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Analysis of Solid Waste Samples per Chinese Method HJ 781

Agilent 5800 VDV ICP-OES provides smart tools to streamline method development and improve confidence in results

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Introduction

Environmental agencies around the world regulate the elemental and metal content of solid wastes and soils to minimize pollution. Chinese standard method HJ 781-2015 outlines the procedure for the determination of 22 elements in solid waste samples, prepared using a four-acid microwave digestion program. The element list includes silver, aluminum, barium, beryllium, calcium, cadmium, cobalt, chromium, copper, iron, potassium, magnesium, manganese, sodium, nickel, lead, antimony, strontium, titanium, thallium, vanadium, and zinc.

Complexity and variation in solid waste and soil samples can cause challenges during analysis. Analysts may face spectral interferences which can lead to sample remeasurement or reporting the wrong results if the interference is not properly identified.

In this study, an Agilent 5800 Vertical Dual View (VDV) ICP-OES fitted with AVS 7 switching valve was used to analyze industrial waste samples according to the HJ 781-2015 standard method.

Agilent ICP Expert smart software tools

Agilent ICP Expert software developed for the Agilent 5900 and 5800 ICP-OES includes smart tools to simplify method development, verify results, and minimize sample remeasurements for this type of analysis.

- IntelliQuant uses data analytics to automatically identify spectral interferences that can lead to false-positive results and recommends the emission wavelength that will give the most accurate result.

- Outlier Conditional Formatting (OCF) compares analytical results from different wavelengths for the same element, providing extra confidence in the results.

- Early Maintenance Feedback (EMF) allows the user to set up alerts to prompt maintenance after a specified number of samples. Maintaining the instrument more frequently when measuring complex samples such as industrial wastes, ensures ongoing high-level analytical performance.

Experimental

Instrumentation

An Agilent 5800 VDV ICP-OES was fitted with the AVS 7 switching valve and SPS 4 autosampler. The AVS 7 features a seven-port valve and a high-speed positive displacement pump to rapidly fill the sample loop. The 5800 ICP-OES combined with the fully integrated AVS 7 switching valve allows for fast sample analysis without compromising on performance. The Agilent Vista Chip III detector offers high-speed continuous wavelength coverage that allows the analyst to choose multiple wavelengths for each element, without adding a time delay to the analysis.

To ensure the accuracy of the method, the ICP Expert software's IntelliQuant function was used to provide sample insight and assist with method development. IntelliQuant can identify up to 70 elements in the sample and identify spectral interferences that arise from elements present in complex samples. IntelliQuant saves valuable time during method development and provides additional data that may not be generated by the quantitative method. With a complex sample digest, lots of extra elements that are not in the full quantitative method can be detected using IntelliQuant. To manage the large data set, the Smart Views function of IntelliQuant was used to filter the semiquantitative results to show only the 27 elements included in the quantitative method.

Lutetium was used as an internal standard at a concentration of 10 mg/L. Lu 296.332 nm was used to correct ionic wavelengths, and Lu 350.738 nm was used to correct atomic wavelengths. Tables 1 and 2 list the 5800 VDV ICP-OES operating conditions and AVS 7 parameters, respectively.

Table 1. 5800 VDV ICP-OES instrument and method parameters.

Parameter	Radial	Axial
Read Time (s)	10	10
Replicates	3	
Sample Uptake Delay (s)	0	
Stabilization Time (s)	10	0
Rinse Time (s)	0	
Pump Speed (rpm)	12	
RF Power (kW)	1.5	
Aux Flow (L/min)	1	
Plasma Flow (L/min)	12	
Nebulizer Flow (L/min)	0.7	
Viewing Height (mm)	8	NA
Nebulizer	SeaSpray concentric	
Spray Chamber	Double Pass Cyclonic	
Torch	Easy-fit demountable VDV, 1.8 mm injector	
Sample Pump Tubing	White-white	
Internal Standard Pump Tubing	Orange-white	
Waste Pump Tubing	Blue-blue	
Background Correction	Fitted/FACT	

Table 2. AVS 7 switching valve system parameters.

