Application Note

Environmental exposure

Workplace Air Monitoring: Multi-Element Analysis of Air-Filters using ICP-OES

Fast, accurate analysis of 44 elements using the Agilent 5110 VDV ICP-OES

Author

Peter Riles

Agilent Technologies,
Melbourne, Australia

Introduction

Monitoring the quality of air within a workplace is important for workers' health, well-being, and productivity. While poor indoor air quality can cause mild symptoms such as tiredness and headaches, long-term exposure may lead to more serious conditions (*1*). Depending on the working environment and potential hazards that may arise from a company's activities, ongoing or regular monitoring is needed to ensure good air quality. Ambient (outdoor) monitoring data can identify if action is required to manage or prevent contaminants from entering the workplace.

Given the risks associated with poor air quality, regulations may develop to include inorganic-components, especially heavy metals. Standard methods for the analysis of multiple elements in outdoor and indoor air already exist. For example, Chinese standard method HJ 777-2015 Ambient air and waste gas from stationary sources emission (*2*) has been developed for the quantitative analysis of 24 elements using ICP-OES. An additional 20 elements are listed in standard methods ISO 15202 Workplace Air and ASTM D7035-16 (*3, 4*).

This study was carried out according to Chinese standard method HJ 777-2015, and includes the 20 additional elements listed in the ISO 15202 and ASTM D7035-16 methods. The method specifies sample preparation and multi-element analysis using ICP-OES. An Agilent 5110 Vertical Dual View (VDV) ICP-OES fitted with the Advanced Valve System (AVS 7) seven-port switching valve was used to analyze 44 elements in filter papers.

Experimental

Instrumentation

An Agilent 5110 VDV ICP-OES was fitted with the AVS 7 switching valve and SPS 4 autosampler. The 5110 ICP-OES uses an Easy-fit torch that automatically connects with all gas lines and aligns with the instrument's optics (*5*). The Easy-fit torch mechanism removes potential operator-to-operator variability when setting up the instrument and allows for fast startup. The mass flow controllers that are used on all torch gases provide excellent plasma stability over extended periods.

The 5110 ICP-OES combined with the fully integrated AVS 7 switching valve (*6*) allows for fast sample analysis without compromising on performance. The AVS 7 features a seven-port valve and a high-speed positive displacement pump to rapidly fill the sample loop. Controlled bubble injection reduces sample uptake, stabilization times, and rinse delays to deliver the highest analytical precision. The faster analysis speed means lower cost per analysis as shorter analysis times result in less argon usage per sample.

To achieve the lowest detection limits (DLs), an axial plasma view was selected for all elements. Agilent's Vista Chip II 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, three wavelengths for each element were tested. Checking the agreement of the results from multiple wavelengths confirmed the analytes were free from spectral interferences. Only one wavelength for each element has been reported in this study.

Europium (Eu) and rubidium (Rb) were selected as internal standards, at 10 mg/L and 50 mg/L respectively. Two Eu wavelengths were used for internal standardization; one atomic (462.723 nm), and one ionic (397.197 nm). Rb was used to correct for easily ionizable elements (EIEs), including potassium and lithium.

Tables 1 and 2 list the 5110 VDV ICP-OES operating conditions and AVS 7 parameters, respectively. RF power was increased to reduce the effect of EIEs. All other parameters are default settings.

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

Parameter	Settings
Read time (s)	15
Replicates	3
Sample uptake delay (s)	0
Stabilization time (s)	8
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
Nebulizer	SeaSpray concentric glass
Spray chamber	Double-pass glass cyclonic
Torch	Easy-fit VDV demountable 1.8 mm injector
Sample pump tubing	Black/black
Internal standard pump tubing	Orange/green
Waste pump tubing	Blue/blue
Background correction	Fitted/FACT
Viewing mode	Axial

Table 2. AVS 7 switching valve system parameters.

