Direct determination of Cu, Fe, Mn, P, Pb and Ti in HF acid-digested soils using the Agilent 4200 Microwave Plasma-Atomic Emission Spectrometer

Application note

Agriculture

Authors

Dave McDonald and
Alejandro Amorin,
Agilent Technologies
Melbourne, Australia

Introduction

Accurate elemental analysis of soils is extremely important for numerous reasons. Lead and cadmium are known for their adverse health and environmental effects. Phosphorus, copper, iron, magnesium are considered important macro and micro nutrients for plants and thus, these elements are of interest for agricultural science, crop selection and soil remediation studies. Titanium minerals in soil are also used as weathering indicators [1].

Laboratories that analyze soil and rock samples must use hydrofluoric acid (HF) during sample preparation to ensure complete dissolution, especially where silicate based minerals may be present. Standard glass sample introduction systems are not suitable for the introduction of HF digests unless the samples are neutralized prior to analysis as the free HF attacks and degrades the glass and quartz components.

Unfortunately, the HF neutralization step reduces laboratory efficiency and introduces a potential source of contamination. Therefore, laboratories that routinely analyze samples prepared using HF digests prefer to work with inert sample introduction components allowing HF digests to be run without the neutralization step.

Agilent has developed an inert torch for the 4200 MP-AES to facilitate the analysis of HF digests without prior neutralization (Figure 1). The inert MP-AES torch features an inert alumina injector. When used in conjunction with the inert double-pass spray chamber and an inert nebulizer, such as the OneNeb nebulizer, it provides a complete inert sample introduction system for use with HF digests. This expands the application range of the Agilent 4200 MP-AES to include the analysis of challenging geochemical samples.

In this study, the concentrations of Cu, Fe, Mn, P, Pb and Ti in a range of soil-based Standard Reference Materials (SRMs) digested using aqua regia and HF have been determined using the 4200 MP-AES and an inert sample introduction system, including the inert MP-AES torch (shown in Figure 1).

Figure 1. The inert MP-AES torch

Experimental

Instrumentation

The 4200 MP-AES is a fast sequential emission based multi-element analytical technique that uses a microwave-induced nitrogen-based plasma for sample excitation. This eliminates expensive and hazardous gases such as acetylene, increasing safety, and allowing unattended operation of the instrument, even in remote locations. 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 to run the MP-AES.

The sample introduction system used for the analysis of HF-digested soil samples featured inert components including an inert double pass spray chamber, the inert MP-AES torch and the inert OneNeb nebulizer.

The instrument was controlled by the powerful and easy-to-use MP Expert software. The MP-AES features continuous wavelength coverage and MP Expert features an extensive wavelength database that allows the selection of wavelengths that are appropriate for the concentration range required for the analysis and which are relatively free of interferences.

Table 1. Agilent 4200 MP-AES operating conditions

Parameter	Setting/setup
Torch	Inert torch with alumina injector
Nebulizer	OneNeb inert nebulizer
Nebulizer flow	
	0.4 L/min for P
	0.6 L/min for Fe, Ti, Cu and Y
	0.9 L/min for Mn and Pb
Spray chamber	Inert double-pass spray chamber
Sample tubing	Solvaflex pump tubing with orange-green tabs
Internal Std tubing	Solvaflex pump tubing with orange-green tabs
Waste tubing	Solvaflex pump tubing with blue-blue tabs
Pump speed	10 rpm
Number of replicates	3
Read time	5 s for Pb
	3 s for P
	1 s for all others
Stabilization time	10 s
Uptake time	45 s (fast pump)
Rinse time	120 s (fast pump)

Standard Reference Materials

Three soil-based SRMs from the National Institute of Standard and Technology (NIST) were analyzed to validate the method used in this study (refer to Table 2) All were sourced from Graham B. Jackson (Aust) Pty Ltd and were used on an as-received basis.

Table 2. Soil-based standard reference materials and their certified concentrations, as used in this study.

