Analysis of domestic sludge using the Agilent 4200 MP-AES

Application note

Environmental

Authors

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Introduction

Managing the treatment and disposal of domestic sludge is an important activity and one that is highly regulated in many countries. After treatment, the effluent may be discharged leaving a mixture of water, organic solids and chemicals, nutrients, heavy metals, and inorganic ions. This sludge can be further treated and the resulting biosolids can then be applied to the land as a fertilizer, sent to landfill or incinerated. It is vital that the sludge or biosolids are tested and conform to regulatory levels in order to protect public health and the environment.

The United States federal biosolids rule is contained in 40 CFR Part 503. The European Union Sludge Directive 86/278/EEC is expected to be revised as several Member States have enacted and implemented stricter limit values for heavy metals and set requirements for other contaminants.

In this work, an Agilent 4200 MP-AES was used to determine major and minor elements in domestic sludge, following microwave digestion.

MP-AES is a fast sequential, multielement analytical technique that uses a microwave-induced nitrogen-based plasma for sample excitation. Without needing expensive and hazardous gases such as acetylene, MP-AES increases lab safety and allows unattended operation, even for overnight runs. Sample throughput can be further enhanced with the use of the high capacity autosampler, the Agilent SPS 4.

The 4200 MP-AES with MP Expert software uses a high number of automated parameters including pre-set methods, auto optimization, suggested wavelengths, and background correction. It has a simple yet powerful user interface and a reliable torch loader that automatically aligns the torch and connects gases for fast start up and reproducible performance.

This application note describes the sample preparation procedure and analytical method used to analyze Zn, Mn, Cr, Ca, Fe, Cu and Mg in a domestic sludge standard reference material (SRM) 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 can be supplied from bottled gas, Dewar or via the Agilent 4107 Nitrogen Generator (with air supplied from an air compressor). For this application, Dewar nitrogen was used. 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 cyclonic glass
Pump rate	15 rpm
Sample pump tubing	Orange/green
Waste pump tubing	Blue/blue
Read time (s)	3
Number of replicates	3
Fast pump during uptake	On
Sample uptake delay (s)	50
Rinse time (s)	45
Stabilization time (s)	10
Background correction	Auto
Gas source	Dewar nitrogen

Sample and sample preparation

Domestic Sludge SRM (SRM®- 2781, NIST, Gaithersburg, MD, US) was used to validate the accuracy of the method. Approximately 0.5 g of the SRM sample was accurately weighed into a microwave vessel followed by the addition of 6 mL HNO_3 and 2 mL H_2O_2. Acid digestion was performed in an UltraWAVE Single Reaction Chamber Microwave Digester. Heating conditions are given in Table 2. After cooling, the digested solution was transferred quantitatively to a volumetric flask and brought to a 50 mL volume with 18.2 MΩ deionized water. The final acid concentration was 12% HNO_3.

Table 2: Parameters used for microwave digestion

Parameter	Setting
Ramp (min)	10
Temp (°C)	150
Hold (min)	5
Ramp (min)	10
Temp (°C)	230
Hold (min)	10
Total (min)	30

Calibration standards

Single element stock solutions (Agilent Technologies) were used to prepare the multi-element calibration standards. One set of multi-element standards was used for the calibration. All working standards were prepared in 12% HNO_3 and HCl. No modifier or ionization buffers were required.

Wavelength selection and calibration range

Details of wavelength selection and nebulizer flow rate are given in Table 3. 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. For example, in this application, the less sensitive Mg 383.829 nm line was selected over the more sensitive Mg 285 nm line because it has a large dynamic range, meets the detection limit requirements of the application, and is free from spectral interferences.