Parameter	Setting
Valve uptake delay (s)	3.5
Pump rate - uptake (mL/min)	35.1
Pump rate - inject (mL/min)	3.1
Sample loop volume (mL)	1
Preemptive rinse time (s)	1.0
Bubble inject time (s)	1.0

Background correction

A combination of automated fitted background correction (FBC) and Fast Automated Curve-fitting Technique (FACT) modeling was used for background correction. An example of FBC is shown in Figure 1. FBC has accurately modelled the Co 226.488 nm and Cr 226.519 nm interfering peaks on Cd 226.502 nm, allowing easy correction. By eliminating the need for the user to manually determine off-peak background correction points, FBC simplifies method development (*7*).

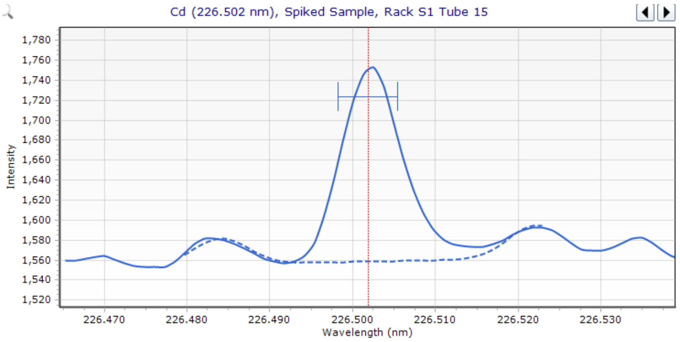

Figure 1. Cd 226.502 nm using FBC.

FACT modeling is used to correct spectral overlaps and the structural background typical of an axially-viewed plasma (*8*). In the FACT spectrum (Figure 2), by modeling the Th interference peak, the contribution to the In signal from Th can be removed, improving the accuracy of the measurement.

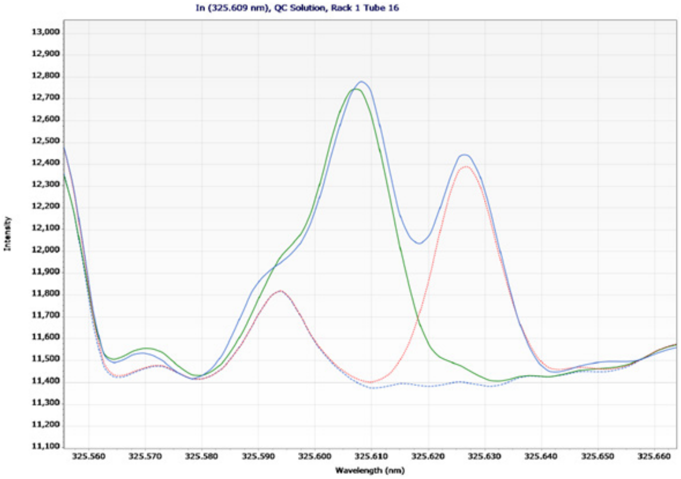

Figure 2. FACT model for In 325.609 nm. Blue solid line represents the total signal. The green solid line represents the indium signal and the red dashed line the thorium signal. The blue dashed line represents the background.

Standards and sample preparation

Working calibration solutions were prepared from Agilent single element calibration standards and Agilent multi-element calibration standard (Calibration mix 2). The standards were made in 10% nitric acid (Emsure, Merck) or 10% hydrochloric acid (Emsure, Merck), at 0.25, 0.5, 1, 5 mg/L and 1, 5, and 10 mg/L for major elements. The QC solution (0.2 mg/L; 2.00 mg/L for major elements) was made in 2% HNO_3 and 10% HCl. Standards containing silver and tantalum where made using 10% HCl matrix to avoid precipitation of these metals. 18.2 MΩ de-ionized (DI) water (Merck Millipore) was used to dilute all solutions. Solutions were separated into three sets to minimize any chemical incompatibilities. Fresh calibration solutions should be prepared every week to avoid precipitation of silver and tantalum.

A calibration blank and an initial calibration blank were prepared to match the matrix of the samples (2% HNO_3 and 7% HCl).