	Certified concentration in mg/kg					
Reference Material	**Cu**	**Fe**	**Mn**	**P**	**Pb**	**Ti**
NIST SRM 2710a Montana I Soil	3420	43200	2140	1050	5520	3110
NIST SRM 2711a Montana II Soil	140	28200	675	842	1400	3170
NIST SRM 2709a San Joaquin Soil	33.9*	33600	529	688	17.3	3360

* reference value

Preparation of calibration standards and samples

Sample preparation included a HNO$_3$–HCl-HF digestion with a nominal sample weight of 0.5 g. The weighed sample was placed into an inert (PTFE) reaction vessel. In order to ensure a homogeneous reaction with the acid mix, 2 mL of de-ionized water was first added to moisten the sample. Subsequently, 2 mL of nitric acid 69% (Merck), 6 mL hydrochloric acid 37% (Merck) and 2 mL hydrofluoric acid 48% (Merck) was added. The samples were digested using the Milestone UltraWave microwave digestion system. The Single Reaction Chamber of the microwave digestion system was pressurized using a nitrogen gas pressure of 40 bar. The samples were made up to a volume of 40 mL using 18 MΩ de-ionized water. Samples were prepared in triplicate.

The temperature program used for the microwave digestion process is shown in Table 3.

Table 3. Parameters for microwave digestion (where t is the time and T1 and T2 are the initial and final vessel temperatures)

Step	t (min)	T1 (°C)	T2 (°C)
1	10	Ambient	150
2	5	150	150
3	10	150	230
4	10	230	230

Calibration standards were prepared from Agilent aqueous single element certified reference materials. Multi-element calibration standards were prepared by diluting the single element stock solutions using an aqueous solution of 20% aqua regia and 5% HF in 18 MΩ de-ionized water. Phosphorus standards were prepared separately due to spectral interferences from Cu, Fe and Mn. The diluent solution, containing 20% aqua regia / 5% hydrofluoric acid in 18 MΩ de-ionized water, was used to match the acid matrix of the digests. The calibration range was determined based on the expected concentration of the analytes in the completed digests of the SRMs. Ten calibration standards were used as shown in Table 4.

Table 4. Calibration standards

Solution	Cu	Fe	Mn	Pb	Ti	P
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Digestion Blank	0	0	0	0	0	0
Cal Std 1	4.0	20	8.0	1.0	4.0	-
Cal Std 2	10	50	20	2.5	10	-
Cal Std 3	20	100	40	5.0	20	-
Cal Std 4	60	300	120	15	60	-
Cal Std 5	80	400	160	20	80	-
Cal Std 6	120	600	240	30	120	-
Cal Std 7	240	1200	480	60	240	-
Cal Std 8	-	-	-	-	-	5.0
Cal Std 9	-	-	-	-	-	20
Cal Std 10	-	-	-	-	-	50

Wavelength selection, background and interference correction

Table 5 lists the emission lines selected for analysis, together with the background and interference correction methods used. The selected wavelengths provide minimal spectral interferences, and wide dynamic range, eliminating time-consuming sample dilutions and re-analysis. An internal standard solution of 10 mg/L Yttrium in 2% HNO$_3$ was delivered on-line using orange/green pump tubing with a Y-connector used to combine the flow with the sample prior to nebulization.

Table 5. Line selection, background and interference correction methods for each element

Element	Wavelength (nm)	Type	Back-ground/ Interference Correction	Interferents
Cu	324.754	Analyte	FLIC	Fe, Mn, Ni, Ti
Fe	248.327	Analyte	FLIC	Co
Mn	403.307	Analyte	FLIC	Co, Fe, V
P	213.618	Analyte	FLIC	Cu, Fe, Mn, Ni, Zn
Pb	405.781	Analyte	FLIC	Co, Fe, Mn, Ti, V
Ti	308.804	Analyte	FLIC	Co
Y	437.494	Internal Standard	Auto	-

Most soil samples contain a wide range of elements at varying concentrations - this can result in some spectral interferences. The MP Expert software has an extensive wavelength database that helps the analyst to choose the best analytical wavelengths, based on intensity and the potential for spectral interferences. When there are interferences and there are no other lines that either provide the required sensitivity or are free of interferences, Agilent's Fast Linear Interference Correction (FLIC)[2] can be used to apply correction. FLIC can be used when multiple, partly overlapping spectral components are present in the spectral window, or if there is only a single component present. FLIC also provides you with the flexibility to correct for structured background. FLIC models are constructed using pure solutions for the blank, analyte and the expected interferences in the sample. The Agilent MP Expert software estimates the amount of each model required to minimize the sum of squared differences between the unknown spectrum and the scaled sum of the models for the blank, analyte and expected interferences. This modeling provides accurate and automatic correction for the interferences identified in your sample spectra.

