

Determination of metals in soils using the 4100 MP-AES

Application note

Agriculture

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Introduction

It is well known that the presence of elevated levels of metals (for example, As, Cr, Cu, Pb, Ni and Zn) is a considerable concern to human health, and agricultural, livestock and aquatic industries. Certain metals (for example, Cu and Zn) are also essential for biotic and human health and, therefore there is an effective threshold for both deficiency and toxicity. The presence of these contaminants in the environment is likely due to discharge of effluents from small to medium industries, emissions from vehicles, disposal of rural domestic sewage, indiscriminate use of fertilizers and metal-containing pesticides, and disposal of solid waste in unprotected sites. These various contaminant sources have the potential to pollute not only agricultural and urban land, but also surface and ground waters used for agriculture and drinking. Therefore, it is clear that monitoring of metal contamination in soils is critically important for environmental monitoring and to determine the effects of metals on human health.



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This application note describes an analytical method for the determination of metals in soils using a new, simple, and relatively inexpensive Microwave Plasma-Atomic Emission Spectrometer (MP-AES). The Agilent 4100 MP-AES generates a self-sustained atmospheric pressure microwave plasma (MP) using nitrogen gas and a torch specifically designed for the MP-AES. Sample introduction to the MP is pneumatic using a concentric nebulizer and cyclonic spray chamber. Emission line isolation and detection is sequential using a Czerny-Turner monochromator and charge-coupled device detector. This MP-AES allows easy entrainment of sample aerosols, both aqueous and organic. The tolerance level of aqueous and organic solvent loads as well as ambient air is significantly higher compared to other analytical plasmas. Refer to Reference [1] for more details about the operational characteristics of the MP-AES.

Experimental

Sample preparation

Soil samples used for analysis were:

- NIST Standard Reference Material 2710 — Montana Soil (Highly Elevated Trace Element Concentrations)
- NIST Standard Reference Material 2711 — Montana Soil (Moderately Elevated Trace Element Concentrations)

For the comparison of MP-AES and NIST results, US EPA Method 3050B sample preparation procedure relating to the acid digestion of sediments, sludges, and soils was used. A short description of this digestion procedure is given below.

Initially, 10 mL of 1:1 HNO₃ was added to 1.00 g of soil sample in a 25 x 150 mm glass digestion tube. The samples were then heated to 95 ± 10 °C for about 15 minutes. When cool, 5 mL of HNO₃ was added and heat was applied for another 30 minutes. The digests were again allowed to cool, before 2 mL of Milli-Q water and 3 mL of 30% H₂O₂ was added and heated to 95 ± 5 °C. After the digests were cooled again, another 1 mL of 30% H₂O₂ was added. Heating continued until the sample volumes reduced to approximately 5 mL. The

digests were then allowed to cool again before being diluted to 50 mL with Milli-Q water. Prior to analysis, the soil digests were further diluted tenfold. The 2% moisture content given in the certificate of analysis for NIST 2710a and NIST 2711a was incorporated into the calculation [2].

Instrumentation

Instrument operating conditions are listed in Table 1.

Table 1. Agilent 4100 MP-AES operating conditions

Instrument parameter	Setting
Nebulizer	Concentric
Spray chamber	Single-pass glass cyclonic
Sample tubing	Black/black
Waste tubing	Blue/blue
Read time	3 s
Number of replicates	3
Stabilization time	10 s
Fast pump during sample uptake	On
Pump speed	15 rpm

Table 2 provides the instrumental parameters used for the sample analysis. The criterion for wavelength selection was to provide a wide working range and to avoid line overlaps.

Table 2. Agilent 4100 MP-AES parameters used for soil digest analysis

Analyte	Wavelength (nm)	Read time (s)	Nebulizer pressure (kPa)	Background correction
Al	396.152	3	240	Auto
As	234.984	3	120	FLIC
Cr	425.433	3	240	Auto
Cu	510.554	3	220	Auto
Fe	259.940	3	120	Auto
Mn	259.372	3	120	Auto
Ni	341.476	3	200	Auto
Pb	405.781	3	120	Auto
Zn	472.215	3	120	Auto

Background and interference corrections

The auto-background correction feature in the MP Expert software was used for background correction. Fast Linear Interference Correction (FLIC), an Agilent proprietary spectral interference correction method, was used to correct and remove the iron interference on determination of As using the 234.984 nm line. As illustrated in Figure 1, this type of interference can easily be corrected by running a blank, and analyte and interferent standards. MP Expert then automatically corrects the relevant interference.