Digestion solution

The sample digestion procedure outlined in HJ 777-2015 was followed in this application. A digestion solution was prepared by adding 55.5 mL of concentrated HNO_3 and 167.5 mL of concentrated HCl to approximately 500 mL of DI water. The digestion solution was then diluted to 1000 mL, mixed, and stored in a sealable glass container.

Filter standards

Three certified reference material (CRM) filter standards were used to evaluate the analytical method. The CRMs included QC-TMFM-D and QC-TMFM-G (High Purity Standards, USA), and SRM-2783 (NIST, USA). The CRMs from High Purity Standards were made using mixed cellulose ester type filters. Each CRM was supplied with blank filters for correction of elements present in the filter. The NIST SRM was made using a polycarbonate filter membrane and was supplied with a blank filter for correction of elements present in the filter.

The three CRMs were prepared for microwave digestion (CEM, USA) by placing the entire filter paper in a sealable PTFE test tube and adding 20 mL of the digestion solution. Sample digestion was carried out according to the conditions given in Table 3. On completion of the microwave digestion program, 10 mL of DI water was added, and the samples were leached at room temperature for 30 minutes. Each solution was then filtered using a vacuum filter system (Merck

Millipore) fitted with a mixed cellulose ester membrane filter. The filtrate was then diluted to 50 mL using DI water.

Another CRM, NIES CRM 28: Urban Aerosols (National Institute for Environmental Studies, Japan) was prepared and used for the spike-recovery and the long-term stability tests.

To enable accurate determination of the method detection limits (MDLs), blank mixed cellulose ester membrane filters (Merck Millipore) were digested and analyzed. The digestion procedure used for the CRMs was also used to prepare the blanks.

Table 3. Microwave digestion system parameters.

Parameter	Setting
Power (W)	0–1800
Temperature (°C)	200
Ramp time (min)	25
Hold time (min)	15

Results and Discussion

MDLs and LOQs

The three sigma MDLs were calculated from 10 measurements of the digested blank filters which were run on two instruments over three days. The MDLs for each element (reported as µg/L and µg/filter) are given in Table 4. The 5110 MDLs are all significantly lower than the DLs specified in HJ 777-2015, ISO 15202, and ASTM D7035-16 standard methods, confirming the suitability of the instrument for the application. The Limits of Quantitation (LOQs), which were calculated as 10 sigma of the blank measurements, also exceed the standard method DL requirements for most elements.

Table 4. MDLs and LOQs for all elements.

Element and wavelength (nm)	Background correction	MDL (µg/L)	MDL µg/filter	LOQ (µg/L)	LOQ (µg/filter)	HJ 777-2015 MDL (µg/L)	ISO 15202 MDL (µg/L)	ASTM D7035-16 MDL (µg/L)
Ag 328.068	Fitted	1.7	0.085	5.7	0.29	9	-	-
Al 396.152	Fitted	6.4	0.32	21	1.1	66	-	-
As 188.980	Fitted	5.9	0.30	20	1.0	12	19	40
B 249.678	Fitted	2.8	0.14	9.3	0.47	-	-	20
Ba 455.403	Fitted	0.39	0.020	1.3	0.065	4	-	2.4
Be 234.861	Fitted	0.095	0.0048	0.32	0.016	8	0.3	0.36
Bi 223.061	Fitted	8.8	0.44	29	1.5	18	-	-
Ca 317.933	Fitted	72	3.6	240	12	200	-	80
Cd 226.502	Fitted	0.37	0.019	1.2	0.060	9	2.8	4
Ce 446.021	FACT	4.5	0.23	15	0.75	-	-	-
Co 228.615	Fitted	0.74	0.037	2.5	0.13	7	3.3	12
Cr 267.716	Fitted	2.1	0.11	7.0	0.35	18	2.3	16
Cu 327.395	Fitted	1.4	0.070	4.7	0.24	7	15	2.8
Fe 259.940	Fitted	6.9	0.346	63	3.2	71	14	80
Hf 277.336	Fitted	6.1	0.31	20	1.0	-	-	-
In 325.609	FACT	9.6	0.48	32	1.6	-	10	-
K 766.491	Fitted	15	0.75	50	2.5	38	-	80
Li 670.783	Fitted	0.63	0.032	2.1	0.11			
Mg 285.213	FACT	3.3	0.17	11	0.55	73	-	20
Mn 257.610	Fitted	0.14	0.0070	0.47	0.024	7	1	0.8

Table 4 continues...

