Application Note

Environmental

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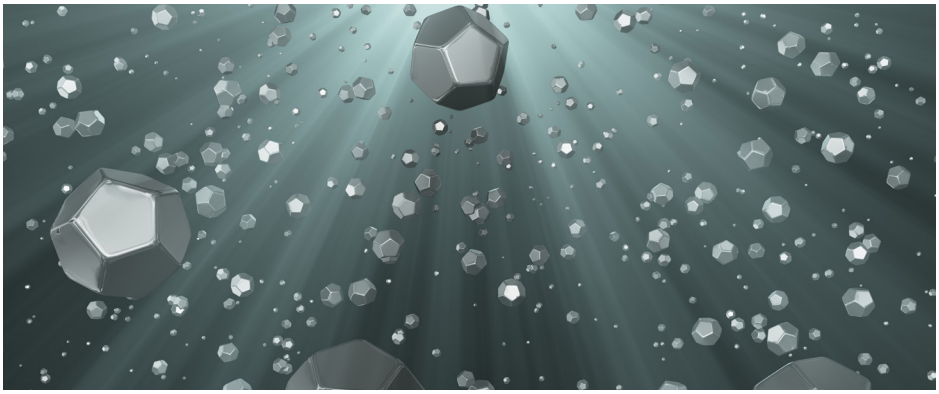
Measuring Metals in Airborne Particulate Matter ($PM_{2.5}$) by ICP-MS

Determination of 26 elements extracted from $PM_{2.5}$ trapped in air filters using an Agilent 7850 ICP-MS



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Introduction

The harmful impact of poor air quality caused by traffic-related emissions is well documented.[1,2] Pollutants arising from exhaust fumes, brake abrasion dust, tires, and road-surface wear are a significant contributor of particulate matter (PM) to the environment. PM, which is the term used to describe solid and liquid particles that are suspended in air, is especially problematic around road networks within densely populated areas. Various industrial, agricultural, and domestic processes and practices, such as burning fossil fuels, can also release particles into the air.

PM is typically categorized as PM_{10} (particles ≤10 µm) or $PM_{2.5}$ (particles ≤2.5 µm). While all PM is of concern to public health, the finer $PM_{2.5}$ particles are increasingly monitored in traffic-heavy parts of cities and urban areas. To help countries meet the World Health Organisation (WHO) Sustainable Development Goal, SDG 11.6.2, 'Air quality in urban areas', policymakers are encouraged to adopt WHO's air quality guidelines.[3]

The WHO specify an annual average concentration limit for $PM_{2.5}$ of 5 µg/m^3 and an average of 15 µg/m^3 over 24 hours.[4] The European Union (EU) is working to align its standards with the WHO.[5] In February 2024, the US EPA strengthened its health-based annual $PM_{2.5}$ standard to 9.0 µg/m^3 and maintained the 24-hour $PM_{2.5}$ standard at 35 µg/m^3.[6] Japan's standards for $PM_{2.5}$, which were first introduced in 2009, specify annual and 24-hour limits of ≤ 15.0 and ≤ 35 µg/m^3, respectively.[7] Currently, the Chinese national ambient air quality standards for $PM_{2.5}$ are an average of 35 µg/m^3 annually and 75 µg/m^3 daily.[8]

In addition to monitoring the total concentration of $PM_{2.5}$ in air samples, which can be calculated by weighing the filters before and after sample collection, regulatory agencies and researchers need reliable methods to measure pollutants contained in the particles. Key pollutants include metals and elements of concern to health or the environment such as heavy metals and transition metals. Agilent ICP-MS instruments provide high sensitivity and a wide dynamic range of 10 to 11 orders of magnitude, making them suitable for the multi-elemental analysis of $PM_{2.5}$ samples.

In this study, a method was developed for the measurement of 26 elements in $PM_{2.5}$ ambient air samples using an Agilent 7850 ICP-MS. The method was developed with reference to the China GB3095-2012 standard[8] and data was acquired to evaluate the sensitivity, accuracy, stability, and robustness of the 7850 ICP-MS method.

Experimental

Standards

Standards were prepared in 5% nitric acid (HNO_3), which was prepared by diluting 69% HNO_3 (BVIII grade, Beijing Institute of Chemical Reagents) with 18 MΩ de-ionized (DI) water.

