

measuring metallics

By Bill Spence & Matthew Cassap

Industrial discharge, the use of agricultural chemicals, vehicle exhaust and natural geological activities such as volcanic eruptions increase the probability of high levels of metallic contaminants in water. Four metals—lead, arsenic, cadmium and mercury—raise particular concern because of their toxicity to humans, especially in cases of chronic exposure.

These metals can accumulate in the body and cause serious organ damage. In response, the U.S. Environmental Protection Agency (EPA) has specified maximum contaminant levels (MCLs) under the Federal Regulation 40 CFR part 141 (see Table 1 and Table 2). In order to comply with these regulations, the water and wastewater industry requires laboratories to use analytical methods capable of monitoring the levels of metallic contaminants in water.

Traditional Methods

Optical inductively coupled plasma (ICP) has traditionally been employed for such measurements. The required detection limit for some analytes such as antimony, arsenic, mercury and thallium, however, are problematic with this technique. Under the Arsenic Rule (part of 66 FR 6976, 2001), the EPA stated that as of January 2006, optical ICP methods were to be withdrawn from approval for the determination of arsenic because the typical detection limit of the technique was not generally thought to be routinely low enough to measure confidently at the MCL level of 10 µg/L.

Although optical ICP methods are no longer approved for regulatory analysis of arsenic in drinking water, methods such as 200.7 are still routinely used for other water analyses and using the more sensitive axial view configuration, some ICP instruments are still able to offer sufficient sensitivity to provide method detection limits suitable for determining arsenic at the 10 ppb level. In this study, an ICP with dual viewing capability (axial and radial) was employed in order to characterize its performance for the analysis of water samples with Method 200.7.

Method 200.7

Method 200.7 is the approved technique for the determination of metallic contaminants in water in compliance with the MCLs specified under the Federal Regulation 40 CFR part 141. The method is also extensively used for regulatory analysis of wastewater samples for compliance with the permits issued within the National Pollutant Discharge Elimination System (NPDES).

Method 200.7 detects a total of 32 metals and trace elements in supplied water, natural water and wastewater. It is also commonly used to ensure compliance with state regulations that require well waters within properties to be analyzed prior to purchase of real estate. Currently, the method serves as the basis

Table 1. Metals MCLs (mg/L) from Primary Drinking Water Standard

Contaminant	MCL
Antimony	0.006
Arsenic	0.01
Barium	2
Beryllium	0.004
Cadmium	0.005
Chromium	0.1
Copper	1.3
Lead	0.015
Mercury	0.002
Selenium	0.05
Thallium	0.002
Uranium	0.03

Table 2. Metals Levels (mg/L) from Secondary Drinking Water Standard

Contaminant	Level
Aluminum	0.05 to 0.2
Copper	1
Iron	0.3
Manganese	0.05
Silver	0.1
Sulfate	250
Zinc	5

for water analysis methods by ICP across the world, especially in regions where environmental monitoring industries developed later than in the U.S.

Method 200.7 suggests preferred wavelengths, calibration and quality control procedures as well as specific procedures for determining method performance characteristics (e.g., detection limits and linear ranges).

It is important that contamination is kept under control, especially for environmentally abundant elements such as aluminium and zinc, because any contamination will degrade the method detection limit (MDL). Interference corrections also affect the MDL, as they employ the monitoring of additional lines and propagate the measurement errors accordingly.

Method 200.7 defines the upper linear range limit of a calibration—termed the linear dynamic range (LDR)—as the concentration at which an observed signal deviates by less than 10% from that extrapolated from lower standards. Sample dilution can

Method 200.7:
principles and application

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facilitate the measurement of high concentrations, but with additional effort, cost and error; therefore, a wide LDR is desirable. In addition, Method 200.7 specifies a variety of quality control standards.

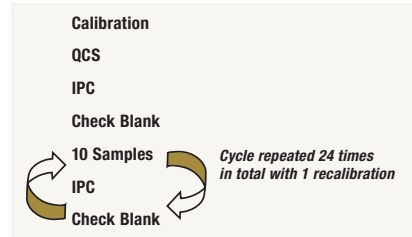
Principles of the Method

To commence the analysis, an aliquot of a well-mixed, homogeneous sample is accurately weighed or measured for sample processing. For total recoverable analysis of a sample containing undissolved materials, analytes are solubilized by gentle refluxing with nitric acid (HNO₃) and hydrochloric acid (HCl). After cooling, the sample is made up to volume, mixed and then centrifuged or allowed to settle overnight prior to analysis. For the determination of dissolved analytes in a filtered sample aliquot, total recoverable determination of analytes in water where sample turbidity is less than 1 NTU, the sample is prepared for analysis by the addition of the appropriate volume of HNO₃. It is then diluted to a predetermined volume and mixed before analysis.

Samples are introduced into the ICP instrument, where they are nebulized, and the resulting aerosols are transported to the plasma. Element-specific light emissions are produced in a radio-frequency inductively coupled plasma. The emitted light is dispersed by a grating spectrometer, and the intensities of the line spectra are monitored at specific wavelengths by a photosensitive detector. Photocurrents from the detector are processed and controlled by a computer system.