Calibration

Analytical calibration was carried out using multi-element standard solutions, except for As. Separate calibration solutions were used for As because of the Fe spectral interference on the As 234.984 nm emission line. Table 3 provides calibration fit types and maximum applicable analyte concentration. Rational fit is a non-linear curve fit and allows an extended working range so that sample analysis can be carried out using a single wavelength without further dilutions being required. Figure 2 depicts a typical non-linear calibration using rational fit. The acceptance criterion for the calibration curve correlation coefficient is 0.999.

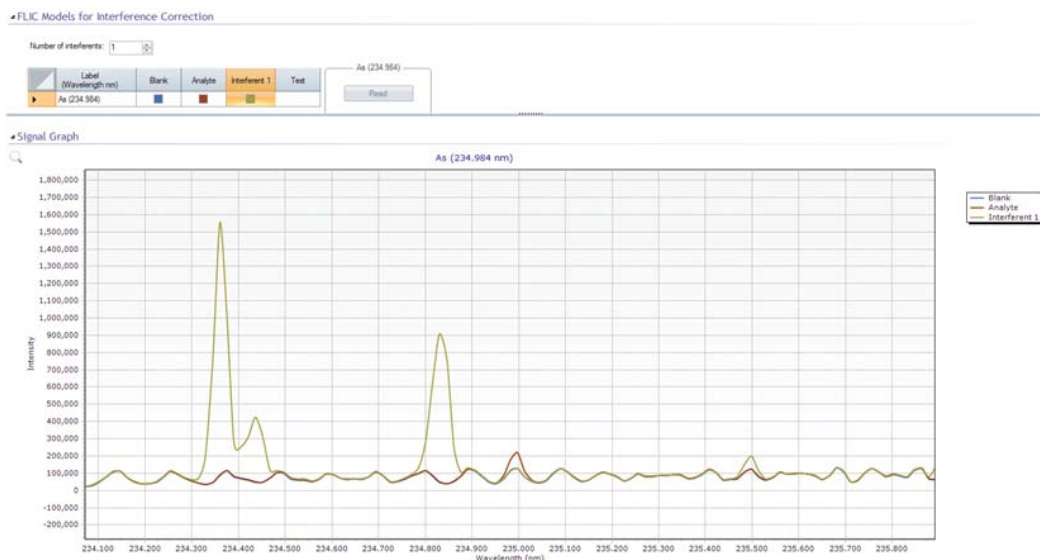


Figure 1. Illustration of spectral interference correction using FLIC. Figure 1 represents the FLIC page showing blank, analyte and interferent spectra

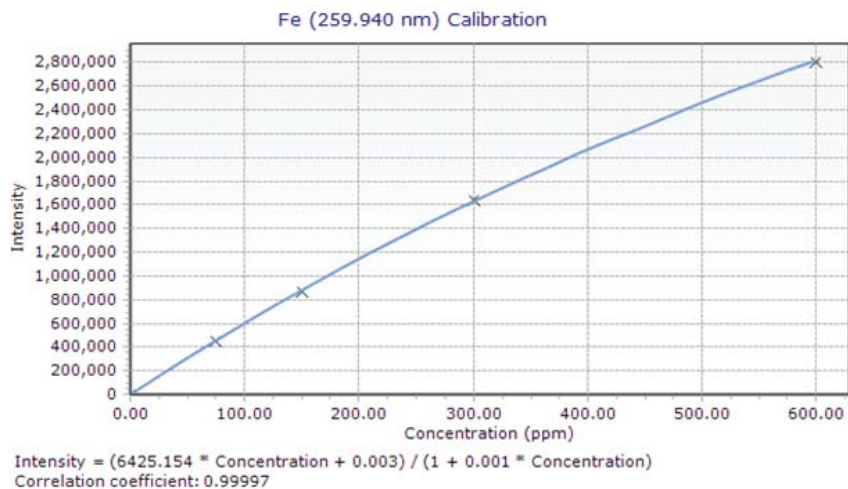


Figure 2. A typical non-linear calibration curve in MP-AES

Table 3. Calibration parameters used for soil digest analysis

Analyte	Wavelength (nm)	Calibration fit	Weighted fit	Through blank
Al	396.152	Rational	On	On
As	234.984	Linear	On	On
Cr	425.433	Rational	On	On
Cu	510.554	Linear	On	On
Fe	259.940	Rational	On	On
Mn	259.372	Rational	On	On
Ni	341.476	Linear	On	On
Pb	405.781	Rational	On	On
Zn	472.215	Rational	On	On

