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Determination of Major and Minor Elements in HF-Digested Soil Samples using an Agilent 5110 ICP-OES

Evaluating an Agilent inert sample introduction system designed for ICP-OES and MP-AES

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Introduction

The accurate elemental analysis of soil and rock samples can depend on reliable and reproducible sample preparation methods. If silicate-based minerals are likely to be present in the samples, laboratories must use hydrofluoric (HF) acid during sample preparation to ensure complete sample dissolution. Regulated methods, such as US EPA 3052, require the use of HF to achieve total sample decomposition (1). Standard glass or quartz sample introduction systems are not suitable for handling HF acid digests as any free HF attacks and degrades the glass and quartz components. To prevent degradation of glassware, the analyst must neutralize any residual HF before analysis, which reduces workflow efficiency and introduces a potential source of contamination. For this reason, laboratories that routinely analyze HF sample digests by atomic spectroscopy use inert sample introduction components which allow the digests to be run directly, without requiring a neutralization step.

Agilent has introduced an inert spray chamber for Agilent 5100/5110 ICP-OES and Agilent 4200/4210 MP-AES instruments to facilitate the analysis of HF digests without prior neutralization. The spray chamber features a removable internal baffle (Figure 1) that allows it to be used as a double or single pass design. The double pass configuration is suitable for the analysis of samples containing high total dissolved solids (TDS) or for the analysis of organic solvents. With the baffle removed, the spray chamber can also be used as a single-pass design when extra sensitivity is required. The internal surfaces of the spray chamber are permanently treated to ensure good drainage, without requiring any periodic recoating, ensuring a long lifetime. The spray chamber can be used with an inert nebulizer, such as the OneNeb Series 2 nebulizer and an inert torch such as the Easy-fit demountable torch. This complete inert sample introduction system is suitable for the direct analysis of HF sample digests.
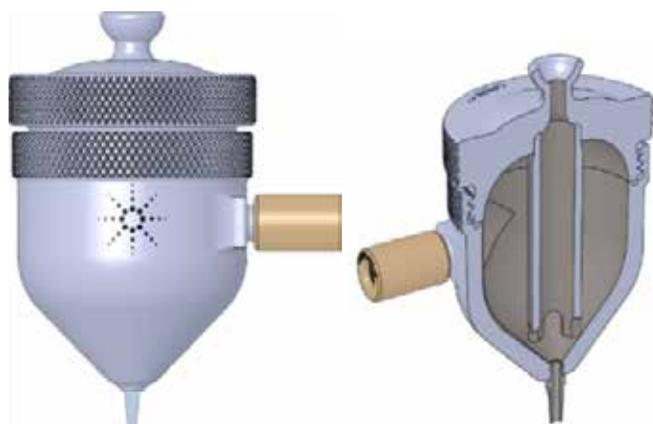

Figure 1. Drawing of an Agilent inert spray chamber designed for ICP-OES or MP-AES, highlighting the removable internal baffle in the center.

The accurate elemental analysis of soils is important in a range of applications. Lead and cadmium are known for their adverse health and environmental effects. Phosphorus, copper, and iron are considered essential macro- and micronutrients for plants. The total and extractable quantitative concentrations of these elements are usually required in agricultural science, for crop selection/production, and soil remediation investigations. Titanium minerals in soil are used as weathering indicators or considered beneficial for crop production (2, 3).

In this study, the concentrations of 11 elements in a digested soil standard reference material (SRM) were determined using an Agilent 5110 Vertical Dual View (VDV) ICP-OES.

Experimental

Instrumentation

All measurements were performed using an Agilent 5110 VDV ICP-OES configured with an SPS 4 autosampler. An inert sample introduction system was used. This consisted of the OneNeb Series 2 nebulizer (part number G8010-60293), the Agilent inert double-pass spray chamber (part number G8014-68002), and Easy-fit inert demountable VDV torch with a 1.8 mm i.d. alumina injector (part number G8010-60231). The Agilent nebulizer gas humidifier (part number G8010-60346) was used to reduce the potential for salt deposits forming in the nebulizer and in the injector of the torch. Instrument method parameters and analyte settings are listed in Table 1.

Table 1. 5110 VDV ICP-OES instrument and method parameters.

