ICP-Optical Emission
Spectroscopy

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Analysis of Trace Metals in Surface and Bottled Water with the Optima 7300 DV ICP-OES

Introduction

Heavy metals are among the most significant freshwater pollutants and pose severe threats to geographical biodiversity. Pollution by heavy metals such as Cd, Pb, etc. not only affects the productivity of crops, but also compromises the quality of the atmosphere and water bodies. By propagation through the food chain, this type of pollution also threatens the health and life of animals and human beings. Such metals are not required for routine functioning of the human body and can be toxic even at low concentrations. The pollution caused by heavy metals is a long-term and irreversible process. Even though small concentrations of some metals (Ca, K, Mg, Na etc.) are required for routine functioning of the human body, their accumulation in higher concentration becomes toxic to most life forms. Certain trace metals such as Cu, Fe, Mn, Zn, etc., at catalytic amounts as metalloenzymes and as cofactors of enzymes, are essential to living organisms for their normal physiological activities. But a high concentration of Cu has been correlated with liver damage and Zn may produce adverse nutrient interactions with copper.[1-4]

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Drinking water from a tap source, such as a private well or public water system, can potentially be a significant source of exposure to environmental contaminants. Usually, the natural contamination of heavy metals originates from the weathering of minerals, rocks and aquatic environments, resulting in their entry into nearby water bodies. Disposal of industrial effluents, wastes (domestic and industrial) such as sewage sludge, and mining effluents are other potential sources of contamination.[5] Many of the metals are retained relatively strongly in surface water and soil and do not readily leach out, causing accumulation that may ultimately pose a threat to humans, animals, plants and microbes. There is still a pressing need to deal with excess metals present in water bodies to protect the environment from metal contaminants. Regulatory bodies have set maximum contaminant levels (MCLs) for various metal ions in drinking water (Table 1).[6] This means that public water supplies are monitored for these metals regularly. Private drinking water systems are not monitored and it is up to the owner or consumer to test and treat their water.

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

Element	U.S. MCL (µg/L)	European Union (µg/L)	WHO (µg/L)	Calculated ICP-OES DL (µg/L)**
Ba	2000	--	700	0.04
Be	4	--	--	0.02
Cd	5	5	3	0.1
Cr	100	50	50	0.3
Cu	1300	2000	1000	0.3
Pb	15	10	10	1.5
Ni	100	20	20	0.5
Al*	50	--	--	1.1
Fe*	300	--	--	0.3
Zn*	5000	--	--	0.2
Na*	20 (mg/L)	--	--	0.1
Mg*	50 (mg/L)	--	--	0.1
Ca*	250 (mg/L)	--	--	0.5
K*	12 (mg/L)	--	--	0.3

* U.S. secondary drinking water contaminants
** Experimentally determined in this study
-- Not a contaminant mentioned by WHO or EU

Markets today are flooded with many choices of bottled drinking waters, which may be regulated in a similar way to drinking water, but at the moment this regulation depends on geographical considerations. Because of poor or uncontrolled preparation methods, bottled waters may become contaminated during the bottling procedure. There is also a possibility that branded names may be counterfeited and the actual water source can be suspect. Hence, bottled water available on the market needs to be monitored routinely for trace and ultra trace levels of metal impurities.

Both inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectroscopy (ICP-OES) are well suited to this type of analysis. For applications where maximum detection power is required, ICP-MS is the method of choice. ICP-OES is more rugged and can handle a higher total dissolved solid content. However, when compared with electro thermal atomic absorption, radially viewed ICPs have had the disadvantage of lower sensitivity. This is especially important in the application of ICP-OES to the determination of trace elements in drinking water. The use of axially viewed ICP-OES has helped in overcoming this disadvantage by extending the measurable concentration limits to sub-ppb levels for many elements. Axial observation samples a larger volume of the plasma emission, potentially yielding improved detection limits by up to a factor of 10.[7] As the analysis of drinking water requires determination of many elements, it can be performed economically by using a simultaneous ICP-OES. Several ICP-OES methods are available for this determination, including U.S. EPA 200.7/200.5 in the USA, DIN 38406E22 in Germany, or ISO11885 on a global level. Table 1 shows the approximate instrument detection limits (IDLs) for ICP-OES for comparison with the maximum contaminant level (MCL) value specified by U.S. EPA/EU/WHO for various metal ions. It is prudent to choose an analytical technique with a detection limit approximately 10 times below the MCL for most reliability at a decision-making point.