Table 3. Element, wavelength and nebulizer flow

Element	Wavelength (nm)	Nebulizer Flow (L/min)
Zn	213.857	0.45
Mn	403.449	0.9
Cr	425.433	0.9
Ca	445.478	0.5
Fe	373.486	0.5
Cu	324.754	0.7
Mg	383.829	0.9

Results and discussion

Calibration

In addition to minimizing spectral interferences, all wavelengths were selected to provide the widest dynamic range. Each element was calibrated using a three point calibration. All calibration curves were linear, except for Ca 455.478 nm, which was rational fit. The curves had a correlation factor 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.

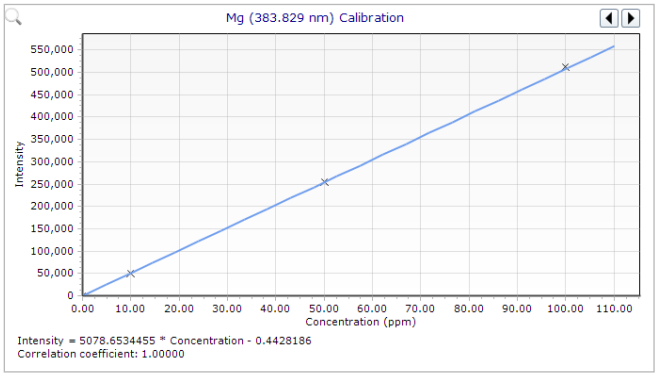

Figure 1. Calibration curve for Mg 383.829 nm.

Table 4 summarizes the calibration standard concentration range and correlation coefficients for all 7 elements. As the working range of MP-AES far exceeds that of FAAS, further dilution of the sample digest was not required to measure all of the elements of interest. Reducing the number of sample dilution steps improves productivity and reduces the risk of sample contamination.

Table 4. Calibration standard concentration range and correlation coefficients

Element / Wavelength (nm)	Standard Conc. Range (mg/L)	Linear Correlation Coefficient - r
Zn 213.857	0-10	0.99987
Mn 403.449	0-10	0.99994
Cr 425.433	0-10	0.99964
Ca 445.478	0-250	0.99999
Fe 373.486	0-250	0.99988
Cu 324.754	0-100	0.99998
Mg 383.829	0-100	1.00000

Sample analysis

Recoveries of the domestic sludge SRM are based on the average of 3 replicate digestions over separate analyses. The mean concentration, standard deviation (SD), and recovery was calculated for each analyte, as shown in Table 5. The results obtained with the method were in good agreement with the SRM values (96–103%), verifying the method.

Table 5. MP-AES recovery of elements in NIST 2781 domestic sludge SRM. Results are compared to the reference leach values.

Element/ Wavelength (nm)	Measured conc in sample (mg/L)	SD	Leachable mass fraction (mg/kg)	Recovery in sample (%)
Zn 213.857	1132.8	94.6	1120	101.1
Mn 403.449	768.3	21.7	745	103.1
Cr 425.433	142.9	3.68	143	99.9
Ca 445.478	35145.3	716.5	36440	96.4
Fe 373.486	25108.0	232.6	24300	103.3
Cu 324.754	599.1	15.3	601	99.7
Mg 383.829	4842.0	252.6	4850	99.8

Method Detection Limits

Method Detection Limits (MDL) were determined using three sigma of ten replicate measurements of the matrix blank solution, then multiplying by the dilution factor to calculate the MDL in the original sample. These MDLs were acquired using a method conditions suitable for routine sample analysis rather than highly optimized conditions. Consequently, they are not best-possible detection limits but are more than sufficient for the method requirements. The results are shown in Table 6.

Table 6. Method Detection Limits in the original sample (mg/kg).

Element	Wavelength (nm)	MDL (mg/kg)
Zn	213.857	0.25
Mn	403.449	0.03
Cr	425.433	0.03
Ca	445.478	1.03
Fe	373.486	0.88
Cu	324.754	0.43
Mg	383.829	0.20

Long term stability

The domestic sludge SRM was analyzed every 10 samples over 12 hours of continuous measurement. Excellent stability was achieved over this period as shown in Figure 2. Average recoveries for most elements were within ± 2%. The long term measurement precision over the full 12 hours was less than 2% RSD (Table 7), demonstrating the suitability of the 4200 MP-AES for routine measurement of metals in domestic sludge samples.

