Determination of 22 Elements Following US EPA Guidelines with a New Megapixel CCD ICP-OES

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

Author

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Introduction

Elemental analysis of environmental samples has always played an important role in preserving our health and environment. With financial pressures applied to laboratories today, it is important to achieve maximum efficiency in the procurement of accurate and precise results. With versatile software and simultaneous measurement of the entire elemental spectrum, the Agilent Vista-MPX measures the 22 US EPA approved ICP elements with one quick method, at under 5 minutes per sample.

What makes this possible is the custom-designed MPX megapixel detector, the first to provide over 1.1 million pixels in a charge coupled device (CCD) array. Full wavelength coverage between 177–785 nm means that spectral interferences are easily avoided, and selecting several elemental wavelengths allows automatic on-line results confirmation throughout an analysis with no time penalty. Simultaneous measurement of all selected wavelengths gives real-time background correction, which improves analytical precision and slashes analysis times. This means you can analyze more samples per day and reduce argon costs.

This work illustrates that a full suite of US EPA elements can be measured simultaneously in compliance with US EPA protocols. For a detailed interpretation of US EPA requirements, please refer to "A Complete Method for Environmental Samples by Simultaneous Axially Viewed ICP-OES following US EPA Guidelines"[1]. The Vista-MPX software simplifies method development significantly by providing a resident template worksheet that incorporates required QCP tests at the appropriate frequency as specified in ILM05.0 [2]. A copy of the supplied worksheet can be modified to suit the requirements of an individual analysis, such as sample number, conditions, or additional QCP tests. If an Agilent SPS-5 autosampler and autodiluter are used, over-range solutions are diluted on-line, thus avoiding the need to re-prepare and re-analyze those solutions. The MultiCal feature of the software takes advantage of the simultaneous full wavelength coverage of the Vista-MPX. MultiCal enables both trace and major concentrations of an element to be determined in one analysis using wavelengths of different sensitivity. It then assigns each result to the appropriate wavelength automatically.

Agilent Technologies

Experimental

Instrumental

A Vista-MPX simultaneous ICP-OES with axially viewed plasma was used for this work. The instrument was fitted with the 3-channel peristaltic pump option for easy introduction of ionization buffer to the sample via a post-pump Y-piece. Instrument operating conditions are set out in Table 1.

Table 1. Instrument Operating Conditions

Power	1.4 kW
Plasma gas flow	15.0 L/min
Auxiliary gas flow	1.5 L/min
Nebulizer type	Glass concentric
Sample tubing	Grey/grey
Internal standard tubing	Orange/white
Drain tubing	Purple/black
Pump speed	15 rpm
Sample delay	35 s
Stabilization time	15 s
Rinse time	60 s
Replicate time	60 s
Replicates	2
Autosampler	AIM 1250*

* Manufactured by A.I. Scientific

Reagents

NIST certified standard reference material 1643d Trace Elements in Water was used for a number of QC tests. All remaining test and standard solutions were from Inorganic Ventures (Lakewood, NJ, USA) using their US EPA 200.7 kit. Solution matrix was 1% nitric acid and 5% hydrochloric acid (both AR Select PLUS grade, Mallinckrodt). The 1000 ppm Cs buffer was prepared from CsCl salt (AnalAR grade, Merck).

Results

Instrument Detection Limits (IDL) and Contract Required Detection Limits (CRDL)

According to ILM05.0 [2], the instrument detection limit for an element is determined by measuring a standard solution containing that element at a concentration of 3–5 times the instrument manufacturer's suggested IDL on three non-consecutive days with seven consecutive measurements on each day (for explanations of alternative terminologies [1]). The IDL is then calculated by multiplying by three the average of the standard deviations obtained for the element on the different days. The IDLs obtained this way must meet the contract required detection limits (CRDLs) specified in Section 1, Exhibit C of the ILM05.0 document. Table 2 shows that the contract required detection limits (CRDLs) are met for all 22 US EPA elements.

