interferences.
- The QC toolkit included within the Qtegra ISDS Software enables easy set up and compliance with the comprehensive QC protocol of EPA Method 200.8. Customizable report templates are available to provide all data required for audit and regulatory purposes.

References

1. U.S. EPA Method 200.8: https://www.epa.gov/sites/default/files/2015-08/documents/method_200-8_rev_5-4_1994.pdf
2. National Primary Drinking Water Regulations: <https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations>
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