



Elemental Analysis of Drinking Water

Using the PerkinElmer AAnalyst 800 Atomic Absorption Spectrometer

Application Note

Water analysis

Author

Ankit Shah
Agilent Technologies, Inc.



Introduction

Inorganic elemental contamination of water supplies occurs from natural deposits, and from industrial, agricultural, and household sources. Major causes of water quality degradation include discharge of toxic chemicals, overpumping of aquifers, long-range atmospheric transport of pollutants, and contamination of water bodies with substances that promote algal growth (possibly leading to eutrophication) [1]. The World Health Organization has noted that there is a pressing need for comprehensive and accurate assessment of water quality [1]. To address the consequences of contamination threats, accurate monitoring of minerals and contaminants in drinking, waste, surface, and ground waters is essential to ensure good water quality.

There are various advanced instrumental methods suitable for the determination of nutrients, minerals, and trace elements in waters. However, for the determination of the major elements (Ca, Cu, Fe, Mg, K, Na, and Zn), flame atomic absorption spectrometry (FAAS) is preferred. Many other trace elements can be determined directly using alternative, more sensitive techniques such as ICP-OES and ICP-MS. The FAAS method is simple, rapid, and appropriate for many environmental samples including ground water, aqueous samples, extracts, industrial wastes, soils, sludge, sediments, and similar wastes [2]. FAAS is used because of its simplicity, low operating cost, and comparatively fast analysis for the major elements. It also requires minimal sample preparation, is element-specific, free from most interferences, and is suitable for analysis at the expected analyte concentrations in these sample types.

In this study, municipal drinking water, recycled water, and bottled water samples were analyzed for seven different elements using the Perkin Elmer AAnalyst 800 FAAS.



Agilent Technologies

Experimental

Instrumentation

A PerkinElmer AAnalyst 800 FAAS was used for this study. This instrument features an adjustable nebulizer that enables optimization of the uptake rate. This feature means that many different sample matrices can be analyzed with good signal stability and minimal carryover. This system also features an automated atomizer-changing system that allows pushbutton change-over between flame AA and graphite furnace AA operation.

In this study, only Agilent supplies for the PerkinElmer atomic absorption instruments were used. Agilent supplies for PerkinElmer instruments are guaranteed to be fully compatible with the equipment for which they are specified. These supplies are designed and manufactured to meet critical specifications set by Agilent engineers to ensure optimal fit and performance with PerkinElmer instruments.

Sample collection and pretreatment

The municipal water samples were collected from two different properties. One of these properties was also supplied with recycled water from a local water authority treatment facility that was also sampled for this study.

Using prewashed bottles, the samples were collected from the first tap after the water meter. A bottle of mineral water was purchased from a local store.

The samples were acidified with 1 % nitric acid, and 0.1 % lanthanum chloride was added. Lanthanum chloride acts as a releasing agent for analysis of calcium (Ca) and magnesium (Mg), and as an ionization suppressant for sodium (Na) and potassium (K) analysis.

To validate the results reported for these drinking and recycled water samples, two independent standards were used. An Agilent Initial Calibration Verification (ICV) standard (p/n 5190-9408) was used as an independent standard to confirm the accuracy of the calibration curve. Table 1 lists the certified concentrations for the elements in the ICV standard, which is prepared in 5 % nitric acid matrix with trace tartaric acid.

A certified reference material from High-Purity Standards was also used as an independent standard to validate the measured results for the different water samples. The CRM selected for this study was Trace Metals in Drinking Water (CRM-TMDW), sourced from Graham B. Jackson (Aust.) Pty. Ltd. Table 2 lists the certified concentrations for the elements in High Purity Standards CRM-TMDW determined in this study.

Table 1. *Certified Concentrations for the Elements in the Agilent ICV Standard (p/n 5190-9408) Used to Validate the Individual Calibrations in this Study*

Element	Certified concentration ($\mu\text{g}/\text{mL}$)
Ag, As, Cr and Tl	10
Al and Ba	200
Be, Cd, and Se	5
Co and V	50
Cu	25
Mn	15
Ca, K, Mg, and Na	500
Fe	100
Sb	60
Ni	40
Zn	20
Pb	3

Table 2. *Certified Concentrations for the Elements in the High-Purity Standards CRM-TMDW Used in this Study*

Element	Certified concentration ($\mu\text{g}/\text{L}$)
Al	120
Sb, Bi, Cd, Rb, Se, Tl, and U	10
As	80
Ba	50
Be, Cr, Cu, and Li	20
Co	25
Mg	9,000
V	30
Zn	70
Mn and Pb	40
Fe, Mo	100
Ni	60
K	2,500
Ca	35,000
Ag	2*
Na	6,000
Sr	250
Te	3*

*Reference values

Instrument conditions

All sample analyses were carried out using the Perkin Elmer AAnalyst 800 AA spectrometer in flame atomizer mode. An Agilent stainless steel self-aspirating nebulizer recommended for aqueous solutions (p/n 8003-0822) was used for sample introduction with the sample uptake optimized for maximum sensitivity. Only Agilent single element 50 mm coded hollow cathode lamps for the PerkinElmer AA instruments were used (Ca (p/n 8003-0891), Cu (p/n 8003-0894), Fe (p/n 8003-0906), Mg (p/n 8003-0910), and Zn (p/n 8003-0942)).