Parameter	Setting
Sample Loop Size (mL)	3
Pump Rate - Uptake (mL/min)	36
Pump Rate - Inject (mL/min)	4
Valve Uptake Delay (s)	12
Bubble Inject Time (s)	2
Pre-emptive Rinse Time (s)	1

Outlier Conditional Formatting

The Outlier Conditional Formatting (OCF) function of the ICP Expert software allows the user to spot any issues with the quality of the quantitative data using color-coded flags. OCF can be configured to highlight overranges, poor RSDs, internal standard failures, or inconsistent results across wavelengths of the same element. Figure 1 shows the Element Concentration % RSD flag. The software compares results for an element between different wavelengths and flags any results that fall outside the set limit; in this case >5%RSD.

Solution Label	Outlier Summary	Pb 220.353 nm ppm	Pb 283.305 nm ppm	Pb 405.781 nm ppm
Sample 1	F	184.5	390.0	206.5
Sample 2	F	4799.4	5512.0	5402.1
Sample 3	F	466.5	1251.5	502.4
Sample 4	F	374.7	603.1	427.3
Sample 5	F	480.0	1265.6	504.4
Sample 6	F	4890.5	5625.9	5511.1

Figure 1. All six sample results were flagged in the Outlier Summary column. The flag informs the analyst that there is a difference in the Pb concentration determined using the different wavelengths.

The difference in the Pb results was investigated using the IntelliQuant function, and a suitable wavelength selection was made. As shown in Figure 2, IntelliQuant results for Sample 3 show an iron interference on Pb 283.305 nm, accounting for the high concentration. Pb 405.781 nm was given a low confidence ranking (one-star ranking). However, Pb 220.353 was given the highest confidence ranking (five stars), so was selected for the quantitative method.

Figure 2. IntelliQuant results for lead in Sample 3. The IntelliQuant star ranking system uses data analytics to rank different emission wavelengths for the same element. Hovering over the "?" symbol displays reasons for the poor ranking on a wavelength.

Background correction

IntelliQuant collects data across the entire spectral range for each sample. This information was used to check if any of the results in the quantitative method had been affected by an interference. IntelliQuant uses a star-ranking system to recommend the best emission wavelength for an element, as shown in Figure 2. Once identified, any interferences can be avoided by selecting a different wavelength or corrected using fitted background correction (FBC), Fast Automated Curve-fitting Technique (FACT), or Inter Element Correction (IEC).

Considering vanadium, IntelliQuant identified an interference on V 292.401 nm from Ti 292.396 nm, as indicated by the low confidence ranking (one-star). V 311.837 nm was given a four-star ranking due to interference from Cr 311.865 nm and OH 311.776 nm. To correct for the interferences on both V lines, a combination of automated FBC and FACT modeling was used for background correction for the vanadium analysis.

An example of FBC is shown in Figure 3. FBC accurately modeled the Cr 311.865 nm and OH 311.776 nm interfering peaks on V 311.837 nm, allowing for easy correction. By eliminating the need for the user to manually determine off-peak background correction points, FBC simplifies method development.
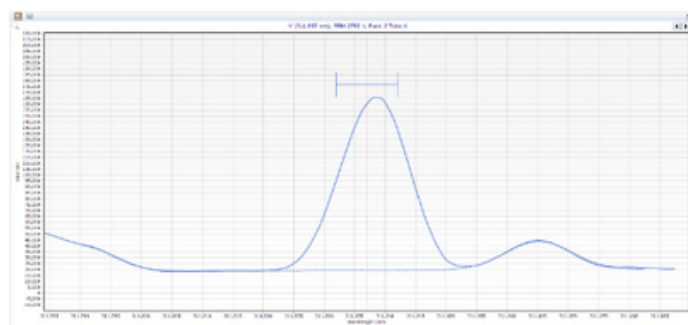

Figure 3. V 311.837 nm using FBC.

Wavelength selection can be used to avoid interferences. However, if a specific wavelength must be used, FACT models can be constructed to correct for interferences and deliver the required accuracy.

Early Maintenance Feedback

Analyzing complex sample types such as industrial waste can be tough on the sample introduction system of an ICP-OES. This can result in deteriorating analytical performance, high consumable costs, and unplanned instrument downtime. Scheduling maintenance tasks according to the number of solutions measured, rather than elapsed time can reduce these impacts. The Early Maintenance Feedback (EMF) function allows the user to set up an alert for a maintenance task after a specified number of samples. Recommended alert settings for specific sample types can be generated automatically. The alert system will result in more frequent instrument maintenance when measuring complex samples, ensuring consistent analytical performance. Figure 4 shows an example of a maintenance counter for the ICP torch based on the number of measured solutions. The AVS 7 extends the life of the torch, as less sample digest goes through it, so the counter was set to a relatively high number.
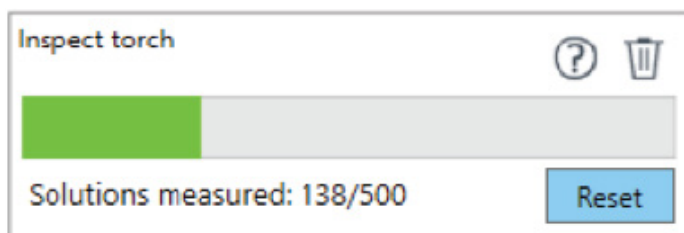

