Application Note

Materials Testing and Research

Agilent

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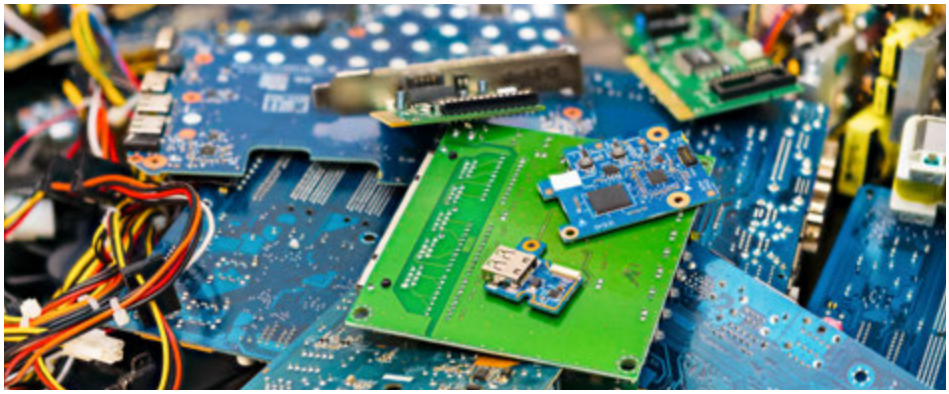
Enhanced RoHS Compliance Testing with Agilent 5800 ICP-OES

Accurate measurement of multiple elements including Cd, Cr, Pb, and Hg in plastic materials



Authors

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Introduction

The volume of waste electrical and electronic equipment (WEEE) is one of the fastest-growing waste streams worldwide. Over 62 million tonnes was generated globally in 2024.[1] However, only a small fraction of this waste is properly recycled, contributing to environmental pollution and the loss of valuable materials. To address this issue and to improve the safety of electrical and electronic equipment (EEE), the EU first introduced the Restriction of Hazardous Substances (RoHS) directive in 2003.[2] By restricting the use of specific hazardous materials such as lead, mercury, cadmium, hexavalent chromium, and certain flame retardants, RoHS helps ensure that products are safer for both consumers and the environment.[3] As the design, type, and production of EEE evolve, ensuring compliance with RoHS regulations becomes increasingly challenging for manufacturers, importers, and distributors. Plastics, such as polyethylene (PE), polycarbonate, polystyrene, polyethylene terephthalate (PET), polyvinylchlorate (PVC), and acrylonitrile butadiene styrene (ABS), are often used in EEE because of their unique properties and cost-effectiveness.[4] Manufacturers must rigorously test these materials using advanced analytical techniques to detect and quantify restricted substances,

ensuring compliance with the stringent limits set by the directive. Among these techniques, Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) is one of the most effective tools for analyzing elements in plastics in accordance with RoHS regulations.[5]

This application note describes a RoHS-compliant testing method for the multi-elemental analysis of plastics using an Agilent 5800 Vertical Dual View (VDV) ICP-OES. The methodology includes detailed procedures for sample preparation of a PE Certified Reference Material (CRM) and two real-life plastic materials used in EEE, instrument parameters, and performance evaluation. Quantitative results for arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg), tin (Sn), antimony (Sb), sulfur (S), and zinc (Zn) are presented. The data set demonstrates the suitability of the method for supporting manufacturers in achieving RoHS compliance with a high level of efficiency and accuracy.

Experimental

Instrumentation

The Agilent 5800 VDV ICP-OES was used for the elemental analysis of plastics. The instrument was equipped with a SeaSpray glass concentric nebulizer, double-pass cyclonic spray chamber, and an Easy-fit semi-demountable torch with 1.8 mm id quartz injector. Sample introduction was performed using an Agilent SPS 4 autosampler. The instrument and method were controlled and optimized using Agilent ICP Expert software version 7.7 (Pro version), which was also used to process the analytical data.