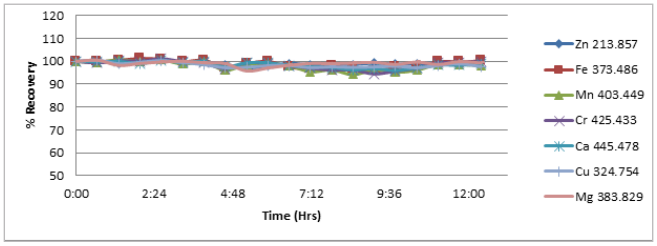

Figure 2. Long-term stability plot. <2.0% RSD over 12 hours analysis of domestic sludge SRM.

Table 7. Long-term precision and average recovery over 12 hours continuous measurement of the domestic sludge SRM.

Element/ Wavelength (nm)	%RSD	Average Recovery (%)
Zn 213.857	0.8	99.2
Mn 403.449	2.0	98.0
Cr 425.433	1.9	98.4
Ca 445.478	1.4	98.5
Fe 373.486	1.7	98.9
Cu 324.754	1.1	98.4
Mg 383.829	1.1	99.0

Potential cost savings with the 4200 MP-AES

The example given in Figure 3 is intended to demonstrate the reduction in running costs and thus potential savings of the MP-AES, compared to operating a flame atomic absorption spectrometer.

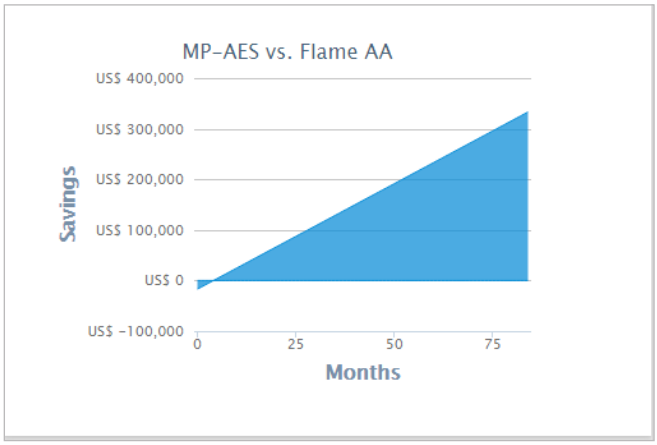

Figure 3. Potential cost savings with MP-AES compared to FAAS over time*

*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.

Operating an MP-AES in place of a FAAS over a 7-year evaluation period could lead to savings of more than USD300K as shown in Figure 3. The cost-comparison was based on the following criteria:

- An FAAS fitted with an air compressor, autosampler, and 1 year of consumables,
- An MP-AES fitted with an air compressor, SPS 4 autosampler and 1 year of consumables
- Seven elements measured under method conditions
- Based on the analysis of 300 samples per week

Conclusions

The Agilent 4200 MP-AES is ideally suited to the analysis of major and trace elements in domestic sludge following a simple microwave digestion sample preparation procedure. Excellent recoveries of the standard reference material were achieved, with good precision. Instrument robustness was demonstrated with exceptional stability over 12 hours—without the need to recalibrate.

The 4200 MP-AES offers multiple benefits over FAAS including:

- Higher performance with fast sequential operation, lower detection limits and wider dynamic range, meaning higher sample throughput and fewer manual dilutions.
- Improved safety and reduced running costs with the use of nitrogen to generate the plasma.
- Simplified workflow with no need to change and optimize lamps, and no need for complicated element specific sample preparation with addition of modifiers or buffers.

In addition to analytical performance advantages, MP-AES is considerably more cost-effective over the long term than FAAS - an important consideration for any lab looking to invest in new or replacement instrumentation.

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Published September 14 2015
Publication number: 5991-6239EN

Agilent Technologies