Calibration standards, spikes, and the quality control (QC) standards were prepared from AccuStandard multi-element standards (New Haven, CT, USA). A single element standard was used for mercury (National Center of Analysis and Testing for Nonferrous Metals and Electronic Materials (Beijing, China).*Six point calibrations including the calibration blank were prepared in 5% HNO_3. Al, Mn, Fe, Cu, Zn, Ba were calibrated up to 500.0 µg/L (ppb), V, Cr, Co, Ni, As, Se, Sr, Mo, Sn, Sb, Pb up to 100.0 µg/L, Li, Be, Ag, Cd, Tl, Bi, Th, U up to 20.0 µg/L, and Hg up to 2.0 µg/L.

For the in-run QC, the initial calibration verification (ICV) and continuing calibration verification (CCV) standards were prepared at the same concentration as the midrange standard.

Sample and spike preparation

The $PM_{2.5}$ samples provided for the study had been collected in a city in Guangdong Province, China, using a quartz-membrane filter-based particle sampler. To prepare the sample and spiked sample, each sample filter was cut into four equal parts using ceramic scissors.

For sample preparation, two parts of the filter were accurately weighed into separate 50 mL centrifuge tubes. To extract the elemental content of the $PM_{2.5}$ into solution, 20 mL of electronic grade 5% HNO_3 was added to the tubes. The tubes were then ultrasonicated at 70 °C for 3 hours in a fume hood. To remove any undissolved particulate matter, the extracts were centrifuged. Once cooled, the extracts were shaken and then filtered through a 0.45 µm filter. The filtrates were diluted in DI water before analysis by ICP-MS.

To check the accuracy of the method, spiked samples and six reference filter samples were prepared using the same extraction preparation method as for the samples.

To prepare the spiked samples, the two remaining parts of the filter were accurately weighed into separate centrifuge tubes. 40 µL of the mixed standard stock solution containing elements at high, medium, or low concentrations and 80 µL of the Hg standard stock solution were then added to the respective sample tubes.

Six reference filter samples with known concentrations of Mn, Zn, Cd, and Pb were also prepared. The reference materials included TMZJ-LMHB-001-1, TMZJ-LMHB-001-2, GBW(E)080211, GBW(E)080212, AK-QC402-1, and AK-QC402-2. The GBW filters were from the Institute of Occupational Health and Poison Control, Chinese Center for Disease Control and Prevention (CDC) and the TM RMs were produced by Tanmo Quality Inspection Technology Co., Ltd (Beijing, China).

An Internal Standard (ISTD) solution containing Sc, Ge, Rh, In, Tb, Re (National Center of Analysis and Testing for Nonferrous Metals and Electronic Materials), and Li (SPEX CertiPrep, Metuchen, NJ, USA) was automatically added online via the ISTD kit for the 7850 ICP-MS.

Instrumentation

The 7850 ICP-MS, which includes the fourth generation ORS^4 collision/reaction cell (CRC), was used in this study. The ORS^4 is optimized for control of polyatomic spectral interferences on the analytes of interest using helium collision mode. The 7850 was fitted with the standard sample introduction system, comprising a MicroMist glass concentric nebulizer, quartz spray chamber, and quartz torch with 2.5 mm injector, and nickel sampling and skimmer cones.

Agilent multi-element, single element, and internal standard mixes are also available.

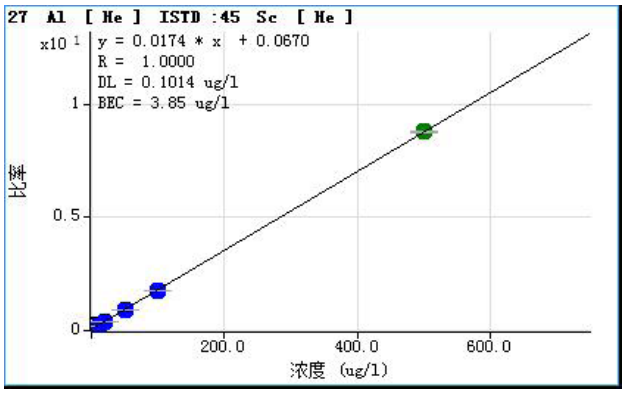
All elements except Li and Be were measured in He mode, which is the standard ORS[4] setting used on Agilent ICP-MS systems, as it can reliably remove the typical polyatomic (molecular) ion interferences on all common analytes using kinetic energy discrimination (KED).[9] The lens voltages were autotuned one time only and the same tune conditions were used for all elements. Instrument operating parameters are summarized in Table 1.

