



Analysis of low levels of metals in drinking water with a SCANNING ARRAY ICP EMISSION SPECTROMETER AND ULTRASONIC NEBULIZATION

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Introduction

Drinking water is an important factor in exposure to environmental contaminants and is used in preparing foods and beverages for human consumption. Therefore, great care is used to verify that it is free of or contains acceptable limits of toxic substances. With respect to heavy metals and other toxicologically relevant elements, atomic spectrometric techniques are frequently used to determine their concentration levels (1). While atomic absorption spectroscopy has been the main technique employed for this application, inductively coupled plasma optical emission spectrometry (ICP-OES) has become more important during the past years. National and international agencies set guidelines and methodology for the use of ICP-OES for water analysis (e.g., EPA 200.7 (2), ISO 11885 (3), the latter has been adopted by the European Community and its participating states).

ICP emission spectrometers equipped with an array detector show a significant advantage over conventional technology with respect to speed, sensitivity and stability(4), which has produced an ever-growing market for this type of instrumentation. The established analytical advantages of array detectors were transferred to a new scanning array-type instrument in order to retain the analytical advantages at a reduced instrument cost. The price of the analysis is composed of many

different factors. These include the instrument and maintenance costs, the speed of analysis, and system usability. Great care was taken to develop a system that can analyze at a high speed with minimum requirements for maintenance and education.

An ultrasonic nebulizer produces a very fine aerosol, so the sample delivered into the plasma is much greater (about a factor 10) than with a pneumatic nebulizer. The enhanced sensitivity can be utilized for the improvement of detection limits by about the same factor, because the signal stability is comparable to that of pneumatic nebulizers.

This work demonstrates that the new scanning array ICP emission spectrometer in combination with an ultrasonic nebulizer is capable of determining extremely low concentrations of elements in drinking water according to the requirements of the strictest national and international laws and regulations. Major elements, such as Ca, Mg, Na, and K, can be measured in the same analysis run, but was not within the scope of this work. Mercury is often combined in a multielement analysis using ICP-MS, but was not considered within the scope of this work.

Regulatory Aspects

The regulatory aspects are twofold: One aspect are the permissible concentrations in drinking water, the other is the regulation that guides the analyst to use a certain technique

and the methodology for an accurate analysis. The issue of setting permissible values is usually a compromise between toxicological and economical issues and is strictly tied to national laws and ordinances. Table 1 lists tolerable concentrations for drinking water in several regions of the world (5-7).

The concentrations given by the World Health Organization (WHO) are recommended values. Similarly, the European Community (EC) suggests concentrations, which are adopted into national laws by the members of the EC. In the EC regulations, there are minimum requirements on the quality of the analytical data generated to verify the quality of the drinking water (7). The limits for accuracy and precision may not exceed 10%, which means that the systematic and statistical deviation may not be higher than 10% at or above the tolerance level. In addition, the detection limit must be less than 10% of the tolerance level. While normally the detection limits are calculated using 3σ , the EC suggests 5σ when using the blank method.

With respect to the analytical technique to be used to determine the tolerable concentrations of heavy metals and other toxicologically relevant elements, all atomic spectroscopic techniques (atomic absorption, ICP emission, and ICP mass spectrometry) may be used. While atomic absorption spectroscopy has been the main technique employed

for this application over many years, ICP optical emission spectrometry (ICP OES) has become more important recently. As an example, ISO 11885 regulates the use of ICP OES for the analysis of water on an international scale since the year 1996 (3). In addition, numerous national regulations set guidelines for the use of ICP OES for water analysis. In many cases, these only have a recommendation character. Guidelines for the analysis of waters do not exist in each country, so the guidelines of another country are often used (e.g., EPA guidelines are often used in the Western hemisphere but also in parts of Asia; in this case: EPA 200.7).

Experimental

Instrumentation and Operating Conditions

A scanning array ICP emission spectrometer (Optima 2000™ DV, PerkinElmer, Norwalk, USA) was used for all measurements. The spectrometer uses a double-pass Echelle optical mount with movable grating and prism in order to slew to any analytical wavelength. A linear CCD detector registers the spectrum around the analyte wavelength, which allows simultaneous background correction in order to minimize flicker noise. The detector is split into two parts, one of which is being used to measure the analyte spectrum, while the other registers a neon spectrum which is travelling the same path as the light originating from the plasma. If the system registers deviations from initial settings, then the wavelength setting is actively changed to its original setting, allowing for wavelength stability in the order of 0.1 pm. In Figure 1, an example for this wavelength stability is displayed for the Cd line at 228.802 nm taken during a long-term stability measurement over 10 hours. Because of this exceptional wavelength stability, this *sequential* spectrometer can measure exactly

on the peak position thus contributing to excellent accuracy under routine conditions.

