

ICP – Optical Emission Spectroscopy

Author

Praveen Sarojam, Ph.D.

PerkinElmer, Inc.
Shelton, CT 06484 USA

Analysis of Trace Metals in Drinking Water with the Optima 7000 DV ICP-OES

Introduction

With the development of mining, smelting and other industrial activities, heavy metals are increasingly being found in freshwater sources which can pose severe threats to human and environmental health. Pollution by heavy metals (such as Cd, Pb, etc.) not only affects the productivity of crops, but also the quality of the atmosphere as well as water bodies and threatens the health and life of animals and human beings by way of the food chain.

The environmental pollution caused by these heavy metals is a long-term and irreversible process. Such metals are not required for routine functioning of the human body and can be toxic even at low concentration. Drinking water from a tap, such as a private well or public water system, is a source of potential exposure to environmental contaminants. Natural contamination of heavy metals usually originates from weathering of minerals, rocks and aquatic environments which result in the entry of heavy metals into water bodies. Disposal of industrial effluents, wastes (domestic and industrial), such as sewage sludge and mining effluents, are other causes of contamination. Many of the metals are retained relatively strongly in the surface water and soil and do not readily leach out – causing accumulation that may ultimately pose a threat to humans, animals, plants and microbes. Regulatory bodies (e.g. U.S. EPA) have set maximum contaminant levels (MCL) for various metal ions in drinking water (Table 1 – Page 2). This requires that public water supplies be monitored for these metals regularly. Private drinking water systems are not monitored and it is the responsibility of the owner or consumer to test and treat their water.

Table 1. Drinking-water regulatory limits and experimentally determined instrument detection limits for ICP-OES.

Analyte	U.S. MCL (µg/L)	Calculated ICP-OES DL (µg/L)**
As	10	2.4
Cd	5	0.1
Cr	100	0.3
Cu	1300	0.3
Pb	15	1.5
Fe*	300	0.3
Zn*	5000	0.2
Ca*	250 (mg/L)	0.5

* U.S. secondary drinking water contaminants.
 ** Experimentally determined in this study.

Inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectroscopy (ICP-OES) are well suited for the analysis of water samples for trace-metal content. For applications where maximum detection power is required, ICP-MS is the method of choice. ICP-OES is more rugged and can more easily handle samples with higher total-dissolved-solid content. However, when compared with graphite furnace atomic absorption (GFAA), traditional, radial-view ICP-OES instruments have the disadvantage of lower sensitivity. This is especially important in the use of ICP-OES for the determination of trace elements in drinking water. The use of axial-view ICP-OES has helped in overcoming this disadvantage by extending the measurable concentration range into sub-ppb levels for many elements.

ICP optical emission spectrometers equipped with a charge-coupled device (CCD) array detector show a significant advantage over conventional technology with respect to speed, sensitivity and stability and are generally available at a lower instrument cost.

This work demonstrates that the Optima™ 7000 DV, a CCD detector-based ICP optical emission spectrometer in combination with a cyclonic spray chamber and MEINHARD® concentric nebulizer, is capable of determining extremely low concentrations of elements in drinking-water certified reference materials, with high speed, according to the requirements of various regulatory bodies.

Experimental

Instrumentation

A PerkinElmer® Optima 7000 DV ICP-Optical Emission Spectrometer (Shelton, CT, USA), equipped with WinLab™ 32 for ICP Version 4.0 software, was used for measurement of all elements of interest (Figure 1). The plasma can be viewed radially or axially and is user-selectable as part of the analytical method. Axial viewing allows ultratrace measurements because it provides a longer emission path for increased sensitivity. Radial viewing permits percentage concentration measurements (for elements like Ca, K, etc.). The read time was set at a variable range from 0.1 s to 0.5 s using the auto-integration mode. This feature takes a snapshot of intensity of the line to be measured before the actual reading begins. For high intensities, a shorter time is used – while for low intensities, a longer time is used thereby optimizing precision of analysis. Longer measurement times are beneficial in reducing shot noise, with little compromise on sample throughput.

The sample-introduction unit included a cyclonic spray chamber and MEINHARD® concentric glass nebulizer (Figure 2). The cyclonic spray chamber was used to provide both high sample transfer into the ICP and very fast sample rinse-in and rinse-out times, which improved productivity. The concentric nebulizer provided excellent sensitivity and precision for aqueous solutions and is well suited for the analysis of water samples. Table 2 (Page 3) lists the instrumental conditions used in this work. Yttrium was used as an internal standard to compensate for any physical interference effects and was added to all standards, blanks and CRMs using an on-line internal standard addition kit.