A robust and stable plasma is needed for long analytical runs of complex sample matrices. To achieve a high level of performance for routine analyses, the 5800 VDV ICP-OES uses a vertical plasma configuration, a solid-state radio frequency (SSRF) generator operating at 27 MHz, and a Cooled Cone Interface (CCI). The CCI deflects the cooler tail of the plasma, preventing interferences that typically form in this region and enabling trace elements to be measured in axial view mode.

The instrument operating conditions were optimized as detailed in Table 1. The total analysis time for one sample varied between 68 and 125 s, depending on the rinse time of between 3 and 60 s applied using the Intelligent Rinse software. To correct for ionization suppression or enhancement of the emission signals in the plasma, an internal standard (IS) solution was added online.

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

Parameter	Setting
Nebulizer Gas (L/min)	0.65
Pump Speed (rpm)	12
Read Time (s)	10
Uptake Time (s)	15
Stabilization Time (s)	10
Rinse Time (s)	3 to 60
Replicates	3
RF Power (kW)	1.3
Aux Flow (L/min)	1.0
Plasma Flow (L/min)	12
Sample Pump Tubing	White/white
Waste Pump Tubing	Blue/blue
Internal Standard Pump Tubing	Orange/green
Intelligent Rinse	Quick

Reagents and standards

High-purity concentrated nitric acid (HNO_3, 69%) and hydrochloric acid (HCl, 30%) were bought from Kanto Chemical, Japan. De-ionized (DI) water was produced by a Milli-Q purification system (Merck Millipore, Germany). Calibration standards were prepared from Agilent multi-elemental standard 2A, which includes As, Cd, Cr, Hg, Pb, and Zn, and single element standard solutions of S, Sn, and Sb were used. Table 2 lists the calibration concentration range that was used for each analyte.

Table 2. Calibration standard concentration range for each analyte.

Analytes	Calibration Concentration (mg/L)
As, Cd, Pb, Cr, Sb	0, 0.05, 0.1, 0.5, 1
Hg	0, 0.01, 0.02, 0.05, 0.1
Zn	0, 1, 5, 10, 50, 100
S, Sn	0, 0.05, 0.1, 0.5, 1, 5

To monitor the stability of the instrument, continuing calibration verification (CCV) solutions, equivalent to calibration level 3, were prepared separately and analyzed after every 10 samples. An IS solution containing Y at 5 mg/L was prepared from an Agilent 1000 ppm stock solution and introduced into the system online.

CRM, samples, and sample preparation

A European Reference Material, ERM-EC681 low density polyethylene (LDPE), bought from the Institute for Reference Materials and Measurements (IRMM), was used to validate the performance of the ICP-OES method. Two test samples

manufactured for real-life electronic consumer products (sample A) and electric vehicles (sample B) were provided to our laboratory. Once all metal parts had been removed from the test samples, they were cut into small pieces ready for digestion.

Microwave digestion is a flexible and powerful tool that provides the highest probability of completely digesting complex materials such as plastics. A MARS 6 microwave digestion system (CEM Corporation, USA) was used in this study. First, 250 ± 0.1 mg of the sample or CRM was weighed into an iPrep vessel (CEM). The solid was then mixed with 10 mL of aqua regia (7.5 mL HCl + 2.5 mL HNO_3) and a single-stage heating program was applied (Table 3). The digests were diluted to 50 mL with DI water, providing clear and particle-free solutions.

Table 3. Microwave digestion procedure using the MARS 6 system.

Stage	Temperature (°C)	Ramp Time (min)	Hold Time (min)	Pressure (psi)	Power (W)
1	250	25	35	800	900 to 1050

Results and discussion

Intelligent Rinse

The Intelligent Rinse feature of the 5800 ICP-OES enables laboratories to enhance both the efficiency and accuracy of sample measurements.[6] Benefits of Intelligent Rinse for the analyst include:

- Adaptive rinse times: Intelligent Rinse adjusts the rinse duration based on the actual time required to rinse out each analyte in a sample. Adapting the rinse means shorter rinse times for samples with lower concentrations of analytes and longer times for those analytes with higher concentrations.
- Monitoring intensities: the software continuously monitors the intensities of nominated analyte wavelengths during the rinse period. It automatically ends the rinse when these intensities reach a user-specified threshold, ensuring thorough cleaning without over-rinsing.
- Increased throughput: by minimizing unnecessary rinse times, Intelligent Rinse significantly increases sample throughput, allowing more samples to be processed in less time.
- Simplified method setup: there is no need to predict the required rinse durations. The system automatically adjusts the rinse cycle, making the setup process easier and more efficient.
- Reduced operating costs: shorter rinse durations mean less consumption of reagents and argon, leading to lower operating costs over time.