In this study, FLIC proved to be the right tool to resolve the interferences encountered in the reference materials analyzed. Table 6 lists the solutions used to build the FLIC models for the soil SRMs in this study. This is one example of how FLIC enables the user to analyze challenging samples with interferences. Measuring the element lead (Pb) represents a challenge since it is usually expected in low concentration in soil samples. Soil samples represent a very complex matrix with multiple potential interferences (Table 5). The wavelength database in the MP Expert software assists the user to choose the appropriate interferent elements. Using FLIC, it is possible to build correction models that can resolve the spectral interferences enabling the user to achieve accurate results.

The Pb content in the SRMs selected for this study ranged from a low of 20 mg/kg to more than 5000 mg/kg. To be able to analyze the samples with low Pb concentration, the most sensitive emission line was selected for analysis (405.781 nm). However in the vicinity of this emission line, a number of interferent elements were observed (Figure 2), with some of them present in the soil SRMs at percent (%) levels.

Figure 2 shows the signal for Pb at 405.781 nm with the interferent elements modeled using FLIC. Cobalt provides an interfering signal at 405.818 nm (green trace). Additionally, there are interferences from iron, which is present at very high levels in the soil SRMs (2.8 - 4.3 % w/w), over the wavelength range from 405.734 to 405.875 nm (purple trace). It was also found that V, which has a signal at 405.707 nm (yellow trace) and Ti signals at 405.762 and 405.814 nm (blue trace), were also introducing interferences at the Pb 405.781 nm wavelength. Finally Mn, which is present in the sample at moderately high levels, was also introducing an interferent signal at 405.795 nm (dark green trace).

Despite the interferences at the Pb 405.781 nm wavelength, FLIC was able to accurately model this complex matrix and achieve good results with excellent recoveries for Pb across a concentration range of two orders of magnitude.

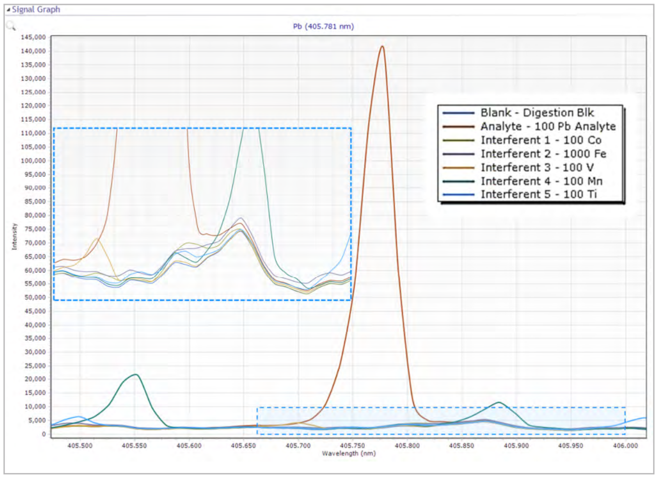

Figure 2. Spectral interferences for Pb 405.781 nm resolved using FLIC

Results and discussion

Method DLs

Method detection limits (MDL) were determined by running the full calibration, including FLIC analytes and interferents—then running 10 replicates of a digested acid blank 10 times. The MDL is defined as 3 times the standard deviation (S) of the concentration reading for each element.

The limit of quantification (LOQ) for this analysis was estimated as 10 times the standard deviation of the concentration readings multiplied by 80. This value (of 80) was selected as this was the total dilution factor used during sample preparation.