A background correction technique is required to compensate for variable background contribution to the determination of the analytes. The background must be measured adjacent to an analyte wavelength

Figure 1. The 10 samples analyzed between each IPC and blank pair consisted of a variety of aqueous matrices. The samples were analyzed multiple times throughout the experiment, replicating a run consisting of a total of more than 300 samples, including quality control and calibration solutions.



during analysis. To reduce potential interferences, dissolved solids should be less than 0.2% (w/v).

Application Example

An iCAP 6500 was used in conjunction with a CETAC ASX-520 autosampler. Wavelengths were selected according to Method 200.7, and additional wavelengths were measured in some cases. Plasma views were selected using the Thermo Scientific iTEVA software's automated view selection function.

The software has a built-in quality control checking capability that is designed to meet the requirements of EPA methods. The package also includes monitored uptake/washout features, reducing the

amount of nonproductive time and maximizing useful analytical time. Axial and radial views were implemented to provide optimum data quality by avoiding easily ionized element interferences in the axial view where necessary.

Solution Preparation

Ultrapure water of resistivity of greater than 15 MΩ cm (Milli-Q) was used, along with Fisher Scientific Primar-grade hydrochloric acid and nitric acid. All analytical standard solutions were prepared from Fisher Scientific stock standards, and reference samples were analyzed along with various unknown water samples. All samples were preserved in a mixture of 2% nitric acid and 2% hydrochloric acid.

Method

LDR and MDL studies were performed as described in Method 200.7. The MDL study was performed with a reagent blank spiked with low concentrations of each element. An interference study was completed using single-element SIC solutions according to Method 200.7. To demonstrate the performance of ICP for typical routine analysis of a variety of water samples with Method 200.7, a sequence was set up as illustrated in Figure 1.

Results

Very few significant interferences were identified during the analysis of the SIC solutions. Those that were observed can easily be corrected by using inter-element corrections when necessary. The high standards

continues on page 44 ▶

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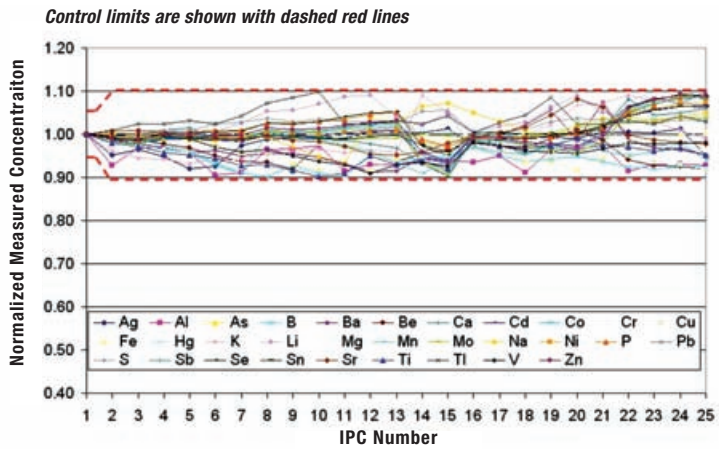
analyzed for the LDR check showed little deviation from their expected values, indicating sufficient linearity for the analysis of typical water samples.

The MDLs calculated from analysis of the MDL solution were generally in the low ppb range for the majority of elements. All MDLs were sufficiently below the typical levels of interest for drinking water analysis, with the exception of antimony, mercury, thallium and aluminium. The MDLs for these elements were of the same magnitude as the level of interest. For this reason, ICP-MS may be a more appropriate alternative for regulatory drinking water measurements for these elements. The use of the axial view can, however, significantly improve the detection limit of some elements measured using the radial view in this study. MDLs for some elements, such as aluminium, may be compromised by spot contamination in the sample tubes.

The iCAP 6500 produced consistently accurate results with minimal intensity drift, as shown by the results for the QCS and IPC solutions. The ongoing IPC results were consistently within the allowed range of 90-110% of the known value, as shown in Figure 2. The precision of the 25 IPC measurements across the 240-sample run were also shown to be very good, with the relative standard deviation (RSD) of these measurements well within 5% across the duration of the run (16 hours). Results also demonstrated that the iCAP 6500 consistently produced accurate and precise data in all of the reference material matrices.

The vast majority of results were within 10% of the certified concentration—the few exceptions tending to be when the measured value was close to the method detection limit.

Figure 2. The Stability of Successive IPC Measurements During a 240-Sample Analysis



Final Review

Elevated concentrations of metallic contaminants in water can prove very harmful to human health due to high toxicity. In response, the EPA has specified MCLs and requires regular monitoring of water. Method 200.7 details the use of Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) for the determination of a total of 32 metals and trace elements in supplied water, natural water and wastewater. This method provides good accuracy and reliability of results

for the vast majority of elements in most environmental samples, as demonstrated by this work. [www](#)

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