The ICP Expert software defines three washout thresholds for Intelligent Rinse, including Quick, Moderate, and Thorough. Factors of 50, 25, and 5 multiplied by the standard deviation (SD) of 10 × 1s readings of the rinse before calibration were used as the thresholds of the three settings in the software, respectively. The software then monitored the intensities of the selected analyte wavelengths and automatically ended the rinse when these intensities reached the user-specified threshold for the chosen setting. So, in this study, rinse times varied from 3 s for the blank samples to 60 s for samples A and B. This approach provided a time saving of between 20 to 30% over the 7-hour long-term stability test, as well as reducing the consumption of gases and utilities used during the analysis. The adaptive rinse method ensures effective, efficient, and accurate rinsing tailored to the specific needs of each sample.

Method linearity

The calibration linearity and method sensitivity performance of each analyte at selected wavelengths are summarized in Table 4. Excellent linearity was achieved for all analytes in their respective working ranges, as demonstrated by the correlation coefficient (R) values close to 1. Representative calibration curves for the critical RoHS elements Cd, Cr, Pb, and Hg are shown in Figure 1.

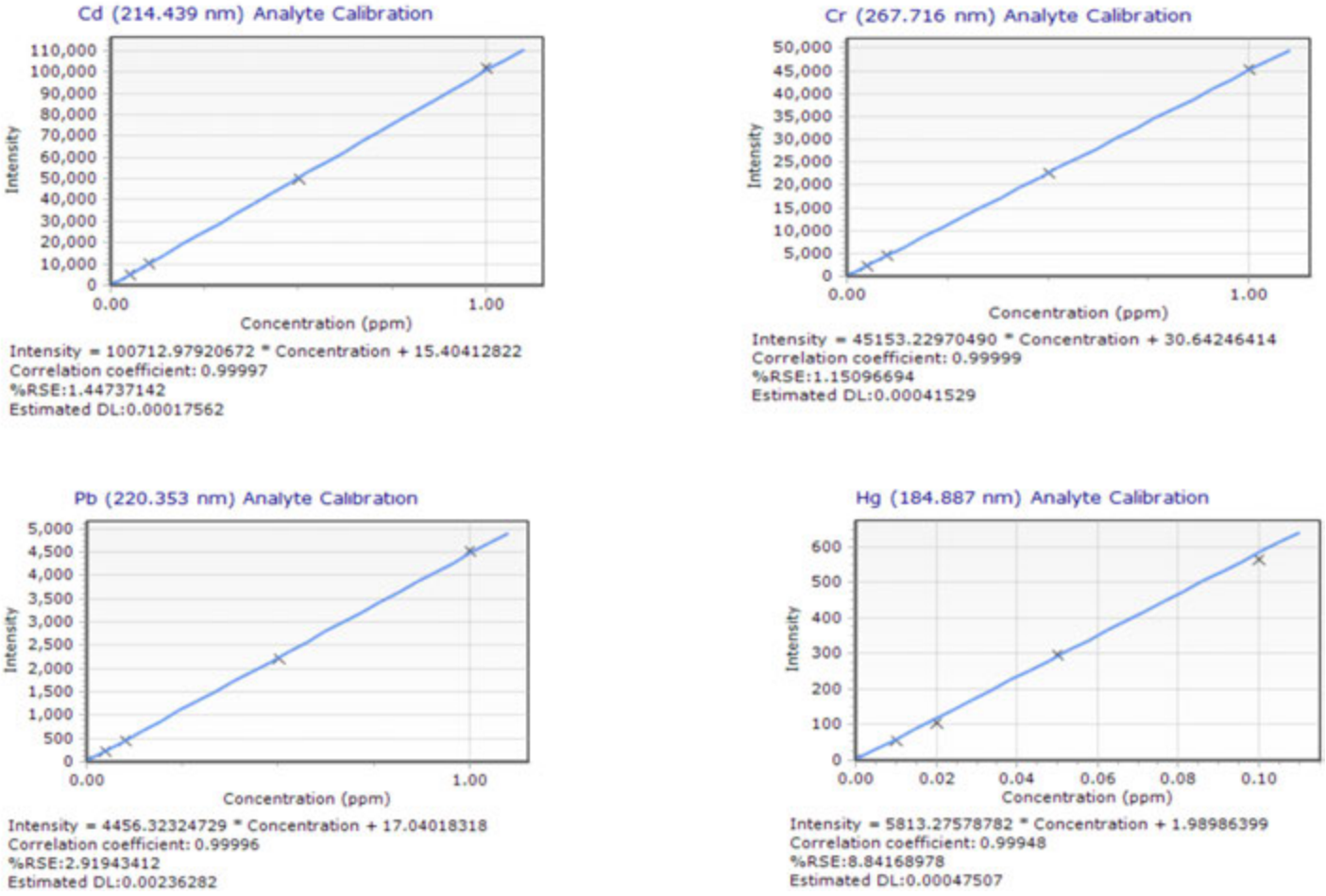

Figure 1. Representative calibration curves of Cd, Cr, Pb, and Hg.

Method sensitivity

The sensitivity of the method was evaluated using LODs, LOQs, and MDLs, as summarized in Table 4. The LODs and LOQs were calculated based on three sigma (3σ) and ten sigma (10σ) of eleven replicates of the blank, respectively. For the four critical RoHS-regulated elements—Cd, Cr, Pb, and Hg—the 5800 ICP-OES achieved LODs of 0.19, 0.30, 3.30, and 1.23 µg/L (ppb), respectively, demonstrating the sensitivity of the instrument.

