Elemental analysis of river sediment using the Agilent 4200 MP-AES

Application note

Environmental: Soils, sludges & sediments

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Introduction

The elemental profile of river sediments provides valuable insight into the health of a river, as well as the wider environment. Some elements that are essential for the ecology of the river at trace levels e.g. manganese, copper and zinc, can be toxic at high concentrations.

Traditionally, the concentration of elements in river sediments is determined via Flame Atomic Absorption Spectroscopy (FAAS). This technique has the drawback of requiring expensive and hazardous gases such as acetylene and nitrous oxide and also requires element-specific sample preparation that adds time and cost to the analysis.

The novel Agilent 4200 Microwave Plasma-Atomic Emission Spectrometer (MP-AES) is the ideal alternative for laboratories looking to transition away from FAAS to a higher performance, lower cost and safer technique. MP-AES is a fast sequential, multielement analytical technique that uses a microwave-induced nitrogen-based plasma for sample excitation. The use of nitrogen eliminates the need for acetylene and nitrous oxide, which can

be generated from surrounding air, using a nitrogen generator. This makes it safer and allows unattended operation of the instrument, even for overnight runs.

This application demonstrates a simple, fast, low cost, and safe method to analyze major and minor elements in river sediment, with no compromise in data quality or ease of use. It describes a simple one step dilution sample preparation procedure and an analytical method that was used to analyze major elements, Ca, K, Mg, Na and Al, and minor elements, Fe, Zn, Cu, and Mn, in a river sediment certified reference material (CRM) using the Agilent 4200 MP-AES.

Experimental

Instrumentation

All measurements were performed using an Agilent 4200 MP-AES fitted with a OneNeb nebulizer, double-pass glass cyclonic spray chamber and easy-fit torch. Nitrogen was supplied from a Dewar, but could also have been obtained via the Agilent 4107 Nitrogen Generator (with air supplied from an air compressor). An Agilent SPS 4 autosampler was used to deliver samples to the instrument, allowing the system to be operated unattended. Method parameters are given in Table 1.

Table 1. MP-AES method parameters

Instrument Parameter	Setting
Nebulizer	OneNeb
Nebulizer flow rate	Optimized
Spay chamber	Double pass glass cyclonic
Pump rate (rpm)	15
Sample pump tubing	Orange/green
Waste pump tubing	Blue/blue
Autosampler	Agilent SPS 4
Read time (s)	3 ; 2 for Na and K
Number of replicates	3
Fast pump during uptake	On
Sample uptake delay (s)	55
Rinse time (s)	45
Stabilization time (s)	10
Background correction	Auto
Gas source	Dewar nitrogen

Sample and sample preparation

River Sediment Solution B CRM (CRM-RS-B) purchased from High Purity Standards (Charleston, SC, USA) was used to validate the method. The CRM was prepared for analysis by diluting 1:10 with 2% HNO_3.

Calibration standards

Single element Reference Materials (Agilent Technologies) were used to prepare a set of multielement calibration standards. The Blank and standards were prepared in 2% HNO_3. No ionization buffers were required.

Wavelength selection and calibration range

Details of wavelength selection and nebulizer flow rate are given in Table 2. The Agilent 4200 MP-AES features continuous wavelength coverage and the MP Expert software includes an extensive wavelength database that allows the selection of wavelengths suited to the concentration range required for the analysis. All wavelengths were selected to provide the widest dynamic range while minimizing spectral interferences. For example, the less sensitive Mg 383.829 nm line was selected over the more sensitive Mg 285 nm line because it has a large linear dynamic range, meets the detection limit requirements of the application, and is free from spectral interferences.

Table 2. Selected wavelength and nebulizer flow for each element being determined

Element	Wavelength (nm)	Nebulizer Flow (L/min)
Zn	213.857	0.45
Fe	373.486	0.5
Ca	422.673	0.6
Cu	324.754	0.7
Mg	383.829	0.9
K	766.491	0.75
Mn	403.076	0.9
Al	394.401	0.95
Na	588.995	0.95

Results and discussion

Calibration

Each element was calibrated using a four point calibration. All calibration curves were linear, with a correlation coefficient greater than 0.999, and less than 10% calibration error on each calibration point. The calibration curve for Mg 383.829 nm (Figure 1) is a typical example, showing excellent linearity across the calibration range.