Table 2. Instrument Detection Limits (EPA defined) at 3σ and 60 Second Read Time

Element and wavelength	CRDL ILM 05.0 (µg/L)	IDL obtained (µg/L)	US EPA pass/fail result
Ag 328.068	5	1	Pass
Al 236.705	200	1	Pass
Al 308.215	200	23	Pass
As 188.980	5	3	Pass
Ba 585.367	20	1	Pass
Be 234.861	1	1	Pass
Ca 370.602	5000	1	Pass
Cd 226.502	2	1	Pass
Co 228.615	5	1	Pass
Cr 267.716	5	2	Pass
Cu 324.754	5	1	Pass
Cu 327.395	5	0.5	Pass
Fe 258.588	100	1	Pass
K 404.721	5000	185	Pass
K 769.897	5000	9	Pass
Mg 279.800	5000	2	Pass
Mn 257.610	10	0.4	Pass
Na 330.237	5000	53	Pass
Na 589.592	5000	17	Pass
Ni 231.604	20	1	Pass
Pb 220.353	3	2	Pass
Sb 206.834	5	1	Pass
Se 196.026	5	4	Pass
Tl 190.794	5	2	Pass
V 311.837	10	1	Pass
Zn 206.200	10	1	Pass

Linear Range Analysis (LRA)

Every three months, a linear range analysis standard (LRS) should be analyzed and reported [2]. The concentration of this sample defines the highest concentration of an element that can be measured without dilution. This sample should be analyzed during a routine analytical run, and the determined concentration of the elements in this solution should be recovered to within ± 5% of their true value. The LRS results obtained in this work are shown in Table 3.

Although it was found that silver was linear up to 10 mg/L, the US EPA recommends that the maximum silver concentration should be limited to 2 mg/L. Therefore, a maximum concentration of 2 mg/L silver was used in this work. Table 4 gives a list of some recommended background correction points.

Table 3. Linear Range Sample Recovery

Element and wavelength	LRA (mg/L)	Recovery %
Ag 328.068	10	101
Al 236.705	500	99
Al 308.215	40	100
As 188.980	10	103
Ba 585.367	200	95
Be 234.861	5	101
Ca 370.602	600	97
Cd 226.502	5	99
Co 228.615	50	97
Cr 267.716	20	100
Cu 327.395	30	101
Fe 258.588	500	95
K 404.721	500	104
K 769.897	200	101
Mg 279.800	600	98
Mn 257.610	50	97
Na 330.237	600	97
Na 589.592	50	98
Ni 231.604	50	97
Pb 220.353	100	101
Sb 206.834	10	103
Se 196.026	100	101
Tl 190.794	100	101
V 311.837	60	99
Zn 334.502	60	102

Table 4. Recommended Background Correction Points

Element and wavelength	BC point left (nm)	BC point right (nm)
Ag 328.068	0.026	0.029
Al 308.215	n.u.	0.052
As 188.980	0.025	n.u.
Ba 585.367	0.068	0.073
Ca 370.602	n.u.	0.057
Cd 226.502	0.021	n.u.
Co 228.615	0.031	n.u.
Cr 267.716	0.020	n.u.
Cu 324.754	n.u.	0.037
Fe 238.204	0.020	n.u.
K 769.897	0.112	n.u.
Mg 279.800	n.u.	0.042
Mn 257.610	0.020	n.u.
Na 589.592	0.066	n.u.
Ni 231.604	0.020	n.u.
Pb 220.353	0.009	0.008
Sb 206.834	n.u.	0.018
Se 196.026	0.022	n.u.
Tl 190.794	0.013	0.008
V 311.837	n.u.	0.048
Zn 206.200	0.024	n.u.

(n.u. indicates "not used")

Inter-Element Corrections (IEC) and Interference Check Samples (ICSA and ICSAB)

Inter-element correction factors are used to compensate for any inter-element interferences that may occur in a sample. Any effect of potentially interfering elements on analyte wavelengths can be calculated using the software, and a table of factors generated automatically. The factors are then automatically applied to produce corrected results during the analysis.