MDLs, which consider the entire sample preparation process, including the dilution factor, are another important metric for evaluating method sensitivity. MDLs can vary depending on the sample preparation procedure and dilution factor.

In this study, MDLs were derived from the LOQ (10σ) multiplied by a dilution factor of 200. Excellent MDLs were achieved for all analytes, easily meeting the RoHS 3 (EU 2015/863) requirements for mandatory elements, even at 1/100 of the RoHS threshold.[7]

Table 4. Summary of calibration linearity and method sensitivity.

Analyte and Wavelength (nm)	Correlation Coefficient (R)	LOD (µg/L)	LOQ (µg/L)	MDL (mg/kg)	RoHS Requirements[7] (mg/L)
As 188.980	0.99992	2.37	7.92	1.58	-
Cd 214.439	0.99997	0.19	0.65	0.13	100
Cr 267.716	0.99999	0.30	1.01	0.20	1000*
Hg 184.887	0.99948	1.23	4.09	0.82	1000
Pb 220.353	0.99996	3.30	11.00	2.20	1000
S 181.972	0.99993	9.43	31.40	3.82	-
Sb 217.582	0.99985	4.70	15.70	6.28	-
Sn 189.925	0.99999	1.38	4.61	0.92	-
Zn 213.857	0.99994	0.26	0.87	0.17	-

** Based on hexavalent chromium*

CRM analysis – method accuracy

Duplicate digestions of the CRM (ERM-EC 681 polyethylene) were prepared and analyzed. The calculated mean concentration and recoveries for each analyte are summarized in Table 5. The measured concentrations of all certified analytes in ERM-EC 681 were well within the acceptable range, with excellent recoveries ranging from 97 to 106% for each certified element. These results confirm the outstanding accuracy of the 5800 VDV ICP-OES method for analyzing multiple elements, including the heavy metals Cd, Cr, Pb, and Hg in a CRM plastic material that is commonly used in the production of EEE.