Parameter	Setting	
Torch	Easy-fit inert demountable VDV torch	
Nebulizer	Inert OneNeb Series 2	
Spray chamber	Inert spray chamber	
Nebulizer gas humidifier	Inline	
Uptake time (s)	15	
Rinse time (s)	60	
Peristaltic pump tubing	Sample	PVC white/white
	Waste	PVC blue/blue
	Axial	**Radial**
Power (kW)	1.2	1.2
Plasma flow (L/min)	12	12
Auxiliary flow (L/min)	1	1
Nebulizer flow (L/min)	0.7	0.7
Uptake time (s)	15	NA
Stabilization time (s)	15	3
Replicates	3	3
Read time (s)	5	5
Viewing mode	As, Cd, Cr, Cu, Mn, P, Pb, V	Fe, Ti, Zn
Viewing height (mm)	NA	10

Preparation of calibration standards and samples

National Institute of Standards and Technology (NIST) SRM 2710a Montana I Soil (Gaithersburg MD, USA) was analyzed to validate the method. The SRM was used as received.

Sample digestion was carried out according to the method specified in US EPA 3052. A Mars 6 microwave digestion

system fitted with iPrep vessels (CEM Corporation, NC, USA) was used. The sample (nominal weight of 0.45 g) was weighed directly into the vessels and 3 mL of de-ionized water (DIW) was added to moisten the sample and to ensure a homogeneous reaction with the acid mix. Then, 10 mL of nitric acid 69% (Merck), 3 mL hydrofluoric acid 48% (Sigma-Aldrich), and 3 mL hydrochloric acid 37% (Merck) were added in that order. The temperature program used for the microwave digestion process is shown in Table 2.

Table 2. Parameters used for microwave digestion.

Step	Time (min)	Temperature 1 (°C)	Temperature 2 (°C)
Ramp	25	Ambient	200
Hold	15	200	200

The digestate was made up to a volume of 40 mL using 18 MΩ DIW. Calibration standards were prepared from Agilent aqueous single element certified reference materials, at the concentrations shown in Table 3. All calibration standards were matrix matched with the same HNO_3-HF-HCl acid mix in DIW. The calibration range was based on the expected concentration of the analytes in the SRM digests.

Wavelength selection and background correction

Table 4 lists the emission lines selected for the analysis, together with the background correction methods used. The selected wavelengths provide minimal spectral interferences and a wide dynamic range, eliminating the need for time-consuming sample dilutions and reanalysis.

The mixed internal standard solution contained 20 mg/L each of lutetium and yttrium in a matrix of 5% HNO_3. The solution was delivered online to the sample before nebulization using a Y-connector. Yttrium (377.433 nm) and lutetium (261.541 nm) were used as internal standards. Radial viewing was used for selected elements to reduce any potential easily ionized elemental interference effects from elements present in the soil-matrix.

Table 4. Line selection, background, and interference correction methods used for each element.

Element (Wavelength, nm)	Calibration Fit	Background Correction	Internal Standard Correction	Correlation Coefficient (R)
As (188.980)	Linear	Fitted	Lu	1.00000
Cd (214.439)	Linear	Fitted	Lu	0.99999
Cr (205.560)	Linear	Fitted	Lu	1.00000
Cu (327.395)	Linear	Fitted	Lu	0.99995
Fe (238.204)	Linear	Fitted	Y	0.99951
Mn (257.610)	Linear	Fitted	Lu	0.99979
P (177.434)	Linear	FACT	Lu	0.99998
P (213.618)	Linear	Off-peak right	Lu	1.00000
Pb (217.000)	Linear	Fitted	Lu	1.00000
Ti (334.941)	Linear	Fitted	Y	1.00000
V (292.401)	Linear	Fitted	Lu	0.99999
Zn (213.857)	Rational	Fitted	Y	1.00000

Most soil samples contain a wide range of elements at varying concentrations, which can cause spectral interferences in the spectrum. The ICP Expert software has an extensive wavelength database that helps the analyst select the best analytical wavelength for the analysis, based on intensity and the potential for spectral interferences. With the full wavelength coverage of the Vista Chip II detector, often a wavelength can be selected that is free of interferences. However, if an interference-free wavelength isn't available, Agilent's Fast Automated Curve-fitting Technique (FACT) can be used. FACT corrects for spectral overlaps or complex background structures, leading to lower detection limits for some elements compared to other correction techniques (4).