Table 3 summarizes the calibration standard concentration range and correlation coefficients for all 9 elements. Due to the wide working range of MP-AES, only one dilution of the sample was required to measure all of the elements of interest. Reducing the number of sample dilution steps improved productivity and reduced the risk of sample contamination and dilution errors. The wide dynamic range of MP-AES eliminates the need for the strategies commonly used on FAAS to determine elements present at high concentration, such as burner rotation or measuring elements in emission mode.

Table 3. Typical MP-AES calibration range

Element/ Wavelength (nm)	Std Conc. Range, mg/L	Linear Correlation Coefficient r
Ca 422.673	0-25	0.99992
Mg 383.829	0-25	0.99999
Na 588.995	0-20	0.99966
K 766.491	0-25	0.99991
Zn 213.857	0-10	0.99996
Fe 373.486	0-50	0.99998
Al 394.401	0-100	0.99994
Cu 324.754	0-5	1.00000
Mn 403.076	0-10	1.99991

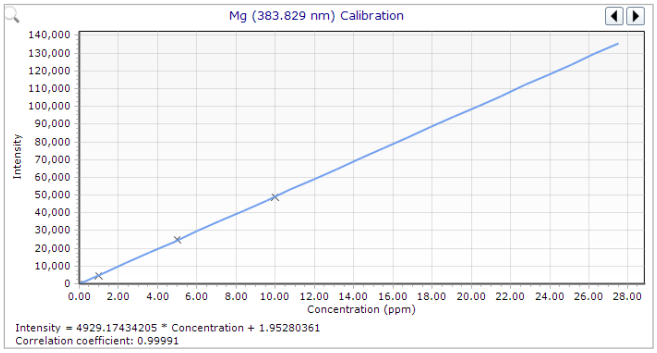

Figure 1. Calibration curve for Mg 383.829 nm

Sample analysis

The river sediment CRM-RS-B was measured three times using two separate MP-AES instruments. The mean concentration, standard deviation (SD), and recovery was calculated for each analyte, as shown in Table 4. All elements were determined in one sample measurement. The precision between the two instruments was excellent, as indicated by the low SD. The mean of the measured results was in good agreement with CRM values (99-107%).

The results demonstrate the ability of the 4200 MP-AES to measure low concentrations (Cu, Zn and Mn), in the presence of major elements (Fe, Ca, Mg, K, Al) and achieve excellent recoveries across a wide concentration range.

Table 4. MP-AES recovery of certified elements in river sediment CRM

Element/ Wavelength (nm)	Measured conc. in solution-Instrument 1 (mg/L)	Measured conc. in solution-Instrument 2 (mg/L)	Mean (mg/L)	SD	Certified conc. (mg/L)	Recovery in solution (%)
Zn 213.857	4.94	5.12	5.03	0.124	5.0	100.7
Fe 373.486	429.6	406.7	418.2	16.2	400.0	104.5
Ca 422.673	305.6	302.4	304	2.28	300.0	101.0
Cu 324.754	1.06	1.08	1.07	0.020	1.00	107.0
Mg 383.829	125.1	121.9	123.5	2.25	120.0	102.9
K 766.491	204.0	204.8	204.4	0.51	200.0	102.2
Mn 403.076	6.08	6	6.04	0.055	6.0	100.7
Al 394.401	597.1	592.1	594.6	3.54	600.0	99.1
Na 588.995	53.2	53.3	53.3	0.015	50.0	106.5

Method Detection Limits

Three sigma Method Detection Limits (MDLs) were calculated from ten replicate measurements of the blank using a 3 second integration time. These MDLs were acquired using a set of conditions suitable for routine sample analysis rather than highly optimized conditions. Therefore, they are not the best possible detection limits but are more than sufficient for the method requirements.

The MDLs were measured three times on two separate instruments. The results shown in Table 5 are the average of the six measurements.

Table 5. Method Detection Limits in ppb (µg/L).

Element	Wavelength (nm)	Average MDL (µg/L), n=6
Zn	213.857	4.44
Fe	373.486	5.39
Ca	422.673	0.310
Cu	324.754	1.21
Mg	383.829	1.91
K	766.491	2.35
Mn	403.076	0.305
Al	394.401	0.452
Na	588.995	3.28

Long term stability

The river sediment CRM was analyzed every 10 samples over 12 hours of continuous measurement, as shown in Figure 2. Excellent stability was achieved over this long term measurement. Average recoveries for most elements were within ± 5%, and all elements in the method were within ± 10% of the certified value. The long term measurement precision over the full 12 hours was less than 2% RSD (Table 6), demonstrating the suitability of the 4200 MP-AES for routine measurement of metals in river sediment samples.