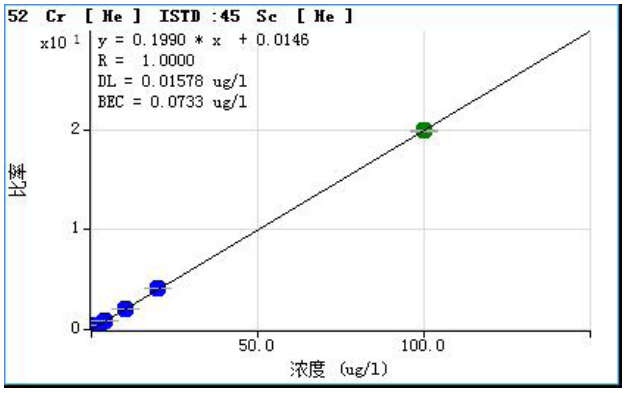
Table 1. Agilent 7850 ICP-MS operating conditions.

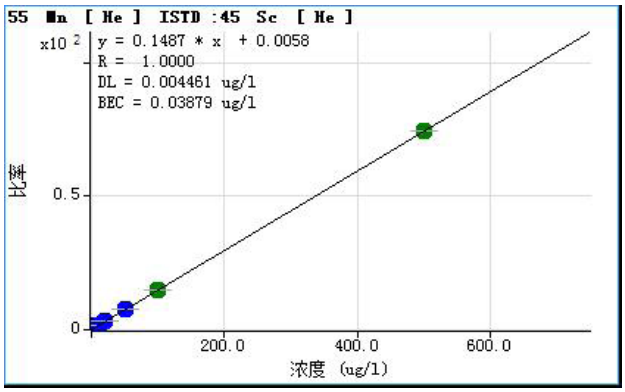
Parameters	No Gas	Helium
RF Power (W)	1550	
Spray Chamber Temp (°C)	2	
Sampling Depth (mm)	8.0	
Nebulizer Gas Flow (L/min)	0.70	
Make-up Gas (L/min)	0.50	
Extract 1 (V)	0	
Extract 2 (V)	−115	−130
He Gas Flow (mL/min)	0	4.3
KED (V)	3.0	
Analytes	Li, Be	Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Cd, Sn, Sb, Ba, Hg, Tl, Pb, Bi, Th, U

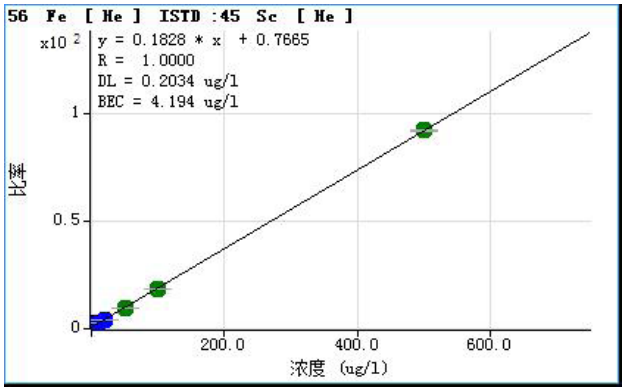
Results and discussion

Representative calibration curves are presented in Figure 1. The plots for Al, Cr, Mn, Fe, Zn, As, Cd, and Pb show excellent linearity across the calibrated range, with correlation coefficients of 1.0000.