Table 5. Analytical results of the measurement of the CRM (ERM-EC 681 polyethylene) using the Agilent 5800 VDV ICP-OES.

	CRM (ERM-EC 681, polyethylene)			
Analyte and Wavelength (nm)	Certified Value (mg/kg)	Acceptable Range (mg/kg)	Mean Measured Value (mg/kg)	Recovery (%)
As 188.980	17	15.8 – 18.2	17.1	101
Cd 214.439	146	141 – 151	150	103
Cr 267.716	45.1	43.2 – 47.0	45.9	102
Hg 184.887	9.9	9.1 – 10.7	10.5	106
Pb 220.353	69.7	67.2 – 72.2	68.4	98
S 181.972	640	540 – 740	627	98
Sb 217.582	86	79 – 93	91.4	106
Sn 189.925	99	93 – 105	103	104
Zn 213.857	1170	1130 – 1210	1134	97

Sample analysis – spike recovery and precision

Spike recovery tests in a sample matrix are an effective way to evaluate the reliability of the sample preparation and/or analytical methods, especially when suitable CRMs are unavailable. In this study, in addition to the analysis of the CRM, two real-life samples (A and B) were analyzed using the 5800 VDV ICP-OES. The measured concentrations of the analytes and spike recovery results are shown in Table 6. The spike recoveries for all analytes were within 94 to 108%, except for Sn in sample A, which had a spike recovery of 88%. This lower recovery could be due to the high measured concentration of Sn in sample A. However, the recovery of Sn in the CRM was 104%, assuring the method's accuracy. The %RSD of the spike recovery measurements (n=3) was used to evaluate the method's precision. As shown in Table 6, the spike recovery RSDs were ≤2.3% for all nine analytes in both samples A and B. This method validation data confirms the effectiveness of the microwave digestion sample preparation procedure for these materials. The results also demonstrate the excellent reproducibility and reliability of the 5800 VDV ICP-OES method for the analysis of complex plastic matrices.

Table 6. Real-life sample analysis results acquired for two plastic materials using the Agilent 5800 VDV ICP-OES.

Analyte and Wavelength (nm)	Spike Conc (mg/kg)	Sample A				Sample B			
		Measured Conc (mg/kg)	Measured Conc in Spiked Sample A (mg/kg)	Spike Recovery (%)	RSD of Spike Recovery (%)	Measured Conc (mg/kg)	Measured Conc in Spiked Sample B (mg/kg)	Spike Recovery (%)	RSD of Spike Recovery (%)
As 188.980	40	<MDL	43.2	108	2.2	<MDL	42	105	1.4
Cd 214.439	40	<MDL	42	105	1.3	<MDL	40	100	0.8
Cr 267.716	40	4	46	105	1.7	4	44	100	0.6
Hg 184.887	7	<MDL	6.52	93	2.3	<MDL	6.89	98	1.4
Pb 220.353	40	8	50	105	1.2	12	50	95	0.4
S 181.972	40	24	66	105	0.4	74	116	105	1.0
Sb 217.582	40	<MDL	40	100	0.7	<MDL	42	105	1.6
Sn 189.925	200	582	758	88	1.4	60	262	101	0.4
Zn 206.200*	2.5	5.3	7.66	94	2.2	5.36	7.8	98	2.1

*The concentration unit for Zn is %

Long-term stability evaluation

The long-term stability of the 5800 VDV ICP-OES was evaluated based on recoveries of the CCV and ISs. The CCV was measured after every 10 unspiked samples (including test samples A and B) over seven hours without recalibration. Recoveries and recovery precision (%RSDs) of all analytes for all 16 CCV measurements were calculated and presented as a stability plot. As shown in Figure 2, recoveries of 100 ±10% were obtained for each analyte, with %RSDs for all wavelengths below 1.4%. These results demonstrate the stability of the instrument over a continuous matrix analysis sequence of more than seven hours.

IS recoveries were also monitored to assess the long-term stability of the 5800 VDV ICP-OES. Yttrium at 5 mg/L was continuously introduced into the instrument, and its recovery was automatically captured by the ICP Expert software. Figure 3 shows IS recoveries within 100 ±7% across the batch analysis of the CRM and real-life samples, well within the generally acceptable range for IS recovery of 100 ±20%. The results are due to the excellent robustness and matrix tolerance of the instrument.