Figure 4. Maintenance counter based on the number of solutions analyzed.

Standards and sample preparation

The IntelliQuant Screening function can be used to quickly determine the approximate concentrations of each element in a sample. This information was then used to determine suitable calibration concentrations. The calibration standards were prepared from Agilent single element calibration standards using a matrix of 5% nitric acid (Emsure, Merck) and 15% hydrochloric acid (Emsure, Merck). 18.2 MΩ de-ionized (DI) water (Merck Millipore) was used to dilute all solutions. The concentrations of the calibration solutions (Table 3) provided a large linear range for each element, while maintaining excellent detection limits. The QC solution was prepared at one-fifth of the highest concentration standard used for each element.

To minimize any chemical incompatibilities, solutions were separated into three sets. A calibration blank and an initial calibration blank solution were prepared to match the matrix of the samples (5% HNO_3 and 15% HCl). Table 3 outlines the viewing mode, background correction method, and concentration ranges for each element.

Standard Reference Material (SRM) 2782 Industrial Sludge (NIST, USA) was used to evaluate the analytical method. An accurately recorded mass of 0.50 g of the SRM was digested using a two-stage microwave digestion procedure. First, the SRM was predigested for 15-minutes at room temperature in 9 mL HNO_3, 1 mL H_2O_2, 3 mL HCl, and 6 mL HF. The SRM was then fully digested using a Mars 6 Microwave Digestion System (CEM Corporation, NC, USA) per the program outlined in Table 4.

Table 3. Plasma viewing mode, background correction method, and calibration information, including percentage relative standard error (%RSE).

Element and Wavelength (nm)	Viewing Mode	Background Correction	Concentration Range (mg/L)	Correlation Coefficient	%RSE
Ag 328.068	Axial	Fitted	1–20	0.99998	4.1
Al 308.215	Radial	Fitted	25–500	0.99996	6.4
As 188.980	Axial	Fitted	2.5–50	0.99999	0.9
Ba 233.527	Radial	Fitted	2.5–50	0.99984	9.2
Be 313.107	Radial	Fitted	0.25–5	0.99997	6.4
Ca 315.887	Radial	Fitted	50–1000	0.99998	4.6
Cd 228.802	Axial	FACT	1–20	1.00000	0.8
Co 230.786	Radial	Fitted	10–200	0.99998	2.2
Cr 267.716	Radial	Fitted	5–100	0.99999	2.7
Cu 327.395	Axial	Fitted	5–100	0.99997	5.3
Fe 273.358	Axial	Fitted	375–7500	0.99989	7.0
K 766.491	Radial	Fitted	12.5–250	1.00000	0.4
La 408.671	Axial	Fitted	2.5–50	0.99999	2.4
Li 670.783	Radial	FACT	0.25–5	1.00000	1.3
Mg 279.800	Radial	Fitted	12.5–250	1.00000	3.2
Mn 257.610	Radial	Fitted	2.5–50	0.99999	2.8
Mo 204.598	Axial	Fitted	2.5–50	1.00000	1.7
Na 589.592	Radial	FACT	25–500	0.99999	1.2
Ni 221.648	Axial	Fitted	5–100	0.99983	11.5
P 213.618	Axial	FACT	35–700	0.99999	1.8
Pb 220.353	Axial	Fitted	10–200	0.99996	5.6
Sb 206.834	Axial	FACT	10–200	0.99998	1.7
Sr 216.596	Axial	Fitted	5–100	0.99997	4.4
Ti 334.941	Radial	Fitted	10–200	0.99998	1.3
Tl 190.794	Axial	Fitted	5–100	0.99987	9.7
V 311.837	Axial	Fitted	5–100	1.00000	0.7
Zn 206.200	Radial	Fitted	10–200	0.99993	4.7

Table 4. Microwave digestion parameters.