The other contribution to good long-term-stability comes from a stable emission source. Here, a stable power supply as well as a robust sample introduction system play a vital role. A newly constructed solid-state RF generator supplies power up to 1500 W with good output stability. Additionally, the sample introduction system can be thermostatted for a constant evaporation rate in the nebulizer chamber. The plasma can be viewed radially or axially and is user-selectable as part of the analytical method. Axial view was used throughout for improved detection limits. Figure 1 also clearly shows that the intensity stability is also excellent. Table 2 lists the instrumental parameters for the Optima 2000 DV.

The read time was set at variable range from 1 s to 10 s using the auto-integration mode. This auto-integration feature will take a snapshot of intensity of the line to be measured before the actual reading begins. For high intensities, a short read time will be used, while for low intensities, a longer read time will be used. Long measuring times are beneficial in reducing shot noise, thereby yielding lower detection limits. This is demonstrated in the Figure 2 with the example of Pb measured at 220 nm. As expected, the detection limit improves by the square root of the factor for time extension. Depending on the magnitude of the signal, the analysis of 11 elements, run at the conditions stated above with three replicates, took from 2 min and 20 s to 4 min and 45 s. For processing the analytical signal, three pixels were grouped to be processed as analytical signal. For background correction, two points and a linear function were used. The ultrasonic nebulizer system used was a CETAC U-5000AT+ (Cetac Technologies, Omaha, NE USA). The heater temperature was

set to 140°C. The condenser, which is cooled by Peltier elements, was set at 3°C. The sample flow rate was 1 mL/min.

Sample Preparation

Solutions at one-tenth of the limit of concentration of the European Community water regulations were prepared using single-element solutions (E. Merck, Darmstadt, Germany), except for Cu and Zn where one-hundredth of the tolerance concentration was used. The samples were diluted with 18 M-Ohm water (ASTM Type 1). The calibration standard was made by diluting a Multielement Verification Standard 2 (PE Pure, PerkinElmer, Norwalk, USA) to a concentration of 100 µg/L.

Results and Discussion

Wavelengths were selected from the lists of the ISO and EPA documents. For this application, those lines with minimum spectral interference and maximum working range were chosen.

To measure accuracy, two standard reference materials (NIST 1643c, National Institute of Standards and Technology, Gaithersburg, USA and SLRS-3, National Research Council Canada, Ottawa, Canada), representing different types of water, were measured. The results are listed in Tables 3 and 4. The agreement between measured and certified concentrations is generally very good. All elements are within the overlap of confidence intervals, except for As in the NIST material and Fe in the Canadian reference material. In both cases, the measured value is within 8% of the true value, which is well within the ±20% generally accepted value for environmental methods.

The detection limits were measured using the blank method: A blank solution was read using 10 replicates per measurement. This was repeated five times. The standard deviations, calculated from each set of 10 replicates, were then averaged. These mean standard deviations were then used in

Table 1: Tolerable concentrations for several toxicologically relevant elements in drinking water (in $\mu\text{g/L}$) according to the WHO (5), in the U.S. (6), and in the EC (7)

Element	WHO	U.S.	EC
Al	200	50	200
As	10	50	10
Ba	700	2000	–
Cd	3	5	5
Cr	50	100	50
Cu	2000	1300	2000
Fe	300	300	200
Mn	500	50	50
Ni	20	100	20
Pb	10	15	10
Zn	3000	5000	–

Table 2. Optima 2000 DV Operating Conditions

RF Power	1300 W (Dry Plasma)
Nebulizer Flow	0.7 L/min
Auxiliary Flow	0.5 L/min
Plasma Flow	15 L/min
Sample Pump Flow	1 mL/min
Plasma Viewing	Axial
Processing Mode	Area
Auto Integration (min - max)	1 - 10 s
Read Delay	40 s
Replicates	3
Background Correction	Manual, two points
Nebulizer	Ultrasonic
Injector	Alumina, 2 mm

Table 3: Certified and measured concentrations for trace elements in water in NIST 1643c

	Cert. Conc. ($\mu\text{g/L}$)	Uncertainty	Meas. Conc. ($\mu\text{g/L}$)	SD
Al	114.6	5.1	125	3.5
As	82.1	1.2	88.3	0.6
Ba	49.6	3.1	48.8	2.0
Cd	12.2	1.0	13.0	0.1
Cr	19.0	0.6	18.9	0.1
Cu	22.3	2.8	26.3	0.1
Fe	106.9	3.0	103.0	0.2
Mn	35.1	2.2	34.1	0.2
Ni	60.6	7.3	57.0	0.7
Pb	35.3	0.9	34.8	0.3
Zn	73.9	0.9	71.0	1.0