The present work demonstrates the development of a simple method for water analysis using a high-speed, segmented charge coupled detector (SCD) based dual-view ICP-OES instrument with the ability to set the plasma viewing orientation (radial or axial) by wavelength.

Experimental

Instrumentation

The measurements were performed using the PerkinElmer® Optima™ 7300 DV ICP-OES instrument (Connecticut, USA) equipped with WinLab32™ for ICP Version 4.0 software for simultaneous measurement of all analyte wavelengths of interest (Figure 1). By combining an SCD detector and an echelle optical system, the Optima 7300 DV ICP-OES can measure all wavelengths simultaneously. Its wavelength flexibility allows the end users to easily add new elements or wavelengths as their program changes. Another benefit of using the Optima for drinking water analysis includes a 40 MHz free-running solid state RF generator designed to run from 750 to 1500 watts in 1 watt increments. High RF power is required to generate a robust plasma which is essential for precise analysis of high matrix samples such as river water.

The ICP torch is physically mounted in a horizontal orientation within the shielded torch box, and can be viewed either axially or radially. This viewing mode is user-selectable on a wavelength-by-wavelength basis. A shear gas minimizes chemical matrix effects by eliminating the cool plasma tail and allowing direct axial observation of the plasma's normal analytical zone.

The sample introduction unit employed included a cyclonic spray chamber and MEINHARD® concentric glass nebulizer (Figure 2). The concentric nebulizer provides excellent sensitivity and precision for aqueous solutions and samples with few dissolved solids (less than 1%), and is hence well suited for the analysis of water samples. The cyclonic spray chamber ensures high sample transfers to the plasma and fast rinse-in and rinse-out times, which improves productivity.

The read time was set at a variable range from 5 to 20 seconds using auto-integration mode. This feature takes a snapshot of the intensities of various lines to be measured before the actual reading begins. For high intensities, a shorter time is used, while for low intensities, the longer time is used thereby optimizing precision of analysis. Longer measurement times are beneficial in reducing shot noise, with little compromise on sample throughput. (Refer to Table 2 for detailed optimized instrumental conditions.)
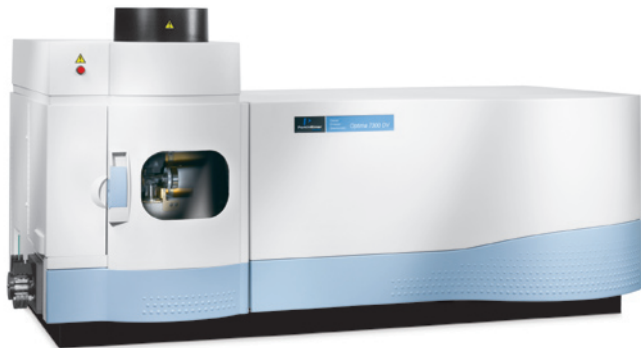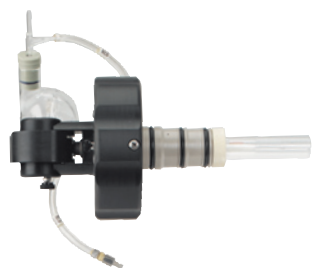
The PerkinElmer S10 autosampler (Figure 3) was used for high-throughput and automated analysis. The autosampler automates introduction of standards and samples for instrument calibration and sample analysis, extending the spectrometer's capabilities to those of an automated analytical workstation.

Figure 3. PerkinElmer S10 autosampler.

Figure 1. PerkinElmer Optima 7300 DV ICP-OES.

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

Table 2. Optimized operating parameters for Optima 7300 DV.	
Parameter	**Optimum Condition**
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	Teflon® 1 mm i.d.
Sample vials	Polypropylene
Source equilibrium delay	15 sec
Plasma aerosol type	Wet
Nebulizer start up	Instant
RF power	1450 Watt
Nebulizer flow	0.8 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)	5-20 sec
Read delay	60 sec
Replicates	3
Background correction	2-point, manual

Standards, Chemicals and Certified Reference Material

PerkinElmer NIST® traceable quality control standards for ICP, Part No. N9300281 (for Be, Ca, Cd, Cu, Cr, Fe, Mg, Mn, Ni, Pb and Zn) and Part No. N9300280 (for K, Al, Ba, Na and Ag) in 5% HNO₃, were used as the stock standards for preparing working standards. A total of four standards were used for calibration and were prepared from the two stock standards so that each metal ion will have two standards (Table 3). ASTM® type I water (from a Millipore® filtration system, Millipore® Corporation, Massachusetts, USA) acidified with Suprapur® nitric acid (Merck®, Germany) was used as the calibration blank and for all dilutions. After constructing the calibration curves which were linear with a correlation coefficient of at least 0.9999, two QC samples (one being a continuing calibration blank (CCB)), were run to monitor the instrument performance and evaluate long-term stability. Quality control check standard prepared at the midpoint of calibrations was Lot 39-86AS from SPEX CertiPrep®, (New Jersey, USA). Working standards were prepared by serial volume/volume dilution in polypropylene vials (Sarstedt®, Germany). Micropipettes (Eppendorf®, Germany) with disposable tips were used for pipetting solutions. NIST® certified drinking water reference material CRM 1643e was used for validating the developed method.