Parameter	Value
Power (W)	0 – 1200
Temperature (°C)	200
Ramp Time (min)	25
Hold Time (min)	25

The second stage of the digestion was completed on a hotplate. The digestion solution was transferred from the microwave vessels to 100 mL PTFE beakers and 3 mL $HClO_4$ was added to ensure that any remaining organic material had oxidized. The samples were then heated at 250 °C on a hotplate in a fume cupboard for 3 to 4 hours to evaporate the solution to a gel-like consistency. This step is required to remove the HF before analysis to prevent damage to the glass sample introduction of the ICP-OES. Once the gel-like consistency had been observed, 1 mL of HNO_3, 3 mL HCl, and 3–5 mL of DI water were added to dissolve the sample. The samples were then left to cool, before diluting to 20 mL final volume with DI water. The final matrix of the samples was 5% HNO_3 and 15% HCl.

This method for the digestion of solid waste samples is based on the method described in HJ 781-2015. However, to ensure complete dissolution, 6 mL of HF was added instead of 3 mL, and the final matrix was changed from the 10% HNO_3 described in the method. Including HCl in the matrix ensured that silver, antimony, aluminum, and iron were stable in solution.

Results and discussion

Method detection limits

The three sigma MDLs were calculated from 10 measurements of the method blank (5% HNO_3, 15% HCl), which were run on two instruments over three days. The MDLs for each element (reported as mg/kg) are given in Table 5. The 5800 MDLs are all significantly lower than the DLs specified in the HJ 781-2015 standard method, confirming the suitability of the instrument for the application.

Table 5. MDLs for each element compared to MDLs specified in HJ 781-2015 standard method and recoveries for certified and reference elements in NIST 2782 Industrial Sludge SRM.

Element and Wavelength (nm)	MDL (mg/kg)	Required MDL (mg/kg)	Measured Concentration (mg/kg)	Certified/ Reference Concentration (mg/kg)	Recovery (%)
Ag 328.068	0.0158	0.1	30.8	30.6*	101
Al 308.215	0.557	8.9	13600	13700*	99
As 188.980	0.0711	–	164	166	99
Ba 233.527	0.0314	3.6	241	254*	95
Be 313.107	0.0027	0.04	0.503	-	-
Ca 315.887	0.19	6.9	6440	6700*	96
Cd 228.802	0.0103	0.1	3.82	4.17	92
Co 230.786	0.0772	0.5	63.2	66.3*	95
Cr 267.716	0.0395	0.5	102	109	94
Cu 327.395	0.0337	0.4	2690	2594	104
Fe 273.358	1.96	8.9	267000	269000*	99
K 766.491	3.99	7.7	2930	3200*	92
La 408.671	0.0168	–	54.3	58.1*	93
Li 670.783	0.0512	–	6.08	-	-
Mg 279.800	0.207	2.3	2450	2600*	94
Mn 257.610	0.0084	3.1	298	-	-
Mo 204.598	0.0299	–	9.98	10.07	99
Na 589.592	0.231	7.8	12300	13000*	95
Ni 221.648	0.0247	0.4	151	154.1	98
P 213.618	0.0421	–	4920	5000*	98
Pb 220.353	0.0571	1.4	533	574	93
Sb 206.834	0.118	0.5	5.51	-	-
Sr 216.596	0.0199	1.3	80.8	-	-
Ti 334.941	0.0109	3	856	880*	97
Tl 190.794	0.104	0.4	<MDL	-	-
V 311.837	0.024	1.5	76.2	80*	95
Zn 206.200	0.0216	1.2	1200	1254	96

<MDL indicates that the result was less than the method detection limit
* Indicates a reference value, as reported by NIST.

SRM analysis

The results for six digestions of the industrial sludge SRM are given in Table 5. The results are reported in mg/kg, based on a sample mass that was accurately recorded during weighing and a final volume of 20 mL. The quantitative SRM recoveries for all certified and reference elements measured above the MDL were within ±10% of the expected value.

IntelliQuant results

Table 6 shows semiquantitative results for certified elements in the industrial waste SRM, plus V (reference value), Cl, and N. The data was obtained using wavelengths with the highest ranking. Typically, semiquantitative measurements are within ±30% of the expected value. Nitrogen (calibrated as % nitric acid) and chlorine (calibrated as % hydrochloric acid) were included in the IntelliQuant calibration. The final concentration of the SRM solutions was 5% HNO_3 and 15% HCl, as confirmed by the IntelliQuant results. Measuring N and Cl allows the operator to check that the sample preparation had been done correctly.