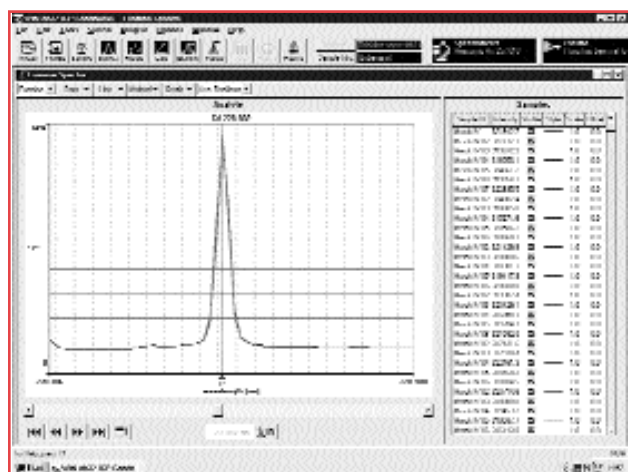


Figure 1: Overlay of 60 spectra at the wavelength of 228.802 nm of a solution containing 1 mg/L Cd taken over the period of 10 hours.

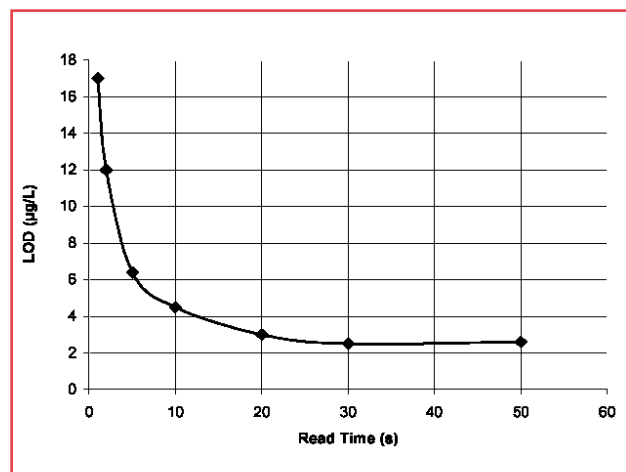


Figure 2: Effect of Read Time on the detection limits for Pb at 220 nm using a cross-flow nebulizer and Scott spray chamber.

the calculation of the detection limits using 5σ (to comply with EC) and 3σ (which is more often used). All detection limits are rounded to one significant figure. As a result, the values tabulated do not always differ by the 0.6 factor expected between 3σ and 5σ . According to the EC regulations, the measurements are made at a concentration required for the detection limits or

in the case of Cu and Zn are an additional factor of 10 below. As can be seen from Table 5, even at these low concentrations, a respectable accuracy and precision can be achieved.

Conclusions

Contaminant elements in drinking water can be successfully determined at very low levels by using a

scanning array ICP emission spectrometer equipped with an ultrasonic nebulizer. The analysis speed is very attractive, while with these conditions, the detection limits achievable are far below the criteria given by the strict European drinking water regulations. Consequently, the accuracy is very good, even at concentrations far below the tolerance levels.

Table 4: Certified and measured concentrations for trace metals in riverine water reference material SLRS-3

	Certified	95% Confid. Limit	Meas. Concn. (µg/L)	SD
Al	31	3	32	0.39
As	0.72	0.05	0.6	0.17
Ba	13.4	0.6	12.2	0.16
Cd	0.013	0.002	< 0.03	
Cr	0.30	0.04	0.28	0.01
Cu	1.35	0.07	1.39	0.11
Fe	100	2	92	1.37
Ni	0.83	0.08	0.87	0.02
Pb	0.068	0.007	< 0.3	
Zn	1.04	0.09	1.09	0.03

Table 5: Results for analysis drinking water at concentrations of at least a factor 10 below the tolerance levels

Element	Wavelength (nm)	C _{add} (µg/L)	C _{meas} (µg/L)	SD _{meas} (µg/L)	c (LOD) (µg/L) 5 σ	c (LOD) (µg/L) 3 σ
Al	396.153	20	20.3	0.22	0.05	0.03
As	188.979	1	0.97	0.37	1	0.6
Ba	455.403	10	9.20	0.12	0.01	0.007
Cd	228.802	0.5	0.42	0.012	0.03	0.02
Cr	283.563	5	4.62	0.080	0.02	0.01
Cu	327.393	20	18.8	0.13	0.06	0.04
Fe	259.939	20	18.6	0.22	0.1	0.07
Mn	257.610	5	4.68	0.31	0.02	0.01
Ni	231.604	2	1.85	0.048	0.2	0.1
Pb	220.353	1	0.93	0.22	0.3	0.2
Zn	206.200	50	47.0	0.40	0.1	0.06

References

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