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Element and wavelength (nm)	Background correction	MDL (µg/L)	MDL µg/filter	LOQ (µg/L)	LOQ (µg/filter)	HJ 777-2015 MDL (µg/L)	IS0 15202 MDL (µg/L)	ASTM D7035-16 MDL (µg/L)
Mo 202.032	Fitted	1.3	0.065	4.3	0.22	-	-	8
Na 589.592	Fitted	73	3.7	240	12	130	-	160
Ni 231.604	Fitted	2.6	0.13	8.7	0.44	12	10	8
P 178.222	Fitted	20	1.0	67	3.4	-	-	80
Pb 220.353	FACT	2.7	0.14	9.0	0.45	14	10	24
Pt 203.646	Fitted	5.5	0.28	18	0.90	-	-	320
Rh 369.236	Fitted	15	0.75	50	2.5	-	-	-
Sb 206.834	Fitted	7.0	0.35	23	1.2	12	-	16
Sc 363.074	Fitted	1.0	0.050	3.3	0.17	-	-	-
Se 196.026	FACT	8.8	0.44	29	1.5	-	17	120
Si 251.611	Fitted	9.5	0.48	32	1.6	-	-	-
Sn 189.925	Fitted	5.2	0.26	17	0.85	28	63	32
Sr 421.552	Fitted	0.13	0.0065	0.43	0.022	9	-	0.8
Ta 263.558	FACT	11	0.55	37	1.9	-	-	-
Te 214.282	FACT	9.4	0.47	31	1.6	-	28	80
Th 283.730	FACT	2.3	0.12	7.7	0.39	-	-	-
Ti 334.941	Fitted	1.7	0.085	5.7	0.29	9	-	8
Tl 190.794	Fitted	5.0	0.25	17	0.85	-	-	36
U 409.013	FACT	16	0.80	53	2.7	-	-	-
V 292.401	Fitted	1.1	0.055	3.7	0.19	11	1.2	4
W 209.475	Fitted	7.8	0.39	26	1.3	-	-	-
Y 377.433	FACT	0.15	0.0075	0.50	0.025	-	0.6	0.8
Zn 213.857	Fitted	2.5	0.13	8.3	0.42	36	15	4
Zr 343.823	Fitted	0.50	0.025	1.7	0.085	-	-	2.4

CRM analysis

The results from the analysis of the three CRMs are given in Table 5. The results are reported in µg/filter, based on the 50 mL final volume of the digested CRMs. The quantitative CRM recoveries for all certified elements measured above the LOQ in the three CRMs were within ±10% of the certified value, where certified values are provided. The only exceptions were the results for resistive metals silicon and titanium in NIST 2783. These elements did not fully recover as the certified value for Ti and reference value for Si are based on results obtained from neutron activation analysis or X-ray fluorescence analysis. These techniques provide a "total" value, where wet chemistry techniques will only extract the leachable portion.

Table 5. Concentration measurements of filter media CRMs using the 5110 VDV ICP-OES. Dashes indicate no certified value.