Although available, inter-element correction factors were not used in this work, as correct results were obtained by simply adjusting the off-peak background correction points. Interference check samples are used to verify whether inter-element correction factors are correct, or to verify they are not required. The concentration of elements in each of the interference check samples is specified in the ILM05.0 document. The interference check sample A (ICSA) contains four interferent analytes only, and is used to verify that samples which do not contain analytes but do have interferents present will report a concentration similar to the blank. US EPA specifies that for target elements with CRDLs below 10 µg/L, the determined concentration of an analyte must be within ± 3 × CRDL. For analytes with CRDLs of 10 µg/L and above, ICSA results are simply reported. Low levels of target elements together with interferent elements are present in the

interference check sample AB (ICSAB). All analytes in the ICSAB must be recovered within ± 20% of their true value. In this work, all target elements meet US EPA limits for ICSA and ICSAB, confirming that the use of IEC was not required. Results are presented in Tables 5 and 6.

Table 5. Interference Check Sample A

Element and wavelength	US EPA CRDL (µg/L)	US EPA ± limit (µg/L)	Found ICSA (µg/L)	US EPA pass/fail/ reported
Ag 328.068	5	15	8	Pass
As 188.980	5	15	9	Pass
Ba 585.367	20	—	6	Reported
Be 234.861	1	3	0.2	Pass
Cd 226.502	2	6	5	Pass
Co 228.615	5	15	2	Pass
Cr 267.716	5	15	1	Pass
Cu 324.754	5	15	-6	Pass
Mn 257.610	10	—	3	Reported
Ni 231.604	20	—	2	Reported
Pb 220.353	3	9	-4	Pass
Sb 206.834	5	15	4	Pass
Se 196.026	5	15	10	Pass
Tl 190.794	5	15	8	Pass
V 311.837	10	—	2	Reported
Zn 206.200	10	—	3	Reported

Table 6. Recovery of Elements from the Interference Check Sample AB

Element and wavelength	Expected ISCBA (mg/L)	Found ICCBA (mg/L)	% Recovery ICSAB	US EPA ± 20% pass/fail
Ag 328.068	0.22	0.20	89	Pass
As 188.980	0.11	0.09	84	Pass
Ba 585.367	0.55	0.49	89	Pass
Be 234.861	0.55	0.47	86	Pass
Cd 226.502	1.10	0.96	88	Pass
Co 228.615	0.55	0.47	87	Pass
Cr 267.716	0.55	0.49	89	Pass
Cu 324.754	0.55	0.52	95	Pass
Mn 257.610	0.55	0.48	88	Pass
Ni 231.604	1.10	0.95	87	Pass
Pb 220.353	0.05	0.05	84	Pass
Sb 206.834	0.66	0.60	91	Pass
Se 196.026	0.05	0.06	116	Pass
Tl 190.794	0.11	0.11	101	Pass
V 311.837	0.55	0.49	89	Pass
Zn 206.200	1.10	0.97	88	Pass

Laboratory Control Sample (LCS)

The purpose of the laboratory control sample (LCS) is to demonstrate that sample preparation procedures are appropriate for the sample type (solid, aqueous, air) analyzed. For example, if aqueous samples have been digested and analyzed, an aqueous LCS should be acquired from the US EPA and digested and analyzed together with the samples. The ILM05.0 documentation requires the LCS to be analyzed for every group of samples in a sample delivery group, or for each batch of samples digested, whichever is more frequent. The limit of recovery for target analytes in the LCS is ± 20% of the true value. In this work, NIST 1643d Water was used as the LCS. Results of the determination of all target analytes are within specification, and are reported in Table 7.