The analysis of Ca, Cu, Fe, Mg, and Zn was completed using absorbance measurement mode. For K and Na, analysis was completed using emission measurement mode. The burner was rotated 30 degrees for K, Na, Ca, and Mg to reduce detector saturation from the high-intensity signals observed, due to the high concentration of these mineral elements. Seven multi-element calibration standard solutions were prepared from Agilent 1,000 µg/mL aqueous single element certified reference materials (Ca (p/n 5190-8273), Cu (p/n 5190-8280), Fe (p/n 5190-8286), Mg (p/n 5190-8292), K (p/n 5190-8305), Na (p/n 5190-8312), and Zn (p/n 5190-8326)). Table 3 lists the instrument operating parameters and the standard concentrations used for instrument calibration in this study.

Table 3. Instrument Operating Parameters and Analytical Conditions Used with the PerkinElmer AAnalyst 800 FAAS

Analyte	Ca	Cu	Fe	Mg	Zn	K	Na
Common instrument operating parameters							
Measurement time	3 seconds	3 seconds	3 seconds	3 seconds	3 seconds	3 seconds	3 seconds
Number of replicates	3	3	3	3	3	3	3
Flame type	Air/Acetylene	Air/Acetylene	Air/Acetylene	Air/Acetylene	Air/Acetylene	Air/Acetylene	Air/Acetylene
Gas flows (Air/Acetylene) (L/min)	10.0/2.0	10.0/2.0	10.0/2.0	10.0/2.0	10.0/2.0	10.0/2.0	10.0/2.0
Element-specific operating parameters							
Measurement mode	Absorbance					Emission	
Wavelength (nm)/SBW (nm)	422.7/0.7	324.8/0.7	248.3/0.2	285.2/0.7	213.9/0.7	766.5/0.7	589.0/0.2
Lamp current (mA)	8	15	30	6	15	10	8
Background correction	Off	Off	On	Off	Off	Off	Off
Burner rotation (deg)	30	0	0	30	0	30	30
Concentration in standard 1 (mg/L)	0.5	0.05	0.05	0.5	0.05	2	2
Concentration in standard 2 (mg/L)	1.0	0.1	0.1	1.0	0.1	5	5
Concentration in standard 3 (mg/L)	2.0	0.25	0.25	2.0	0.25	10	10
Concentration in standard 4 (mg/L)	5.0	0.5	0.5	5.0	0.5	20	20
Concentration in standard 5 (mg/L)	10.0		1.0	10.0		30	30
Concentration in standard 6 (mg/L)	20.0					40	40
Concentration in standard 7 (mg/L)	40.0					50	50

Results and Discussion

All calibrations for each of the elements determined in this study provided a correlation coefficient (R^2) of 0.999 or greater.

The validity of the calibration was assessed by measuring the ICV or independent standard immediately after calibration of the instrument. The Agilent ICV standard (p/n 5190-9408) used for testing the validity of the calibration was diluted 100 times. This dilution ensured that the concentrations of the target elements fell within the range of the calibration curve. Table 4 shows the results for the ICV solution.

Excellent recoveries, within $\pm 10\%$ of the certified value, were achieved for all elements determined in this study. These recoveries demonstrate the accuracy of the calibration.

Having demonstrated that the calibration for each element was accurate, the performance of the method was validated using the High Purity Standards CRM-TMDW certified reference material. Table 5 shows the results. Excellent recoveries, within $\pm 10\%$ of the certified value, were achieved for all elements determined in this study. These recoveries demonstrate the suitability of the methodology for achieving accurate results with water samples.

The water samples collected from the municipal drinking and recycled water supplies, and the bottled water sample were also measured, using the prepared and validated calibration. Table 6 shows the results.

Table 4. Achieved Recoveries for the Elements Determined in the Initial Calibration Verification (ICV) Solution (p/n 5190-9408)

Analyte	Measured result (mg/L)	Analyte concentration with 100x dilution (mg/L)	Recovery (%)
Ca	4.85	5.00	97
Cu	0.25	0.25	100
Fe	1.05	1.00	105
Mg	4.86	5.00	97
K	4.86	5.00	97
Na	5.35	5.00	107
Zn	0.21	0.20	105

Table 5. Achieved Recoveries for the Elements Determined in the High Purity Standards Trace Metals in Drinking Water (CRM-TMDW)

Analyte	Measured result (mg/L)	Certified concentration (mg/L)	Recovery (%)
Ca	36.6	35.0	105
Cu	0.019	0.020	95
Fe	0.102	0.100	102
Mg	8.43	9.00	94
K	2.33	2.50	93
Na	5.90	6.00	98
Zn	0.071	0.070	101

Table 6. Measured Results for the Municipal Water and Bottled Mineral Water Samples