Table 7. Method detection limits and estimated limit of quantification

	Cu	Fe	Mn	P	Pb	Ti
MDL in mg/L in solution	0.0009	0.03	0.0005	0.119	0.010	0.018
LOQ in mg/L in solid	0.2	7.0	0.1	31.7	2.7	4.7

Long term stability

To check instrument stability during a long term measurement, a sample of NIST SRM 2710a Montana I soil digest was analyzed every 12 minutes over 8 hours of continuous measurement. A periodic calibration re-slope, which included the blank and one standard, was performed every 2.5 hours. Excellent stability was achieved over this long term measurement with all elements in the method having average recoveries within ±10% and the long term measurement precision over the full 8 hours was less than 5% RSD (Table 8). Further studies performed with the same sample type have shown that the long term stability could be improved by using a humidifier for the nebulizer gas flow. With the humidifier, the long term measurement precision over the full 8 hours was reduced to less than 3% RSD for all elements.

Table 6. FLIC sequence matrix (the numbers in parenthesis represent the concentration of the solutions in mg/L). MB = matrix blank

		Interf-1	Interf-2	Interf-3	Interf-4	Interf-5	Interf-6	Interf-7	Interf-8
Blank	**Analyte**	**Co**	**Cu**	**Fe**	**Mn**	**Ni**	**Ti**	**V**	**Zn**
MB	Cu (100)	-	-	Fe (1000)	Mn (100)	Ni (100)	Ti (100)	-	-
MB	Fe (100)	Co (100)	-	-	-	-	-	-	-
MB	Mn (100)	Co (100)	-	Fe (1000)	-	-	-	V (100)	-
MB	P (100)	-	Cu (100)	Fe (1000)	Mn (100)	Ni (100)	-	-	Zn (100)
MB	Pb (100)	Co (100)	-	Fe (1000)	Mn (100)	-	Ti (100)	V (100)	-
MB	Ti (100)	Co (100)	-	-	-	-	-	-	-

Table 8. Long-term precision for 8 hours continuous measurement of the NIST SRM 2710a Montana I soil digest

Precision (%RSD)					
Cu	Fe	Mn	P	Pb	Ti
3.2	2.8	3.2	4.2	2.2	2.0

Spike recoveries

An aliquot of acid blank was spiked with the analytes of interest at concentrations representative of ~40% of the concentration in the 2710a Montana I soil. The recoveries for the spiked matrix blank are listed in Table 9. An aliquot of the Montana I soil digest was also spiked with the analytes of interest at ~40% of the expected concentration in the soil. The recoveries for the spiked soil digest sample are listed in Table 10.

Table 9. Spike recoveries: Matrix Blank + 40% spike

	Cu (mg/L)	Fe (mg/L)	Mn (mg/L)	P (mg/L)	Pb (mg/L)	Ti (mg/L)
Spike conc	16	200	10	5	28	16
Measured	14.9	188	9.9	4.7	27.7	15.6
% Recovery	93.3	94.1	99.1	93.0	98.9	97.3

Table 10. Spike recoveries: NIST SRM 2710a Montana I Soil + 40% spike

	[Cu mg/L)	Fe (mg/L)	Mn (mg/L)	P (mg/L)	Pb (mg/L)	Ti (mg/L)
Spike conc	16	200	10	5	28	16
Measured	14.5	189	10.1	5.7	26.8	13.7
% Recovery	90.3	94.6	101	114	95.8	85.6

Recoveries of the soil based SRMs

The recoveries for the elements determined in the SRMs included in this study were all within the range of 100 ± 10 % which highlights the suitability of this method for the different soil matrices covered by this study (Tables 11-13). These results are the average of three separate digestions made in triplicate, measured using two different instruments with two different inert MP-AES torches. The results also demonstrate the wide dynamic range capability of the Agilent 4200 MP-AES, as elements were determined over a wide concentration range from ppm to % level in a single reading.

Table 11. Recoveries for NIST SRM 2710a Montana I Soil

Element (λ, nm)	Certified (mg/kg)	Measured (mg/kg)	Uncertainty (mg/kg) U^{95**}	Std Dev (n=9)	Recovery (%)
Cu (324.754)	3420±50	3435	53	85.5	100
Fe (248.327)	43200±800	42527	461	743.3	98
Mn (403.307)	2140±60	2254	38	60.8	105
P (213.618)	1050±40	1022	62	99.6	97
Pb (405.781)	5520±30	5395	185	297.8	98
Ti (308.804)	3110±70	2955	57	91.4	95