Duplicate and spike sample analysis

These quality control tests are performed on samples. One duplicate analysis is required for each group of samples with a similar matrix, or for each sample delivery group. The relative percent difference (RPD) between sample and duplicate concentrations for each element measured is calculated as follows:

$$\text{RPD} = \frac{|\text{Sample} - \text{Duplicate}|}{(\text{Sample} + \text{Duplicate})/2} \times 100$$

For samples with a concentration greater than or equal to 5 × CRDL, a control limit of 20% RPD applies. For samples with a concentration less than 5 × CRDL, but greater than the CRDL, an absolute difference in concentration of ± CRDL applies. If sample and duplicate concentrations are both lower than the CRDL, the difference is not reported. Sample spike analyses are used to identify whether the sample matrix has an adverse effect on analyte recovery. At least one pre-digestion spike (PDS) analysis must be performed for each group of samples of similar matrix type. Required spiking levels for target analytes are listed in Table 2, Exhibit D (ICP-OES) of the ILM05.0 document. The control limits for percent spike recovery is 75–125%. If this specification is not met, a post-digestion spike may be required [2].

All results for duplicate and spike analysis in this work meet US EPA requirements, as shown in Table 7.

Table 7. Laboratory Control Sample, Duplicate and Spiked Sample Analyses

Element and wavelength	LCS (mg/L) certified NIST 1643d	% Recovery LCS	Sample (mg/L)	Duplicate (mg/L)	CRDL (mg/L)	Calculated limit of difference	Absolute difference (mg/L)	%RPD or QC spike concentration (mg/L)	% Recovery spike
Ag 328.068	0.00127	110	0.0041	0.0025	0.005	Not Reported		0.05	100
Al 308.215	0.1276	86	0.11	0.12	0.2	Not Reported		2	105
As188.980	0.05602	102	0.057	0.057	0.005	20% RPD	0.2%	0.04	103
Ba 585.367	0.5065	102	0.53	0.53	0.02	20% RPD	0.2%	2	103
Be 234.861	0.01253	103	0.013	0.013	0.001	20% RPD	0.3 %	0.05	105
Ca 370.602	31.04	104	32.5	32.3	5	20% RPD	0.2 %	Not Required	
Cd 226.502	0.00647	96	0.0064	0.0064	0.002	0.002 mg/L	0.00005 mg/L	0.05	107
Co 228.615	0.025	102	0.025	0.027	0.005	20% RPD	4 %	0.5	106
Cr 267.716	0.01853	97	0.018	0.017	0.005	0.005 mg/L	0.0004 mg/L	0.2	106
Cu324.754	0.0205	91	0.022	0.022	0.005	0.005 mg/L	0.0004 mg/L	0.25	104
Fe 238.204	0.0912	100	0.091	0.091	0.1	Not Reported		1	105
K 769.897	2.356	116	2.7	2.7	5	Not Reported		Not Required	
Mg 279.800	7.989	105	8.4	8.3	5	5 mg/L	0.04 mg/L	Not Required	
Mn 257.610	0.03766	103	0.038	0.039	0.01	0.01 mg/L	0.0004 mg/L	0.5	104
Na 589.592	22.07	103	22.7	22.7	5	5 mg/L	0.03 mg/L	Not Required	
Ni 231.604	0.0581	103	0.061	0.061	0.02	0.02 mg/L	0.0007 mg/L	0.5	104
Pb 220.353	0.01815	99	0.024	0.023	0.003	20 % RPD	2 %	0.02	83
Sb 206.834	0.0541	97	0.054	0.054	0.005	20 % RPD	0.6 %	0.1	100
Se 196.026	0.01143	103	0.015	0.012	0.005	0.005 mg/L	0.004 mg/L	0.01	116
Tl 190.794	0.00728	115	0.008	0.010	0.005	0.005 mg/L	0.002 mg/L	0.05	111
V 311.837	0.0351	104	0.039	0.034	0.01	0.01 mg/L	0.005 mg/L	0.5	104
Zn 206.200	0.07248	107	0.079	0.080	0.01	20 % RPD	0.4 %	0.5	109

Continuing Calibration Verification (CCV)