These stability tests confirm the suitability of the method for long analytical runs of complex-sample matrices commonly found in routine testing laboratories.

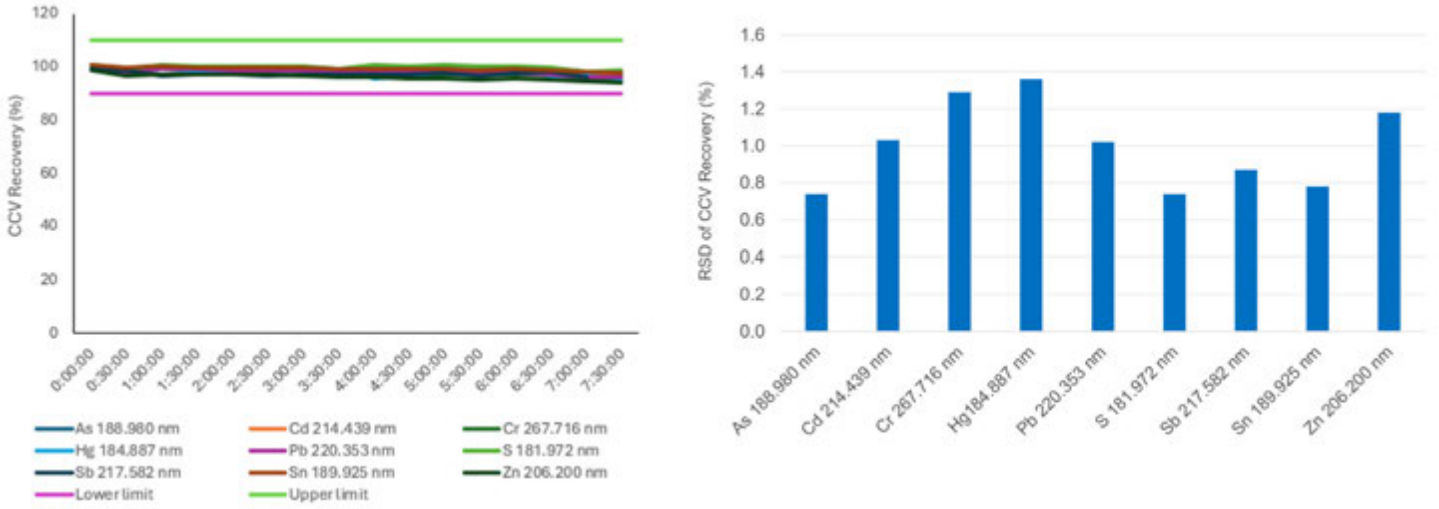

Figure 2. CCV recoveries (left) and recovery %RSD (right) over more than seven hours of continuous measurement of real-life EEE test samples A and B using the Agilent 5800 VDV ICP-OES.