	QC-TMFM-D			QC-TMFM-G			SRM-2783		
Element and wavelength (nm)	Measured (µg/filter)	Certified (µg/filter)	Recovery (%)	Measured (µg/filter)	Certified (µg/filter)	Recovery (%)	Measured (µg/filter)	Certified (µg/filter)	Recovery (%)
Ag 328.068	1.02	1.0	102	5.25	5.0	105	<MDL	-	-
Al 396.152	50.7	50.0	101	<LOQ	-	-	22.1	23.21	95
As 188.980	10.0	10.0	100	50.5	50.0	101	<MDL	0.0118	-
Ba 455.403	2.53	2.5	101	9.51	10.0	95	0.319	0.335	95
Be 234.861	0.110	0.1	110	9.47	10.0	95	<LOQ	-	-
Cd 226.502	1.01	1.0	101	9.86	10.0	99	<LOQ	-	-
Co 228.615	2.50	2.5	100	9.60	10.0	96	<MDL	0.0077	-
Cr 267.716	2.41	2.5	96	9.30	10.0	93	<LOQ	0.135	-
Cu 327.395	2.47	2.5	99	24.0	25.0	96	0.369	0.404	91
Fe 259.940	2.52	2.5	101	23.4	25.0	94	27.2	26.5	103
K 766.491	<LOQ	-	-	<MDL	-	-	4.84	5.28	92
Mg 285.213	<MDL	-	-	<MDL	-	-	7.88	8.62	91
Mn 257.610	1.03	1.0	103	9.67	10.0	97	0.331	0.32	103
Ni 231.604	2.54	2.5	102	9.59	10.0	96	<MDL	0.0068	-
Pb 220.353	2.43	2.5	97	24.8	25.0	99	<LOQ	0.317	-
Tl 190.794	2.33	2.5	93	9.60	10.0	96	<MDL	-	-
U 409.013	<MDL	-	-	4.78	5.0	96	<MDL	0.001234	-
V 292.401	2.46	2.5	98	9.49	10.0	95	<LOQ	0.0485	-
Zn 213.857	2.62	2.5	105	48.0	50.0	96	1.89	1.79	106

<MDL indicates result was less than method detection limit. <LOQ indicates result was less than limit of quantification.

Table 6. Recoveries for spiked samples.

Element and wavelength (nm)	Measured spiked blank (µg/L)	Sample (µg/L)	Spiked sample (µg/L)	Recovery (%)	Element and wavelength (nm)	Measured spiked blank (µg/L)	Sample (µg/L)	Spiked sample (µg/L)	Recovery (%)
Ag 328.068	30.6	<MDL	31.0	101	Ni 231.604	37.0	<MDL	38	103
Al 396.152	35.4	363	402	110	P 178.222	104	35.8	142	102
As 188.980	34.6	<MDL	36.3	105	Pb 220.353	10.8	3.43	14.4	102
B 249.678	23.0	10.4	33.9	102	Pt 203.646	23.3	7.27	28.4	91
Ba 455.403	1.05	8.67	9.71	99	Rh 369.236	32.9	<MDL	34.6	105
Be 234.861	0.798	0.026	0.839	102	Sb 206.834	45.7	<MDL	43.7	96
Bi 223.061	45.3	0.912	45.3	98	Sc 363.074	1.10	<MDL	1.18	107
Ca 317.933	139	293	436	103	Se 196.026	71.0	<MDL	73.1	103
Cd 226.502	2.60	0.403	3.15	106	Si 251.611	126	874	989	91
Ce 446.021	17.2	0.808	18.7	104	Sn 189.925	50.3	<MDL	51.3	102
Co 228.615	2.12	0.142	2.19	97	Sr 421.552	0.956	2.23	3.24	106
Cr 267.716	4.48	4.01	8.64	103	Ta 226.230	23.6	<MDL	24.1	102
Cu 327.395	18.9	0.363	20.8	108	Te 214.282	44.9	<MDL	45.2	101
Fe 259.940	23.3	294	316	94	Th 283.730	9.54	<MDL	9.43	99
Hf 277.336	8.27	<MDL	8.57	104	Ti 334.941	5.38	21	26.7	106
In 325.609	13.0	<MDL	12.0	92	Tl 190.794	21.8	<MDL	21.6	99
K 766.491	43.9	153	200	107	U 409.013	54.8	<MDL	55.2	101
Li 670.783	9.90	<MDL	10.7	108	V 292.401	3.00	<MDL	3.31	110

Table 6 continues..