Table 3. **List of wavelengths selected and calibration standards used.**

Analyte	Wavelength (nm)	Standards (mg/L)	Spike Concentration (mg/L)
Al	396.153	1, 10	1.0
Ag	328.068	0.5, 10	1.25
Ba	493.408	1, 10	1.0
Be	313.107	1, 10	0.1
Cd	226.502	1, 10	0.1
Ca	317.933	1, 10	2.5
Cr	205.560	1, 10	0.1
Cu	327.393	1, 10	0.1
Fe	238.204	1, 10	0.1
K	766.490	10, 100	10.0
Mg	285.213	1, 10	2.5
Mn	257.610	1, 10	0.1
Na	589.592	1, 10	2.5
Ni	231.604	1, 10	0.1
Pb	220.353	1, 10	0.1
Zn	213.857	1, 10	0.1

Sample Preparation

Two well waters, one river, one lake and one ground water sample were collected from various parts of India. Also, six bottled-water samples from reputed firms were directly purchased from the market. The river, lake and well water samples were collected and brought to the lab and were kept undisturbed overnight. The samples were then flushed into plastic bottles containing 1% Suprapur® nitric acid. Similarly, the bottled waters were each poured into 50.0 mL graduated polypropylene vials and 500 µL of nitric acid was added. Spiked samples were similarly prepared with the addition of known quantities of analyte ions from the stock standard solution. For drinking water compliance monitoring, a "total" element determination (dissolved plus suspended) is required. For this total determination of trace and matrix elements in drinking water, samples are not filtered, but acidified with nitric acid to a pH < 2. Preservation may be done at the time of collection or when returned to the laboratory, depending upon regulatory requirements.

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 against 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 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 the 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 system performance, water samples (Table 5 – Page 5) were measured along with certified reference materials, for which results are presented in Table 4 (Page 5). The accuracy and precision are considered very good for the analysis performed. The reproducibility of the measurement is generally below 1%. The validity of the calibration was monitored by the Quality Control Check module within WinLab32 for ICP software. The quality control check standards were run at selected intervals in an unattended automated analysis run to ensure that the instrument performance remained consistent over the length of the analysis (more than 6 hours). Table 7 (Page 6) provides the QC recoveries in % at the beginning and

at the end of analysis, thereby validating consistent performance. In order to further validate the developed method, spike recovery studies were performed at the midpoint of calibrations for all elements in all samples except Bottle Water 6 (as sample quantity was not enough to perform the recovery study). The recoveries were well within the regulatory agencies' set limits (Table 6 – Page 6). The instrument detection limits (IDLs) were determined by running 10 replicate analyses of a series of calibration blank solutions and then multiplying the standard deviation (SD) by a factor of 3. This can be done automatically within the software. The extremely low value obtained for all elements indicates that reliable analysis can be performed at the limits specified by various regulatory bodies.

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

Analytes	Optima 7300 DV Values (µg/L)	Certified Values (µg/L)
Al	139 ±6.0	141 ±8.6
Ag	1.10 ±0.1	1.06±0.08
Ba	507 ±17	544 ±5.8
Be	14.0 ±0.6	14.0 ±0.17
Cd	6.20 ±0.2	6.56 ±0.07
Ca	31400 ±210	32300 ±1100
Cr	20.0 ±0.1	20.4 ±0.24
Cu	42.0 ±2.7	42.7 ±0.31
Fe	96.0 ±1.7	98.1 ±1.4
K	2010 ±10	2034 ±29
Mg	8040 ±41	8037 ±98
Mn	39.6 ±4.0	39.0 ±0.45
Na	19900 ±89	20740 ±260
Ni	61.7 ±2.2	62.4 ±0.69
Pb	19.7 ±0.5	19.6 ±0.21
Zn	79.8 ±3.8	78.5 ±2.2

Table 5. Analysis of surface and bottled water samples with Optima 7300 DV ICP-OES.