Table 12. Recoveries for NIST SRM 2711a Montana II soil

Element (λ, nm)	Certified (mg/kg)	Measured (mg/kg)	Uncertainty (mg/kg) $U^{95\,**}$	Std Dev (n=9)	Recovery (%)
Cu (324.754)	140±2	147	2.3	3.7	105
Fe (248.327)	28200±400	28640	366.3	591.0	102
Mn (403.307)	675±18	716	14.1	22.7	106
P (213.618)	842±511	804	52.3	84.4	96
Pb (405.781)	1400±10	1420	57.6	93.0	101
Ti (308.804)	3170±80	3061	86.3	139.2	97

Table 13. Recoveries for NIST SRM 2709a San Joaquin soil

Element (λ, nm)	Certified (mg/kg)	Measured (mg/kg)	Uncertainty (mg/kg) U^{95} **	Std Dev (n=9)	Recovery (%)
Cu (324.754)	33.9±0.5*	34.3	0.7	1.1	101
Fe (248.327)	33600±700	32941	689.0	1112	98
Mn (403.307)	529±18	550	9.5	15	104
P (213.618)	688±13	633	47.3	76	92
Pb (405.781)	17.3±0.1	18	1.0	1.6	106
Ti (308.804)	3360±70	3189	57.5	93	95

*These values have not been certified but are provided for reference

** The uncertainty is calculated at the 95% confidence interval using a t-distribution ($tS/n^{½}$); conditions: t(8)=1.86

Recoveries of the soil based SRMs without HF

HF is needed in the digestion process to ensure complete dissolution of titanium in the soil samples. To demonstrate the effectiveness of HF in achieving complete digestion, a set of samples were digested using only HCl-HNO_3 and analyzed. The recoveries for titanium were compared against those obtained using the HF digest, from a single digest prepared in triplicate at the same time. As expected the recoveries were quite poor when using only aqua-regia (Figure 3).

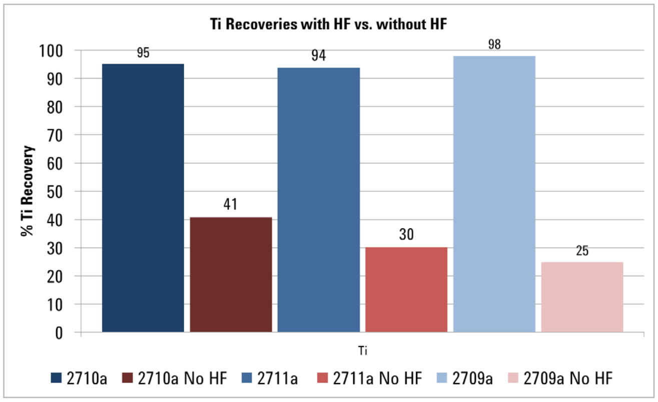

Figure 3. Recoveries for titanium in 3 different soil based NIST SRMs, comparing digests prepared with aqua regia only (show as red columns) with those using HF + aqua regia (shown as blue columns).

Conclusions

The results from analysis of the soil based SRMs included in this study demonstrate that the Agilent 4200 MP-AES is an excellent technique for the analysis of soils and challenging geochemical samples. The wide dynamic range capability was demonstrated as elements were determined over a wide concentration range from ppm to % level in the same sample, in a single reading, with excellent recoveries. When equipped with an inert sample introduction system, comprising an inert double pass spray chamber, the inert MP-AES torch and the inert OneNeb nebulizer, it is possible to analyze HF digests directly without a prior neutralization step. This eliminates one sample preparation step, increasing efficiency and minimizes potential sources of sample contamination.

Despite the numerous interferences, FLIC correction algorithm was able to model the complex interferent signals and produce good results for all elements with excellent recoveries across a concentration range of two orders of magnitude. The FLIC correction algorithm proved to be the right tool to resolve the interferences encountered in the reference materials analyzed.

References

1. Aide M. et al. Soil Science 168(3) (2003) 200–221

2. Agilent MP Expert Software, Technical Overview. Agilent Publication number 5990-8975EN

www.agilent.com/chem

Published July 9 2015
Publication number: 5991-5991EN

Agilent Technologies