Figure 2 shows how FACT modeling was used to correct the background interference on P 177.434 nm from copper at 177.421 nm. The P 213.618 nm emission line was

Table 3. Composition and concentration of calibration standards.

	As (mg/L)	Cd (mg/L)	Cr (mg/L)	Cu (mg/L)	Fe (mg/L)	Mn (mg/L)	P (mg/L)	Pb (mg/L)	Ti (mg/L)	V (mg/L)	Zn (mg/L)
Digestion Blank	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Std 1					250.0				30.00		
Std 2					500.0				60.00		
Std 3					750.0				90.00		
Std 4	1.250	0.125	0.125	1.250		1.250	1.250	2.500		0.125	2.500
Std 5	12.50	1.250	1.250	12.50		12.50	12.50	25.00		1.250	25.00
Std 6	45.00	4.500	4.500	45.00		45.00	45.00	90.00		4.500	90.00

also measured to confirm the P 177.434 nm result. The good agreement between the results at the two different P emission lines (Table 7) confirms that FACT modeling provides accurate correction of multiple interferences.
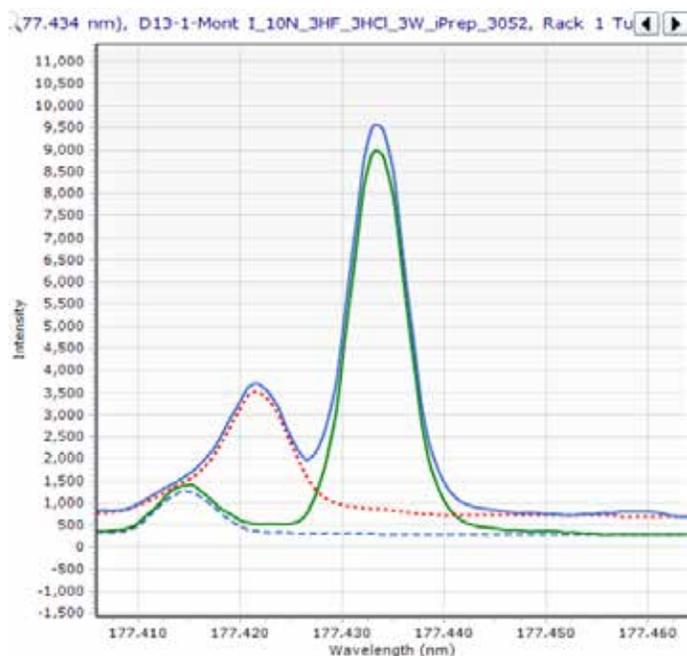

Figure 2. FACT correction used to remove the Cu interference on P 177. 434 nm. Sample signal (blue), corrected analyte signal (green), Cu interferent (dotted red), blank (dotted blue).

Results and discussion

The recoveries for the 11 elements measured in the soil SRM digests were all within ± 10% (Table 7). The results show the suitability of this method for the analysis of samples where complete sample decomposition is required. The results also demonstrate the wide dynamic range capability of the 5110 VDV ICP-OES, as elements from low ppm to % level were determined in a single reading.

Method detection limits

Method detection limits (MDL) were determined by running the full calibration, followed by 10 repeat analyses of 10 replicates of the digested acid blank (Table 5). The MDL is defined as three times the standard deviation 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 the dilution factor (90).

Table 5. Method detection limits and estimated limits of quantification.

Element and Wavelength (nm)	MDL (µg/kg)	LOQ (mg/kg)
As 188.980	8.27	2.23
Cd 214.439	0.44	0.12
Cr 205.560	1.78	0.48
Cu 327.395	0.88	0.24
Fe 238.204	4.53	1.22
Mn 257.610	3.80	1.03
P 213.618	5.65	1.53
P 177.434	11.2	3.01
Pb 217.000	25.0	6.74
Ti 334.941	1.42	0.38
V 292.401	0.62	0.17
Zn 213.857	1.58	0.43