Analyte	Municipal (drinking) water 1 (mg/L)	Municipal (recycled) water 2 (mg/L)	Municipal (drinking) water 3 (mg/L)	Bottled mineral water (mg/L)
Ca	3.85	13.92	4.88	1.17
Cu	0.12	0.03	0.13	<LOD
Fe	0.05	<LOD	0.03	<LOD
Mg	1.86	7.87	1.14	1.82
K	0.59	20.56	0.61	0.53
Na	4.10	Over range	4.17	7.76
Zn	0.04	2.47	0.14	<LOD

Table 6 shows that there are some apparent differences in the measured concentrations for the mineral elements in the municipal water samples. The results in Table 6 suggest that the samples do differentiate slightly between the areas where they have been collected. Municipal water samples 1 and 2 are expected to have differences as they are different types of water. Municipal water 1 is water that was sampled from a domestic water supply suitable for drinking purposes. This water is classified as fit for human consumption. Municipal water 2 is water that was sampled from a Class A rated recycled water supply. This recycled water is specified for use in domestic applications such as flushing toilets, watering gardens, washing clothes, and washing cars. Class A rated recycled water is the highest class of recycled water available, but it is not suitable for human consumption. The supplier does report that recycled water contains higher levels of chlorine, nutrients, and salt. It must satisfy the water quality standards set by the local Environmental Protection Authority and Department of Health [3]. Those regulations specify the maximum allowable levels of chlorine, turbidity, and microorganisms such as *E. coli* and other viral, bacterial, or protozoan pathogens. These differences in the water quality are clearly visible when comparing the results in Table 6. Higher levels of Ca, Mg, K, Zn, and especially Na were measured in the recycled water (municipal water 2).

Municipal water 3 was sourced from a different locality. However, it was later determined that municipal water samples 1 and 3 originated from the same discharge point at a local water reservoir. The differences in the measured mineral levels between those two water samples are most likely due to a combination of factors. These factors include the condition of the water supply pipework, the distance from the water discharge point at the reservoir, and the time the water has been held in the pipework before sample collection.

The bottled mineral water sample was found to be free of Cu, Fe, and Zn, which was expected, due to the water purification methodologies applied before bottling. It was anticipated that bottled mineral water would have different mineral content to the municipal water samples due to the different source of the water. These variations originate from the different geologies in the area where the water was sourced. Although there are differences in the Ca and Na levels, the Mg and K concentrations were remarkably similar to those levels measured in the municipal drinking water.

Limits of detection (LOD) were calculated for Cu, Fe, and Zn as a three sigma value. That is, three times the standard deviation for 10 replicate measurements of a nitric acid blank, measured after completing a full calibration. Table 7 lists the measured LODs. Detection limits were not calculated for the other elements, as they are present in the sample at higher concentrations, and were measured using low sensitivity conditions.

Table 7. Measured LODs for Cu, Zn, and Fe Using the PerkinElmer AAnalyst 800 FAAS

Analyte	Detection limit (mg/L)
Cu	0.003
Fe	0.007
Zn	0.004

Conclusion

The results obtained in this study demonstrate the ability to use the Agilent supplies with the PerkinElmer AAnalyst 800 FAAS. This enables rapid, direct, and simple measurement of the nutrients and mineral elements in both municipal water supplies and bottled water samples. Measuring high concentration elements such as Ca, K, Mg, and Na using reduced sensitivity conditions with a rotated burner position in emission mode, enabled both high and low concentrations to be measured in the same samples.

The performance and dynamic range of the technique was demonstrated by the excellent recoveries obtained for the analysis of High Purity Standards CRM-TMDW. Sample concentrations in this CRM covered four orders of magnitude, yet excellent recoveries were achieved for elements at both low and high concentrations. This reinforces the suitability of this methodology for analysis of municipal water supplies, and bottled water samples.

References

1. J. Bartram, R. Ballance (ed.); Water Quality Monitoring - A Practical Guide to the Design and Implementation of Freshwater Quality Studies and Monitoring Programmes. *United Nations Environment Programme and the World Health Organization*, 1996.
(Accessed online May **2016** at: http://www.who.int/water_sanitation_health/resourcesquality/waterqualmonitor.pdf).
2. US Environmental Protection Agency SW-846 Test Method 7000B: Flame Atomic Absorption Spectrophotometry.
(Accessed online May **2016** at: <https://www.epa.gov/sites/production/files/2015-12/documents/7000b.pdf>).
3. Environment Protection Authority Victoria, Guidelines for Environmental Management - Dual Pipe Water Recycling Schemes – Health and Environmental Risk Management, (Publication 1015.1) Feb. **2015**. (Accessed on-line May 2016 at: http://www.epa.vic.gov.au/~/_/media/Publications/1015%201.pdf).

For More Information

These data represent typical results. For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Agilent shall not be liable for errors contained herein or for incidental or consequential damages in connection with the furnishing, performance, or use of this material.

Information, descriptions, and specifications in this publication are subject to change without notice.

© Agilent Technologies, Inc., 2016
Printed in the USA
June 22, 2016
5991-7046EN



Agilent Technologies