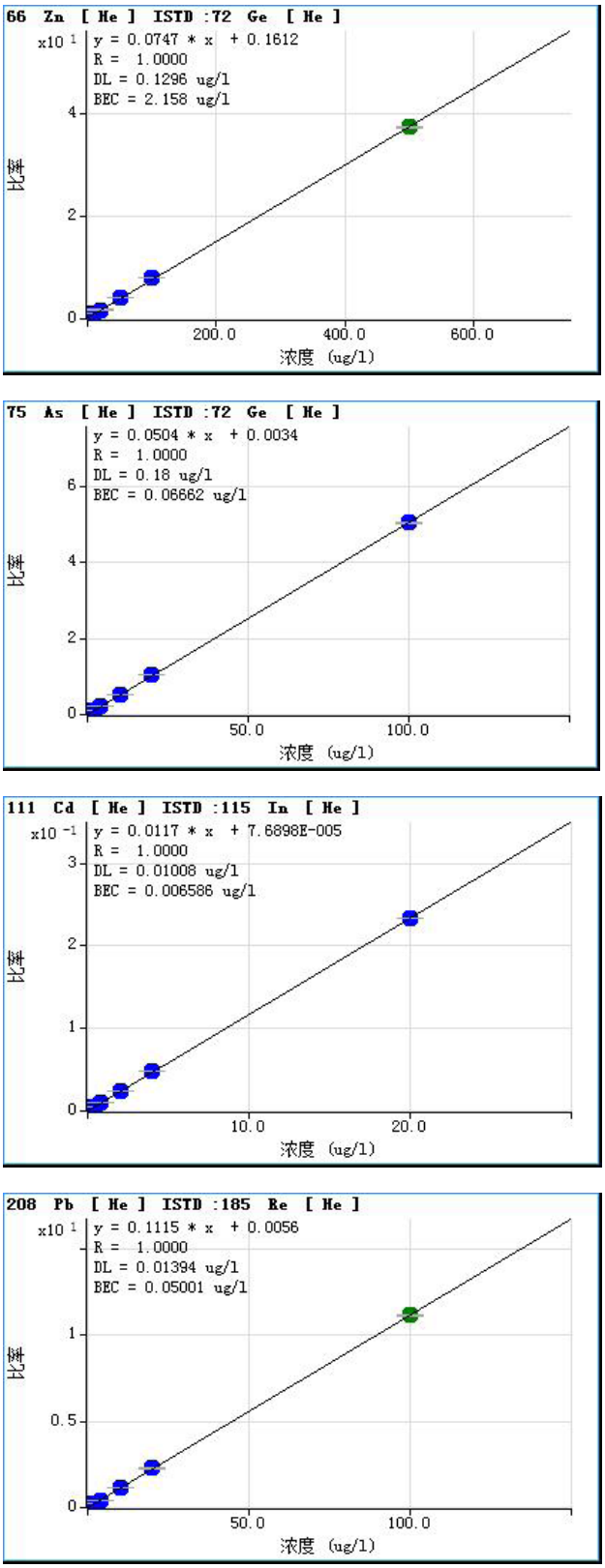


Figure 1. Representative calibration curves for major, minor, and trace elements.

Detection limits

The limits of detection (LOD) and Method Detection Limits (MDLs) reported in Table 2 are based on an air sampling volume of 144 m^3, sample preparation volume of 20.0 mL, and the amount of particulate matter on the membrane (average of 0.0100 g.) The MDLs for most elements were below 1 ng/m^3, with only Al, Fe, and Zn at 3 ng/m^3, confirming the sensitivity of the 7850 ICP-MS for the application.

Table 2. Detection limits.

	LOD	MDL	
Element	Solution Concentration µg/L	Particle Concentration* µg/kg	Air Concentration* ng/m^3
7 Li	0.1	8.00×10^2	0.06
9 Be	0.1	8.00×10^2	0.06
27 Al	5	4.00×10^4	3.0
51 V	0.2	1.60×10^3	0.12
52 Cr	1.25	1.00×10^4	0.70
55 Mn	0.5	4.00×10^3	0.3
56 Fe	5	4.00×10^4	3.0
59 Co	0.2	1.60×10^3	0.12
60 Ni	0.2	1.60×10^3	0.12
63 Cu	1	8.00×10^3	0.6
66 Zn	5	4.00×10^4	3.0
75 As	0.2	1.60×10^3	0.12
78 Se	0.5	4.00×10^3	0.3
88 Sr	0.1	8.00×10^2	0.06
98 Mo	0.1	8.00×10^2	0.06
107 Ag	0.1	8.00×10^2	0.06
111 Cd	0.05	4.00×10^2	0.03
120 Sn	0.1	8.00×10^2	0.06
121 Sb	0.2	1.60×10^3	0.12
137 Ba	1	8.00 × 103	0.6
202 Hg	0.01	80	0.006
205 Tl	0.005	40	0.003
208 Pb	0.2	1.60×10^3	0.12
209 Bi	0.1	8.00×10^2	0.06
232 Th	0.1	8.00×10^2	0.06
238 U	0.05	4.00×10^2	0.03

**Analysis conditions: the air sampling volume was 144 m^3 (standard state), the sample pretreatment volume was 20.0 mL, and the average amount of particulate matter on the membrane was calculated as 0.0100 g.*

Method accuracy

The filtrates obtained from the six reference filters were analyzed using the 7850 ICP-MS method, and the concentration and recoveries were calculated for each of the four analytes (Table 3). All elements gave recoveries within 100 ±10%, although the recovery for Mn in two of the filters was within 100 ±25%. The providers of the reference filters report the element concentration as mass per filter (piece).

Table 3. Recovery of certified values for Mn, Zn, Cd, and Pb in six reference filters. Concentration units µg/piece.