Long-term stability

To check instrument stability during long-term measurements, 140 HF-digested soil samples were analyzed. A digested sample of the NIST SRM 2710a Montana I soil was analyzed approximately every four samples (around every 12 minutes). No recalibration or reslope was applied. Figure 3 shows that excellent long-term stability was achieved over more than 7 hours of operation. The average recovery for all elements in the method was within ±10% with a %RSD less than 3% (Table 6).
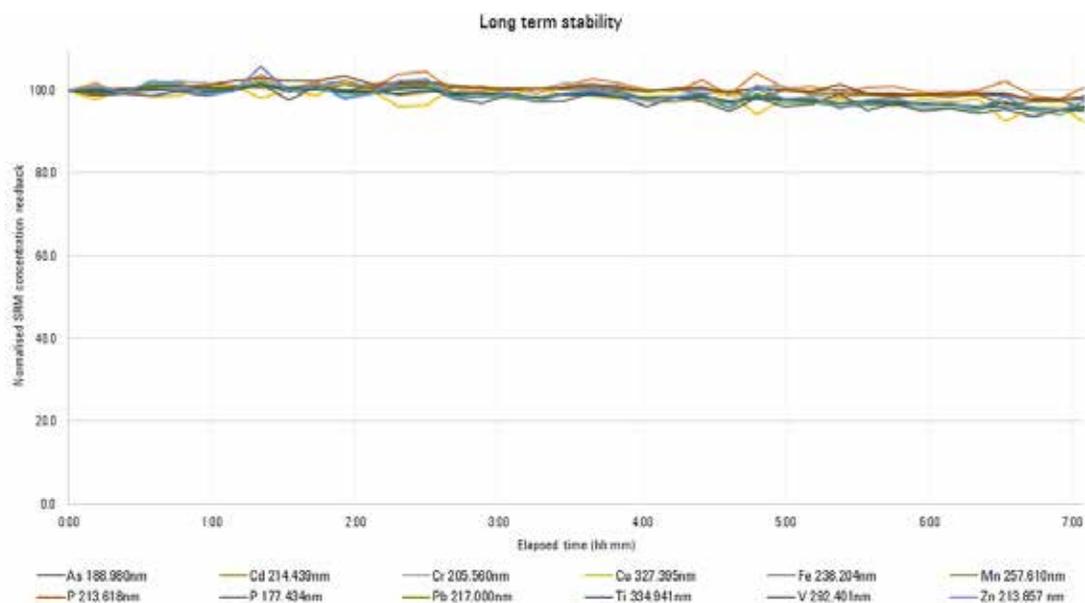
Figure 3. Long-term stability for repeated measurement of the soil digests over 7 hours.

Table 6. Long-term precision (%RSD) for repeated measurement of the soil digests over 7 hours.

Element	As	Cd	Cr	Cu	Fe	Mn	P^{213}	P^{177}	Pb	Ti	V	Zn
Mean Conc (mg/kg)	1441	12.2	22	3578	42974	1986	995	954	5405	3069	80	3912
RSD % (n=38)	1.1	1.6	1.4	2.3	2.3	2.2	1.3	2.2	1.2	1.6	1.7	2.3

Table 7. Measured recoveries for elements determined in the digest of the NIST 2710a Montana I Soil SRM.

Element and Wavelength (nm)	Certified Concentration (mg/kg)	Certified Uncertainty (mg/kg)	Measured Concentration (mg/kg)	Standard Deviation (n=10)	U_{95}#	Precision (% RSD)	Recovery (%)
As 188.980	1540	100	1441	70	40.6	4.9	93.6
Cd 214.439	12.3	0.3	12.2	0.8	0.4	6.1	99.5
Cr 205.560	23*	6.0	22	1.1	0.6	4.8	95.6
Cu 327.395	3420	50.0	3424	115	66.7	3.4	100.1
Fe 238.204	43200	800.0	42343	1041	603.5	2.5	98.0
Mn 257.610	2140	60	2043	104	60.5	5.1	95.4
P 213.618	1050	40	991	62	36.1	6.3	94.3
P 177.434	1050	40	977	68	39.4	7.0	93.1
Pb 217.000	5520	30	5210	170	98.7	3.3	94.4
Ti 334.941	3110	70	3054	100	57.7	3.3	98.2
V 292.401	82*	9	81	3.2	1.8	4.0	98.1
Zn 213.857	4180	150	3992	139	80.3	3.5	95.5

*Reference values
The uncertainty is calculated at the 95% confidence interval using a t distribution (tS/n½); conditions: t(9)=1.833

Recoveries for the soil SRM without HF

To achieve a near-total digestion of soil samples and/or to ensure complete dissolution of certain elements, HF acid is required. To assess the effectiveness of HF, a set of samples were digested using only HCl-HNO$_3$ (aqua regia). The results were compared against those obtained using aqua regia plus HF.