...Table 6 continued

Element and wavelength (nm)	Measured spiked blank (µg/L)	Sample (µg/L)	Spiked sample (µg/L)	Recovery (%)	Element and wavelength (nm)	Measured spiked blank (µg/L)	Sample (µg/L)	Spiked sample (µg/L)	Recovery (%)
Mg 285.213	5.63	99.5	105	98	W 209.475	37.8	<MDL	37.4	99
Mn 257.610	4.45	4.61	9.03	99	Y 377.433	1.23	0.173	1.49	107
Mo 202.032	6.81	<MDL	7.20	106	Zn 213.857	7.36	10.7	17.7	95
Na 589.592	225	293	524	103	Zr 343.823	1.91	0.738	2.55	95

<MDL indicates result was less than method detection limit. For these results, the recovery has been calculated assuming a concentration of 0 ug/L.

Spike recovery test

After depositing the NIES CRM 28 suspension solution onto a filter, the sample was digested to perform the spike recovery test. The sample was spiked with a low concentration (<10 times LOQ) of each analyte to determine recoveries of these elements. All recoveries are within ±10% of the expected concentration, as shown in Table 6, demonstrating the high performance of the 5110 to accurately determine low concentrations of metals in filters.

Long-term stability

Approximately 350 solutions, consisting of CRMs and samples, were analyzed over a 6-hour period without recalibrating. During the run, a QC solution was analyzed every 10 samples. The QC stability plot in Figure 3 shows the recovery of all elements over the 6-hour period to be within ±10%. The relative standard deviation (% RSD) was less than 2.1% for all elements except Te, with 4% RSD. The results demonstrate the excellent robustness and precision of the 5110 VDV ICP-OES over the extended run.

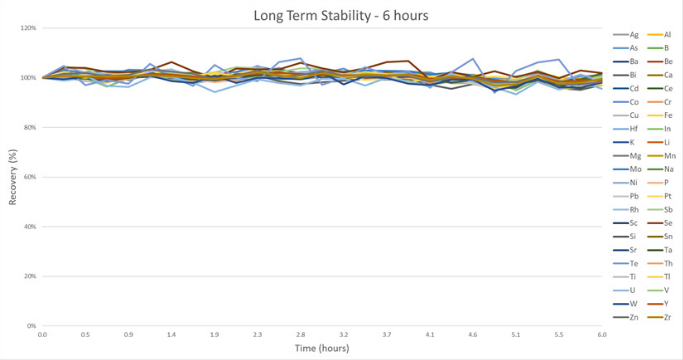

Figure 3. Long-term stability: recovery of a QC solution analyzed every 10 samples over a 6-hour period.

Analysis times and total argon gas consumption

Analysis times and total argon consumption per sample are given in Table 7. As this method is an axial-view only method, the snout purge was turned off, reducing the volume of argon needed. When calculating argon consumption, all gas flows within the instrument were considered to ensure an accurate calculation of gas usage.

Table 7. Analysis time and total argon gas consumption per sample using the 5110 VDV ICP-OES with AVS 7.

Parameter	5110 VDV ICP-OES
Analysis time per sample (s)	63
Total argon gas consumption per sample (L)	21

Conclusions

Accurate, routine measurements of metals in filter media can be carried out using the Agilent 5110 VDV ICP-OES with AVS 7 switching valve. The AVS 7 increases productivity and maintains excellent precision over extended runs.

Good accuracy was demonstrated by the recovery data of multiple elements in three CRMs. Each CRM was prepared for analysis according to the method specified in Chinese standard method HJ 777-2015. A recovery test of low-concentration (µg/L) spikes added to a CRM showed good recoveries for all 44 elements.

Benefits of the 5110 VDV ICP-OES for accurate measurement of metals in filter media include:

- FACT correction for highly complex background structures and automatic correction of spectral interferences.
- Simple-to-use fitted background correction, which provides automatic correction for complex backgrounds.
- Stable results over extended analytical periods, as shown by the QC stability results over a 6-hour run.
- Accurate and precise results, while maintaining low operating costs. Sample analysis time was 63 seconds and argon consumption was 21 L per sample.

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