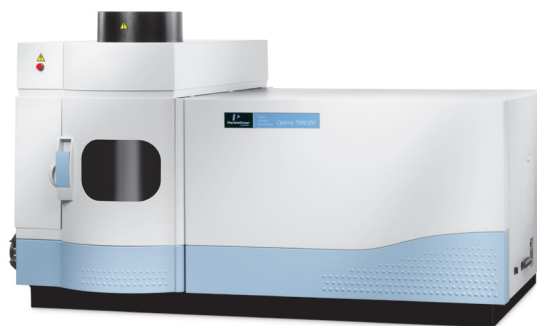


Figure 1. PerkinElmer Optima 7000 DV ICP-OES.



Figure 2. Demountable torch assembly with cyclonic spray chamber and MEINHARD® concentric nebulizer.

Injector:	Alumina 2 mm i.d.
Sample tubing:	Standard 0.76 mm i.d.
Drain tubing:	Standard 1.14 mm i.d.
Quartz torch:	Single slot
Sample capillary:	PTFE 1 mm i.d.
Sample vials:	Polypropylene
Source equilibrium delay:	15 sec
Plasma aerosol type:	Wet
Nebulizer start up:	Instant
RF power:	1450
Nebulizer flow:	0.7 L/min
Auxiliary flow:	0.2 L/min
Plasma flow:	15 L/min
Sample pump rate:	1.5 mL/min
Plasma viewing:	Axial, radial
Processing mode:	Peak area
Auto integration (min-max):	0.1-0.5 sec
Replicates:	2
Background correction:	1 or 2-point, manual

Standards, Chemicals and Certified Reference Material

PerkinElmer NIST® traceable quality control standards for ICP/AAS (N9300141, N9300281 and Spex Certiprep® Standard Lot# 36-60 AS) were used as the stock standards for preparing working standards. A total of six standards were used for calibration and were prepared from the three stock standards so that each metal ion would have three calibration points (Table 3). ASTM® Type I water (from a Millipore® filtration system, Millipore® Corporation, Billerica, Massachusetts, U.S.) acidified with suprapure nitric acid (Merck®, Germany) was used as the calibration blank and for all dilutions. After constructing the calibration curves (refer to Appendix 1 for a few selected elements) which were linear with correlation coefficients of at least 0.9999, two QC samples (one being a CCB, i.e. continuing calibration blank) were run to monitor the instrument performance and evaluate long-term stability. Working standards were prepared by serial volume/volume dilution in polypropylene vials (Sarstedt®, Germany). Micropipettes (Eppendorf®, Germany) with disposable tips were used for pipetting all solutions. NIST® certified drinking-water reference material CRM 1643e and high purity standards certified reference material for drinking water (CRM-TMDW-B) were used for validating the developed method.

Analyte	Wavelength (nm)	Standards (mg/L)	
As	188.979	0.100	1.00
Cd	226.502	0.100	1.00
Ca	315.887	6.00	60.0
Cr	267.716	0.100	1.00
Cu	327.393	0.100	1.00
Fe	259.939	5.00	50.0
Pb	220.353	0.100	1.00
Zn	206.200	0.100	1.00

Results and Discussion

Wavelength selection followed U.S. EPA Method 200.7 and ISO regulation 11885 and took into consideration, (a) the freedom from spectral interferences; (b) the different sensitivities versus expected concentration in the samples. The selected analytical wavelengths are compiled in Table 3. Note that in some cases the most sensitive line was not used in order to avoid spectral interferences. The instrument detection limits were calculated as an average, over 3 non-consecutive days, of 3 times the standard deviation of 10 replicate analyses of a blank standard. For all of the chosen analytes, the calculated detection limits were well below those set by the regulatory agencies (Table 1 – Page 2) which ensures accurate analysis at those levels. The resolution of the system is sufficiently good to warrant undisturbed measurements for typical analysis of environmental samples. In order to safeguard against any unexpected spectral interferences, all spectra generated during an analysis run was stored for post-analysis review. In this work, observed interferences were compensated for by modifying the processing parameters (e.g. adjusting the background correction points).