Table 6. IntelliQuant results for certified elements in SRM 2782, plus V, Cl, and N.

Element	IntelliQuant Concentration (mg/kg)	Certified Concentration (mg/kg)	Recovery (%)
As	136	166	82
Cd	5	4.17	128
Cl (%)	15	-	NA
Cr	81	109	74
Cu	2100	2594	81
Mo	8	10.07	79
N (%)	4	-	NA
Ni	119	154.1	77
Pb	430	574	75
V	67	80*	84
Zn	1030	1254	82

*Indicates a reference value

Spike recovery test

A spike recovery test was done to determine the accuracy of elements not certified in the industrial waste SRM but required by HJ 781. All recoveries were within ±10% of the spike level, as shown in Table 7.

Table 7. Spike recoveries results for some non-certified elements added to the SRM.

Element and Wavelength (nm)	Unspiked Sample (mg/kg)	Spiked Sample (mg/kg)	Spike Level (mg/kg)	Spike Recovery (%)
Be 313.107	0.483	1.51	1	103
*Li 670.783	4.52	53.6	50	98
Mn 257.610	286	790	500	101
Sb 206.834	0.306	11	10	107
Sr 216.596	76.9	259	200	91
Tl 190.794	<MDL	18.4	20	92

*Not listed in HJ 781.

Long-term stability

To assess the stability of the instrument, 172 solutions, consisting of digested soil samples and SRM digests, were measured over a six-hour period without recalibrating. During the analytical run, a QC solution was measured every 10 samples. The QC stability plot in Figure 5 shows the recovery of all elements over the six-hour period to be within ±10%. The relative standard deviation (%RSD) was less than 2.2% for all elements. The results demonstrate the excellent robustness and precision of the 5800 VDV ICP-OES for the analysis of complex industrial waste samples over an extended period.
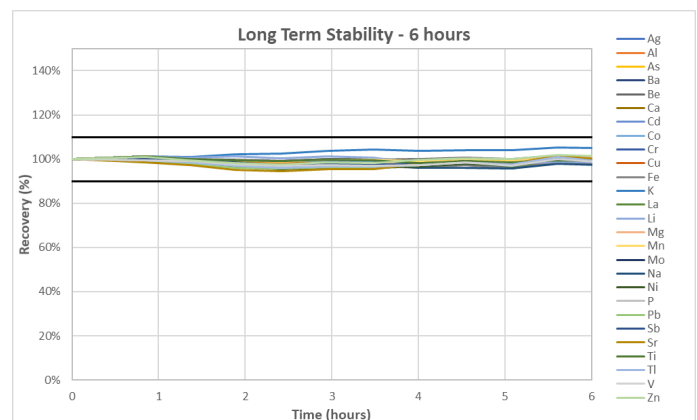

Figure 5. Long-term stability test showing recovery of a QC solution analyzed every 10 samples over a six-hour period.

Conclusion

Accurate, routine measurements of metals in solid wastes can be carried out using an Agilent 5800 VDV ICP-OES with an AVS 7 switching valve in accordance with Chinese National Standard HJ-781. The AVS 7 reduces the maintenance requirements on the VDV torch and improves sample throughput. The high performance of the 5800 was demonstrated by the recovery data for 21 elements in an industrial waste SRM and spike recoveries of six more elements. All recoveries were within ±10% of the certified, reference, or spiked values.

The smart tools developed for the Agilent ICP Expert software add an extra layer of quality assurance to the analysis. The IntelliQuant function helps with wavelength selection, as shown by the wavelength star-ranking system. The software also identifies interferences on analyte wavelengths, even if those elements are not in the quantitative method. The Outlier Conditional Formatting function gives a quick, visual flag of any results that need further attention, allowing you to troubleshoot before you report inaccurate results. To maximize instrument performance and minimize unplanned downtime, the Early Maintenance Feedback function generates alerts for maintenance tasks, based on the number of samples run.

Other benefits of the 5800 VDV ICP-OES for the accurate measurement of metals in industrial waste samples include:

- Simple to use fitted background correction for automatic correction of complex backgrounds.

- FACT background correction for highly complex background structures and automatic correction of spectral interferences.

- Stable results over an extended analytical period, as shown by the six-hour QC stability-test results.

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