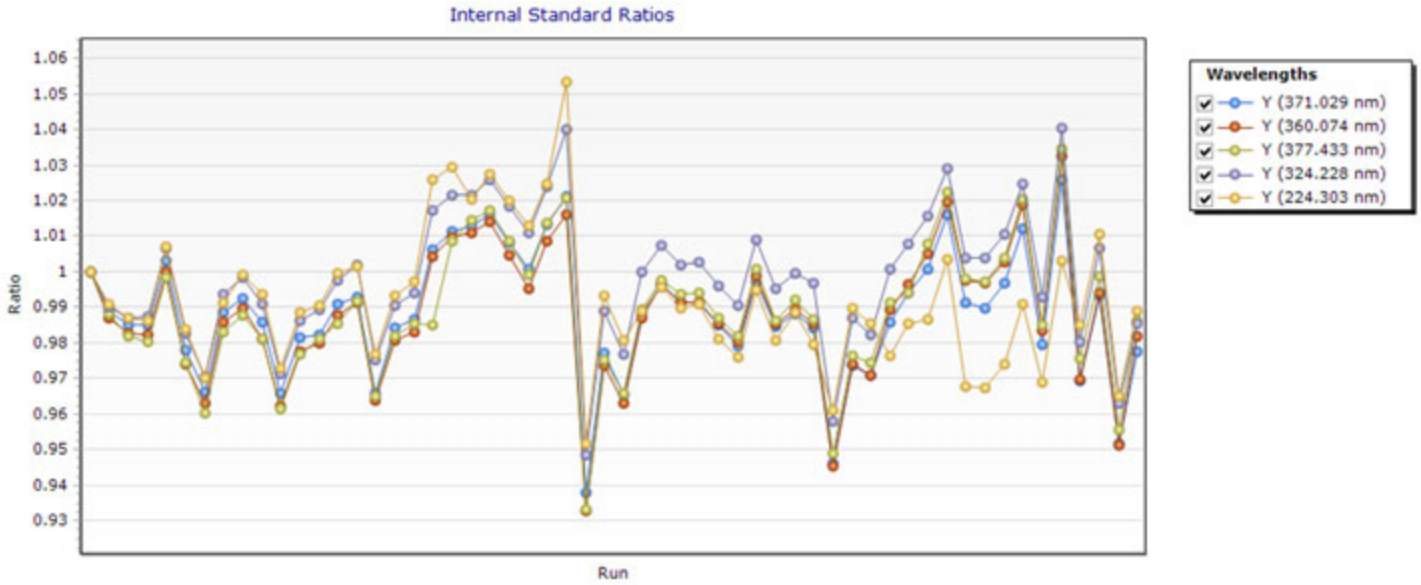

Figure 3. IS stability throughout the batch analysis of the CRM and real-life EEE samples using the Agilent 5800 VDV ICP-OES.

Conclusion

The Agilent 5800 VDV ICP-OES was used for the quantitative analysis of nine elements including RoHS-specified elements, Cd, Cr, Pb, and Hg, in plastics that are typically used in electrical and electronic equipment (EEE). The samples included a plastic-based CRM (ERM-EC 681, polyethylene) and two real-life plastic matrices used in consumer electronics and electric vehicles. A one-stage microwave digestion sample preparation procedure ensured the complete digestion of these tough thermoplastic materials, facilitating accurate analysis by ICP-OES.

The 5800 ICP-OES demonstrated outstanding sensitivity, accuracy, and stability, making it a reliable solution for EEE manufacturers required to comply with RoHS or equivalent testing standards. The Intelligent Rinse software feature of Agilent ICP Expert Pro streamlined operations by automatically adjusting rinse times based on user-defined thresholds, saving time and resources, and lowering the overall costs of analysis. This study highlights the 5800 ICP-OES instrument's capability to deliver precise and consistent results, supporting the industry's need for rigorous and reliable RoHS compliance testing.

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7. RoHS 3 (EU Directive 2015/863), https://www.rohsguide.com/rohs3.htm (accessed March 2025)

Agilent part numbers

G8020-68005	Easy-fit fully demountable torch with 1.8 mm quartz injector for Agilent 5000 series ICP-OES
G8010-60256	Double-pass spray chamber, glass cyclonic design with ball joint socket and UniFit drain outlet, for Agilent 5000 series ICP-OES
G8010-60255	SeaSpray concentric glass nebulizer for Agilent 5000 series ICP-OES
3710034400	Peristaltic pump tubing, PVC, white/white, 12/pk
3710034600	Peristaltic pump tubing, PVC, blue/blue, 12/pk
3710068300	Peristaltic pump tubing, PVC, orange/green, 12/pk
1610132400	Y-piece connector for online addition of internal standard/ionization buffer
8500- 6940	Multi-element calibration standard-2A
5190-8530	Agilent 1000 ppm single element stock solution for S
5190-8243	Agilent 1000 ppm single element stock solution for Sn
5190-8245	Agilent 1000 ppm single element stock solution for Sb
5190-8256	Agilent 1000 ppm single element stock solution for Y

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