	TMZJ-LMHB-001-1			TMZJ-LMHB-001-2			GBW(E)080211		
Element	**Certified Conc**	**Measured Conc**	**Recovery (%)**	**Certified Conc**	**Measured Conc**	**Recovery (%)**	**Certified Conc**	**Measured Conc**	**Recovery (%)**
^{55}Mn	20	18.7	93.4	60	63.3	105.5	19	23.7	124.5
^{66}Zn	100	90.8	90.8	300	313.5	104.5	98	103.6	105.8
^{111}Cd	5	4.9	98.1	15	15.7	104.6	5.2	4.9	94.4
^{208}Pb	5	4.7	93.5	15	15.7	104.7	5.0	5.2	103.9
	GBW(E)080212			**AK-QC402-1**			**AK-QC402-2**		
Element	**Certified Conc**	**Mean Measured Conc**	**Recovery (%)**	**Certified Conc**	**Mean Measured Conc**	**Recovery (%)**	**Certified Conc**	**Mean Measured Conc**	**Recovery (%)**
^{55}Mn	59	70.2	119.1	25.6	25.2	98.3	75.7	72.7	96.0
^{66}Zn	302	317.2	105.0	74.0	78.1	105.5	224.2	212.2	94.6
^{111}Cd	16.2	16.7	103.1	7.6	7.7	101.7	22.9	22.3	97.4
^{208}Pb	15.4	15.8	102.6	5.1	5.1	99.4	15.5	14.4	92.7

A spike recovery test was carried out to check the recovery and accuracy of the 7850 ICP-MS method for the measurement of 26 elements in the blank and four $PM_{2.5}$ filter extract samples.

The filter samples were spiked at a low, medium, or high concentration level, depending on the quantitative elemental concentration in the unspiked (native) sample extract. The recoveries for all elements in the spiked samples were within ±20%, as shown in Table 4.

Table 4. Quantitative results (unspiked concentrations) and spike recovery for the blank and four $PM_{2.5}$ filter extract samples.

	Method Blank		Spike Level (µg/L)	Sample 1		Sample 2		Sample 3		Sample 4	
Element	Method Blank Conc (µg/L)	Recovery Spike (%)		Unspiked Conc (µg/L)	Recovery Spike (%)	Unspiked Conc (µg/L)	Recovery Spike (%)	Unspiked Conc (µg/L)	Recovery Spike (%)	Unspiked Conc (µg/L)	Recovery Spike (%)
7 Li	<DL	94.9	4	<DL	98.1	0.4512	83.5	0.6332	88.7	0.2382	99.0
9 Bi	<DL	95.9	4	<DL	98.1	<DL	91.7	<DL	95.8	<DL	94.8
27 Al	42.05	100.5	100	231.5	101.9	239.2	100.2	214.0	105.4	293.2	88.4
51 V	<DL	96.3	20	0.4943	101.3	1.365	99.4	0.4957	100.4	0.6720	95.4
52 Cr	1.605	94.2	20	2.916	98.9	4.005	96.8	3.050	97.8	2.868	92.5
55 Mn	0.5942	94.7	100	19.75	102.0	27.7	100.1	18.69	99.4	16.24	92.5
56 Fe	16.87	98.8	100	317.1	116.4	368.9	108.4	293.6	115.9	365.6	92.5
59 Co	<DL	94.7	20	0.2147	99.5	<DL	97.2	0.2315	97.7	0.2453	94.0
60 Ni	0.8571	98.1	20	1.214	103.6	1.759	101.4	1.548	101.8	1.527	97.4
63 Cu	1.141	101.0	100	7.427	106.9	10.17	103.2	13.04	104.4	8.299	102.0
66 Zn	<DL	98.7	100	58.57	102.4	161.4	99.9	70.55	101.0	50.72	95.4
75 As	<DL	94.6	20	2.154	99.6	9.337	96.9	16.24	99.4	4.775	94.2
78 Se	<DL	88.9	20	0.9980	95.4	2.914	91.1	2.630	93.7	1.531	90.4
88 Sr	0.6690	89.7	20	3.819	94.8	3.324	92.7	3.403	97.1	5.621	89.1
98 Mo	0.3738	89.6	20	0.6135	103.0	0.9891	98.2	0.7070	98.2	0.6656	91.6
107 Ag	<DL	96.0	4	<DL	102.4	0.1605	99.4	0.1624	100.4	0.1171	95.7
111 Cd	<DL	98.0	4	0.8119	103.6	2.270	100.9	2.519	102.1	1.296	95.8
120 Sn	<DL	94.6	20	1.364	107.2	3.228	99.6	4.059	100.2	1.635	94.7
121 Sb	<DL	92.9	20	3.048	104.2	3.437	99.8	5.579	100.3	2.225	92.7
137 Ba	2.762	95.9	100	13.52	99.8	24.47	95.7	14.24	97.8	18.29	93.2
202 Hg	<DL	86.4	0.4	0.0319	94.0	0.0521	88.6	0.0566	89.8	0.0330	88.8
205 Tl	<DL	97.9	0.4	0.2331	104.0	0.5566	98.5	0.4834	101.4	0.3116	99.7
208 Pb	0.6733	98.1	20	13.58	105.2	43.83	98.6	47.84	102.2	19.57	100.2
209 Bi	<DL	93.1	4	0.4515	100.3	1.875	97.3	3.332	99.0	1.783	95.7
232 Th	<DL	90.5	4	0.1493	106.3	0.1804	99.5	0.1354	98.3	0.1520	93.8
238 U	<DL	96.8	4	0.0539	103.5	0.0614	99.4	0.0528	100.8	0.0552	98.7