Results and discussion

There are several digestion methods available for the analysis of soils. For example, US EPA Method 3050B: Acid digestion of sediments, sludges, and soils is a strong acid digest, but it is not a total digest. US EPA Method 200.2: is a sample preparation procedure for spectrochemical determination of total recoverable elements. It is common practice for routine analytical laboratories to use US EPA Method 200.2 because of its simplicity for large-scale routine use. However, analytical results can be different to those obtained using US EPA Method 3050B, because leachable metal content depends on several factors such as leach medium, leach time and temperature, and the pH of the sample-leach medium.

The results for the analysis of NIST 2710 and 2711, along with the target values [3], for the selected metals using US EPA Method 3050B, can be seen in Tables 4 and 5. The digestions were performed in triplicate before analysis by MP-AES. It should be noted here that the range values quoted in Tables 4 and 5 for the NIST results were provided by several laboratories as a part of contract work for US EPA. Some of the laboratories used different or modified digestion procedures and therefore, as can be seen, the NIST results cover a wide concentration range. Therefore, these NIST soil results are not certified values. The results obtained using MP-AES are well within the acceptable range provided by NIST, and therefore clearly indicate that MP-AES is a suitable analytical atomic spectrometric technique for soil analysis.

Table 4. Results for the analysis of NIST Standard Reference Material 2710 — Montana Soil (Reference values only)

Analyte	MP-AES results Average \pm SD (mg/kg)	NIST results Range (mg/kg)
Al	24300 \pm 400	12000–26000
As	550 \pm 20	490–600
Cr	21 \pm 1	15–23
Cu	2800 \pm 20	2400–3400
Fe	28000 \pm 300	22000–32000
Mn	8500 \pm 200	6200–9000
Ni	9.5 \pm 0.6	8.8–15
Pb	5600 \pm 300	4300–7000
Zn	6100 \pm 200	5200–6900

Table 5. Results for the analysis of NIST Standard Reference Material 2711 — Montana Soil (Reference values only)

Analyte	MP-AES results Average \pm SD (mg/kg)	NIST results Range (mg/kg)
Al	20000 \pm 200	12000–23000
As	90 \pm 15	88–110
Cr	21 \pm 3	15–25
Cu	90 \pm 1	91–110
Fe	23000 \pm 2000	17000–26000
Mn	600 \pm 10	400–620
Ni	17 \pm 3	14–20
Pb	1400 \pm 30	930–1500
Zn	300 \pm 10	290–340

Table 6 provides the results for the analysis of the highest calibration standard, used as a continuing calibration verification standard (CCV). It was analyzed at the end of the sequence, about four and a half hours after the beginning of the run. CCV recoveries for all analytes are within 100 \pm 15% after four and a half hours of continuous operation of the instrument, with most elements within 100 \pm 5%. Note that As was not present in the CCV solution, as explained previously. These CCV recoveries indicate that MP-AES is stable for long hours of continuous operation, which removes the need for time-consuming recalibration over longer instrument runs.

Table 6. Recoveries for CCV solution analysis after four and a half hours of operation

Analyte	Al	As	Cr	Cu	Fe	Mn	Ni	Pb	Zn
CCV recovery (%)	101.8	N/A	99.9	104.1	98.0	97.8	112.1	97.9	100.4

Conclusions

The results obtained using the Agilent 4100 MP-AES indicate that MP-AES is a suitable atomic emission spectrometric technique for metal analysis of soils. Method development, instrument optimization and sample analysis can be easily carried out using the intuitive MP Expert software. The analytical working range can easily be extended using non-linear rational curve fitting for a single wavelength, therefore eliminating most sample dilutions. Spectral interferences can be easily corrected using the proprietary Agilent algorithm (FLIC). A highly stable, self-sustained atmospheric pressure plasma is generated using nitrogen, and therefore the running costs for busy commercial laboratories are very low. The simplicity of the instrument and easy-to-use MP Expert software is even suitable for novice analysts, with minimal training required for routine sample analysis.

References

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