Analyte	Lake Water	Well Water	Bottle Water 1	Ground Water	Bottle Water 2	Bottle Water 3	Bottle Water 4	Bottle Water 5	River Water	Well Water 2	Bottle Water 6
Al	31.0	22.0	BDL	37.0	BDL	BDL	BDL	BDL	1720	BDL	4.60
Ag	BDL	1.10	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.70	0.80
Ba	11.0	2.60	1.90	3.20	BDL	BDL	BDL	2.20	30.0	39.0	191
Be	2.50	2.40	BDL	BDL	1.30	0.40	2.20	1.60	12.0	0.80	2.60
Cd	BDL	0.30	BDL	BDL	BDL	BDL	BDL	BDL	0.20	0.20	BDL
Ca*	12.0	108	6.80	8.60	0.21	0.15	4.60	6.20	3.90	4.80	52.0
Cr	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	1.0	BDL	3.10
Cu	1.20	6.50	BDL	2.10	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Fe*	51.0	46.0	BDL	34	BDL	BDL	BDL	BDL	472	8.70	BDL
K*	1.60	0.51	2.60	0.72	0.04	0.06	0.15	5.20	5.50	4.50	1.60
Mg*	9.50	38.0	3.80	3.10	0.06	3.0	1.30	2.90	8.70	3.0	5.80
Mn	2.60	1.30	BDL	1.70	BDL	BDL	1.00	BDL	1.50	2.40	BDL
Na *	40.0	36.0	25.0	4.50	1.40	2.80	15.0	4.10	72.0	32.0	15.8
Ni	0.70	5.70	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	11.0
BDL	BDL	3.30	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Zn	0.50	596	4.00	73.0	BDL	BDL	1.80	15.0	1.40	78.0	0.55

*in mg/L, Others in µg/L
BDL = Below Detection limit

Table 6. Spike recovery studies.

Analyte	Blank	Lake Water	Well Water	Bottle Water 1	Ground Water	Bottle Water 2	Bottle Water 3	Bottle Water 4	Bottle Water 5	River Water	Well Water 2
Al	93.0	100	99.0	96.0	94.0	93.0	90.0	95.0	93.0	82.0	98.0
Ag	100	105	98.0	103	102	100	98.0	107	100	91.0	92.0
Ba	96.0	93.0	91.0	92.0	94.0	98.0	91.0	93.0	93.0	90.0	90.0
Be	103	101	99.0	100	105	100	101	105	104	90.0	104
Cd	103	99.0	93.0	99.0	99.0	102	101	101	99.0	96.0	98.0
Ca	101	**	**	**	**	95.0	93.0	**	**	**	**
Cr	102	98.0	93.0	98.0	98.0	101	101	100	98.0	96.0	95.0
Cu	102	107	101	101	100	104	101	103	102	102	102
Fe	101	92.0	87.0	97.0	94.0	101	100	100	98.0	**	94.0
K	102	98.0	94.0	92.0	96.0	97.0	98.0	98.0	97.0	90.0	92.0
Mg	103	**	**	**	**	100	**	96.0	**	**	**
Mn	107	101	95.0	100	102	105	105	103	101	98.0	99.0
Na	104	**	**	**	**	91.0	96.0	**	**	**	**
Ni	101	97.0	81.0	97.0	96.0	101	99.0	100	97.0	95.0	96.0
Pb	100	98.0	93.0	97.0	99.0	102	102	101	105	96.0	97.0
Zn	108	109	105	106	103	108	109	110	107	108	100

*** Native concentration too high for spiking. All results are in %.*

Table 7. Quality control check standard recoveries.

Analyte	First QC Recovery (%)	Last QC Recovery (%)
Al	99	104
Ag	103	102
Ba	98	99
Be	101	100
Cd	101	96
Ca	97	100
Cr	100	98
Cu	99	104
Fe	99	95
K	98	104
Mg	98	103
Mn	103	97
Na	98	105
Ni	99	97
Pb	98	98
Zn	103	100

Conclusions

The simultaneous ICP-OES (Optima 7300 DV) used in this study has the capability of analyzing 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 16 elements taking only 16 seconds for three replicates, the analysis speed is extremely good for measuring the drinking water certified reference materials used in this study. This excludes the sample rinse-in and rinse-out times, which may add another 45-60 seconds to the analysis time, depending upon the sample matrix, but can be reduced considerably by using special sample introduction systems. The trace metal constitutions of water samples were determined successfully and accurately at very low levels by using the Optima 7300 DV ICP-OES.

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