Long-term stability

To demonstrate the robustness of the 7850 ICP-MS, more than 80 $PM_{2.5}$ samples were analyzed over five hours. The recoveries of the ISTD elements remained within the QC limits of 80–120% throughout the run, with no mass-dependent drift (Figure 2). The ISTD plot also shows that the 7850 provides excellent control of signal suppression, with ISTD signals being consistent for elements covering a range of masses and ionization potentials. The results show the long-term robustness and high matrix tolerance of the 7850 ICP-MS for the application.

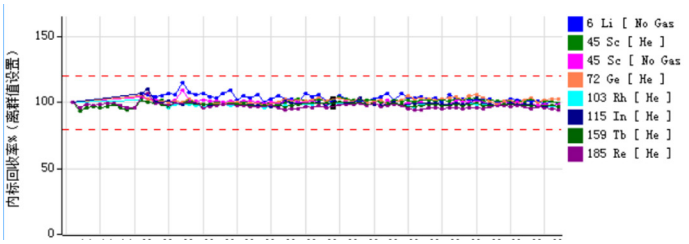


Figure 2. ISTD stability of more than 80 samples measured using the Agilent 7850 ICP-MS. ISTD recoveries were normalized to the calibration blank for all samples.

The CCV solution was measured after every 10 samples. All the CCV recoveries were within ±10% (Figure 3), confirming the excellent matrix tolerance and stability of the 7850 ICP-MS.

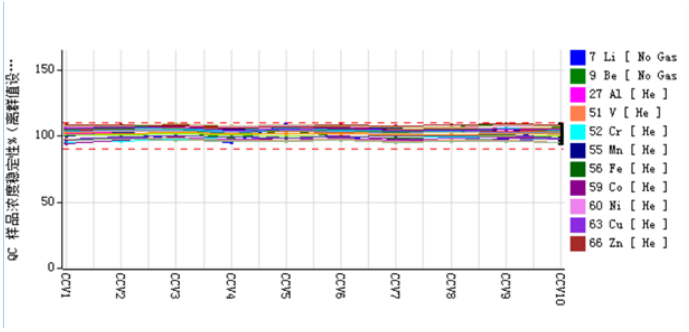


Figure 3. CCV stability over the five-hour sequence. All CCV recoveries were within ±10%.

Conclusion

The study has shown the suitability of the Agilent 7850 ICP-MS for the quantification of 26 elements in $PM_{2.5}$ samples collected from a city in Guangdong Province using a quartz-membrane filter-based particle sampler.

The high sensitivity, wide dynamic range, and control of interferences using the ORS[4] in He-KED mode for most elements was confirmed by the reported detection limits and excellent recoveries of certified elements in six reference filter papers. Recoveries within 100 ±20% from the spike recovery test for all 26 elements in the blank and four samples provided further assurance of the accuracy of the method.

The stability of the internal standards and QC sample over five hours demonstrated the robustness and high matrix tolerance of the 7850 ICP-MS. Instrument stability is important for the productivity of routine, high throughput applications that are typical of environmental testing applications as it reduces drift, QC failures, sample reanalysis, and maintenance.

The data generated by the 7850 ICP-MS method can provide regulatory agencies and researchers with a better understanding of the elemental content of $PM_{2.5}$. This information would help assess the impact of poor air quality on health, as well as providing monitoring data on the elemental content of $PM_{2.5}$ over time.

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