As shown in Figure 4, the recovery of most elements was poorer when HF was not included in the acid digestion mix. The recoveries for Cr, Mn, Ti, and V were significantly affected by the absence of HF.

Spike recoveries

A digested soil SRM sample was spiked with 11 analytes at the concentrations given in Table 8. All recoveries were within ±10%, as shown in Table 8, validating the 5110 VDV ICP-OES method. There was good agreement between the concentration measurements for the two P wavelengths (within ±3%).
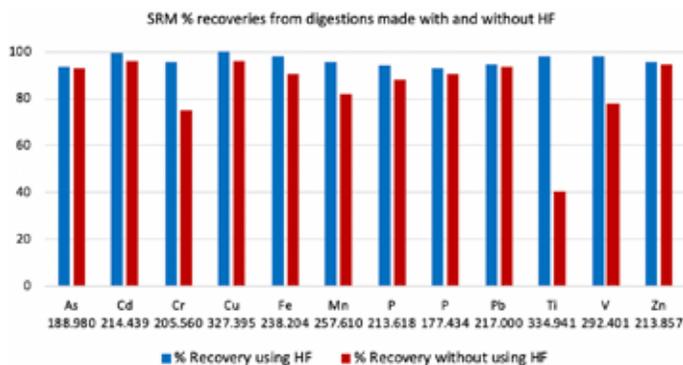

Figure 4. Measured recoveries for elements determined in the NIST 2710a Montana I Soil SRM. Comparison of results from digests prepared using aqua regia only (red bars) with those prepared using HF + aqua regia (blue bars).

Table 8. Spike concentrations and spike recoveries for the NIST 2710a Montana I Soil SRM   .

Element and Wavelength (nm)	Sample Solution Concentration (mg/L)	Spiked Solution Concentration (mg/L)	Spike Concentration (mg/L)	Measured Spike Concentration (mg/L)	Spike Recovery (%)
As 188.980	14.19	23.56	10.0	9.38	93.8
Cd 214.439	0.12	1.05	1.0	0.93	92.6
Cr 205.560	0.21	1.18	1.0	0.97	96.7
Cu 327.395	34.30	44.37	10.0	10.07	100.7
Fe 238.204	422.28	431.67	10.0	9.40	94.0
Mn 257.610	20.23	29.61	10.0	9.38	93.8
P 213.618	9.69	19.22	10.0	9.53	95.3
P 177.434	9.85	19.10	10.0	9.25	92.5
Pb 217.000	51.88	61.21	10.0	9.33	93.3
Ti 334.941	30.24	40.15	10.0	9.91	99.1
V 292.401	0.79	1.76	1.0	0.97	96.5
Zn 213.857	39.30	48.86	10.0	9.56	95.6

Conclusion

The Agilent 5110 VDV ICP-OES fitted with an Agilent inert sample introduction system is an excellent technique for the rapid multi-element analysis of silicate-based matrices, such as soils and geochemical samples. The inert sample introduction system comprised an inert double-pass spray chamber, the Easy-fit inert demountable VDV torch, and the inert OneNeb nebulizer. A NIST soil SRM was fully decomposed using microwave assisted acid (HNO_3-HF-HCl) digestion, following the sample preparation procedure outlined in US EPA method 3020. Using the inert sample introduction system, it is possible to analyze HF digests directly, without a neutralization step to remove excess HF. Simplifying the sample preparation procedure increases workflow efficiency and removes a potential source of sample contamination.

The study showed improved data quality using a total decomposition analysis using HF. Better recoveries of elements such as Cr, Mn, Ti, and V were achieved in HNO_3-HF-HCl-digests of the soil SRM compared to HNO_3-HCl digests.

The 5110's vertical torch orientation provides the robustness and stability required for the determination of a large number of digested soil samples. This performance was shown by the excellent precision (<3% RSD) over seven hours of continuous measurement of the soil SRM.

The dynamic range of the 5100's Vista Chip II detector was demonstrated by the excellent recoveries of analytes ranging from low ppm to %-level spiked into a digested soil SRM sample. Having a large dynamic range of up to eight orders of magnitude allows for both macro- and micro- elements to be analyzed from a single sample preparation method in a single reading.

References

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