The purpose of the continuing calibration verification standard (CCV) is twofold. One is to prove that the calibration standards supplied are the correct concentration, and the second is to prove that conditions remain stable throughout an analysis. According to ILM05.0 guidelines, the CCV must be prepared from an alternative source to the calibration standards. This provides verification of the concentration of each element in the calibration standards. The CCV should contain all elements to be measured, and each element must be present at a concentration equivalent to the mid-point of their respective calibration graphs. The CCV must be analyzed every 10 solutions or every 2 hours, whichever is more frequent. It must be analyzed at the beginning of a run, and after the last analytical sample. Since the measured concentration of each element in the CCV must be within ± 10% of their true value during the entire analysis, CCV results are a good measure of the stability of instrumental conditions. Figure 1 shows that instrument conditions remain stable over an 8-hour period. The precision of the results for all elements over the 8 hours was better than 2%.

Speed of Analysis

An analysis that adheres strictly to US EPA protocols is inherently time-consuming due to the large number of quality control solutions required to ensure compliance. The total analysis time per sample was 4 min 39 s, which included two 60 second replicate read times, a rinse delay of 60 seconds, plus sample uptake and stabilization times.

Conclusion

The Vista-MPX software provides complete automation of US EPA QC protocols, and supplies a resident worksheet template to speed method development. The available QC tests can be easily customized to comply with other regulatory bodies. Internal standardization is unnecessary, and inter-element correction factors were not required owing to excellent anti-blooming protection and spectral resolution. If an Agilent SPS-5 autodiluter is used, over-range solutions can be diluted and analyzed automatically on-line, thus

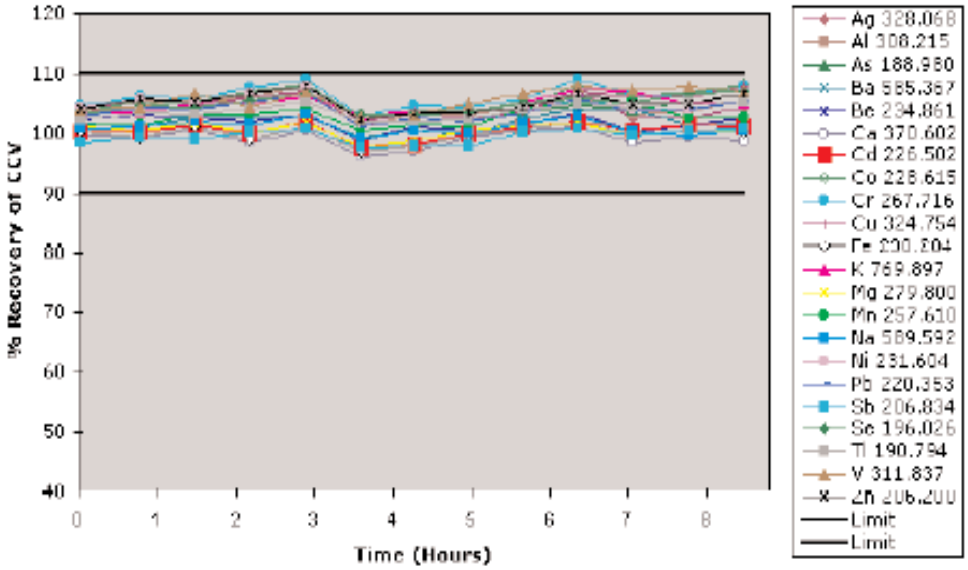

Figure 1. Percent recoveries of target analytes in the CCV over 8 hours without internal standard correction for all 22 US EPA elements. All recoveries were within 90–110% control limits.

saving on analysis time, whilst the MultiCal feature enables automatic results confirmation and extends linear dynamic range.

Although US EPA protocols require further tests not included here, the scope of this work illustrates that a full suite of US EPA elements can be analyzed successfully in under 5 minutes per sample using the Agilent Vista-MPX in complete compliance with US EPA protocols.

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2. ILM05.0 documentation was placed at the following website for review. This website was current at the time of publishing: http://www.epa.gov/oamsrpod/pollard/hq9915909/ilm050c.pdf

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