In order to establish the system performance, drinking-water certified reference materials were analyzed as per the developed method and the results are presented in Tables 4 and 5 (Page 4). The validity of the calibration was monitored using the Quality Control Check section of the WinLab™ 32 for ICP software. The quality control check standards were run at selected intervals during the analysis to ensure that the instrument performance remained consistent over the length of the analysis. Table 6 (Page 4) provides the QC recoveries at the beginning and at the end of the analysis, thereby validating consistent performance.

Table 4. Analysis of NIST® CRM for drinking water 1643e.

Analyte	Certified Values (µg/L)	Optima 7000 DV Values (µg/L)
As	60.45 ±0.72	60.4 ±1.8
Cd	6.568 ±0.073	6.39 ±0.12
Ca	32300 ±1100	32600 ±184
Cr	20.40 ±0.24	20.3 ±0.2
Cu	22.76 ±0.31	23.5 ±0.8
Fe	98.1 ±1.4	103 ±5.0
Pb	19.63 ±0.21	20.0 ±0.4
Zn	78.5 ±2.2	76.5 ±0.6

Table 5. Analysis of high purity standards CRM for drinking water (CRM-TMDW-B).

Analyte	Certified Values (µg/L)	Optima 7000 DV Values (µg/L)
As	10.0 ±0.5	9.60 ±0.8
Cd	10.0 ±0.2	9.60 ±0.4
Ca	31000 ±160	31400 ±460
Cr	20.0 ±0.2	20.4 ±0.9
Cu	20.0 ±0.2	20.9 ±1.1
Fe	90.0 ±0.9	93.7 ±3.2
Pb	20.0 ±0.2	20.6 ±0.6
Zn	75.0 ±0.8	74.5 ±1.8

Table 6. Quality control check standard recoveries.

Analyte	First QC Recovery (%)	Last QC Recovery (%)
As	101	102
Cd	99.7	103
Ca	98.3	101
Cr	99.7	101
Cu	99.8	99.0
Fe	101	101
Pb	99.0	102
Zn	98.8	103

Conclusion

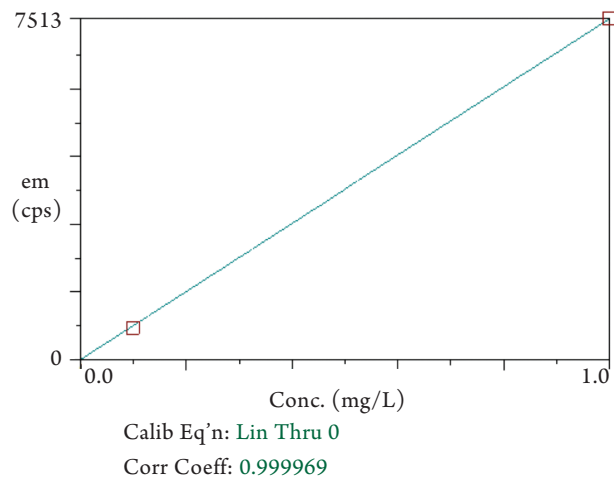
Contaminant elements in drinking water were successfully determined at very low levels by using the Optima 7000 DV ICP optical emission spectrometer equipped with a MEINHARD® concentric nebulizer and cyclonic spray chamber. The Optima 7000 DV used in this study has the capabilities to analyze environmental samples with good accuracy, precision, analysis speed and robustness and hence fulfills the requirements normally set for the analysis of water samples. Long-term stability (evident from QC recoveries over a period of more than 6 hours) ensures that the calibration will be monitored during the analysis run, requiring fewer QC actions and possible reruns. With 10 elements taking only 80 seconds for two replicates, the analysis speed is more than adequate for measuring the drinking-water certified reference materials used in this study. This excludes the sample wash in/out times, which may add another 60-90 seconds to the analysis time, depending upon the sample matrix. Including a time of 60 seconds for sample wash in and out, approximately 200 samples can be analyzed over a period of 8 hours.

References

1. U.S. EPA Method 200.7: "Determination of metals and trace elements in water and wastes by Inductively Coupled Plasma Optical Emission Spectrometry", Cincinnati, Ohio, U.S.
2. ISO 11885: "Water Quality-Determination of 33 Elements by Inductively Coupled Plasma Optical Emission Spectrometry".
3. PerkinElmer Application Library for ICP-OES.

Appendix 1. Calibration Graphs for Selected Elements.

As 188.979



Ca 315.887