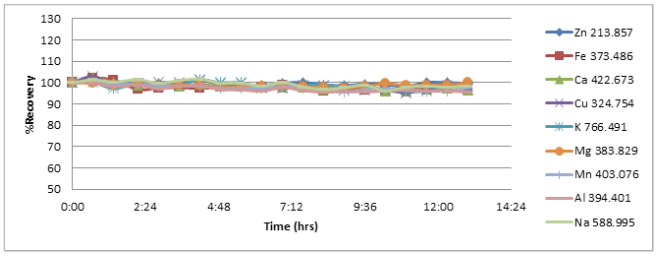

Figure 2. Long-term stability plot. <2.0% RSD over 12 hours analysis of river sediment sample

Table 6. Long-term precision and average recovery over 12 hours of continuous measurement of the river sediment CRM

Element/ Wavelength (nm)	%RSD	Average Recovery (%)
Zn 213.857	0.9	96.4
Fe 373.486	1.8	96.8
Ca 422.673	1.5	93.3
Cu 324.754	1.8	95.2
K 766.491	1.2	93.3
Mg 383.829	0.8	102.4
Mn 403.076	1.3	103.1
Al 394.401	1.6	99.6
Na 588.995	1.5	107.3

Potential cost savings with the 4200 MP-AES

The example given in Figure 3 allows comparison of the running costs and potential savings of the MP-AES compared to operating a FAAS.

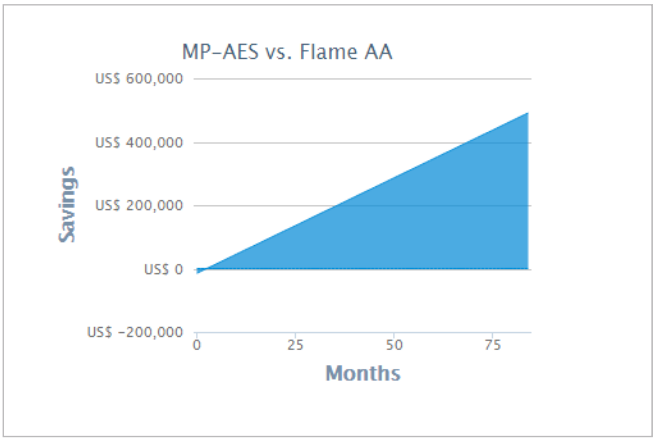

Figure 3. Potential cost savings with MP-AES compared to FAAS over time*

The lower operating costs of the MP-AES, compared to FAAS could deliver savings of close to USD500k over a 7-year evaluation period, as indicated in Figure 3. The cost-comparison was based on the following criteria:

- An FAAS fitted with an air compressor and 1 year of consumables, including acetylene gas
- An MP-AES fitted with an air compressor, SPS 4 autosampler and 1 year of consumables
- Nine elements measured under method conditions, all with air/acetylene flame.
- Based on the analysis of 300 samples per week

Conclusions

The Agilent 4200 MP-AES is suited to the analysis of major and trace elements in river sediments, as demonstrated in this study. The instrument's wide dynamic range ensured that only one dilution of the samples was required to measure the complete set of elements, increasing laboratory productivity and reducing the risk of errors. Excellent recoveries of the certified standard material were achieved, with good precision across two separate instruments.

The robust plasma and sample introduction system consisting of the OneNeb nebulizer and mass flow controlled nebulizer gas flow ensured excellent stability over 12 hours period—without the need to recalibrate. Automated wavelength selection reduced all potential chemical and ionization interferences, greatly simplifying method development.

MP-AES is an ideal replacement technique for FAAS for those labs looking to boost their productivity and realize significant cost benefits.

*This example is intended to help you compare the running costs and savings of the MP-AES vs. flame AA. The applied formulas and parameters are correct to the best of our knowledge, but we cannot guarantee the results. Savings may vary depending on factors such as local gas and electricity costs, operator costs, number and types of elements.
For this calculation, operator labor costs were set to USD 25 per hour and electricity costs were set to USD 0.2 per kW.

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