

Challenge

Determination of precious metals in electronic waste

Solution

HR ICP-OES with exceptional sensitivity and industry leading high-resolution optical system for interference-free detection of precious metals

Intended audience

Electronic waste recycling companies in the waste management and heavy industry

Precious Metal Analysis in Electronic Waste by HR ICP-OES

Introduction

Precious metal recycling in electronic waste involves recovering valuable metals like gold, silver, platinum, and palladium from discarded electronic devices. This process helps to reduce electronic waste and conserve natural resources while also providing a sustainable source of precious metals. Electronic waste is a rapidly growing global problem due to the increasing use of electronic devices and their short life cycles. However, e-waste also represents a significant opportunity for recycling precious metals, which are often used in electronic components due to their excellent conductivity, durability, and resistance to corrosion. The recycling of precious metals from e-waste is an important aspect of sustainable development as it reduces the environmental impact of mining and conserves natural resources. Additionally, it also provides a secure and sustainable source of these precious metals, which are essential for the production of new electronic devices. However, precious metal recycling from e-waste requires specialized equipment and expertise to extract the metals safely and efficiently. Therefore, it is essential to work with

certified e-waste recycling companies that adhere to best practices for handling and processing e-waste, ensuring the safe recovery of precious metals while protecting human health and the environment. The recycling process involves collecting and sorting the e-waste, then using various techniques such as chemical leaching, smelting, and electrolysis to recover the precious metals. The environmental footprint of these technologies can vary depending on the specific method used, the type and quantity of materials being processed, and the energy source used. Chemical leaching, for instance, involves the use of chemicals such as acids and cyanide to dissolve the precious metals from electronic waste. While the process is effective, it can generate toxic waste products and harm the environment if not handled and disposed properly. Smelting involves heating and melting the materials to extract the precious metals. The process requires a significant amount of energy and can generate emissions of greenhouse gases and other pollutants if fossil fuels are used as the energy source. Electrolysis involves the use of an electric current

to extract the precious metals. The process requires a substantial amount of electricity, and if the energy source is not renewable, it can result in significant greenhouse gas emissions and other environmental impacts.

In order to reduce the environmental impact of these precious metal recycling processes, it is important to use intelligent methods for processing the recyclate and measuring equipment that can detect even the finest traces of precious metals. This guarantees a moderate use of environmentally harmful chemicals in combination with a maximum recycling rate.

From a technical point of view, ICP-OES technology is particularly suitable for detecting exact precious metal

concentrations in the metal compound of the recyclate.

While many ICP-OES analyzers easily deal with base metal determination, their limited sensitivity and severe spectral interferences from the complex matrix often impair the detection of precious metals. The robust plasma of the PlasmaQuant 9100 Elite can effortlessly tolerate metallurgical samples and offers long-term stability.

For this application note, a finely ground electronic waste sample was submitted to the analysis of Ag, Au, Pd, and Pt by high-resolution (HR) ICP-OES on PlasmaQuant 9100 Elite equipped with a HF-Kit after microwave assisted digestion in a mixture of HNO₃, HCl, and HF.

Materials and Methods

Sample preparation

All laboratory equipment was washed with deionized (DI) water from a PURELAB system (18.2 MΩ-cm, ELGA LabWater, High Wycombe, England). Chemicals were of analytical reagent grade.

Approximately 0.25 g of a finely ground electronic waste sample was accurately weighed (0.0001 g) into a digestion vessel (DAK-100). Afterwards, 2 mL HNO₃, 6 mL HCl, and 2 mL HF were added. The mixture was swirled carefully and left standing for at least 15 minutes before the vessel was closed. Subsequent heating was performed stepwise (160 °C for 5 min, 190 °C for 5 min, 210 °C for 5 min; 230 °C for 30 min) in a speedwave XPERT microwave digestion system. Afterwards the vessels were allowed to cool to room temperature to avoid foaming and splashing. 10 mL of a saturated H₃BO₃ solution were added and the complexation of free HF was carried out at a temperature of 190 °C. The solutions were transferred to a graduated polypropylene tube, diluted to 50 mL with DI water, and centrifuged (1125xg, 10 min). The supernatants were directly submitted to the analysis.

Calibration

All multi-element stock solutions were made up using single element standard solutions (Merck, Sigma-Aldrich). The working standards were prepared by serial volume/volume dilution in polypropylene tubes of the stock solutions using an acidic mixture of 4% (v/v) HNO₃, 12% (v/v) HCl, 4% (v/v) HF, and 20% (v/v) H₃BO₃. Calibration levels for each element were chosen based on the expected concentration ranges. Three calibration standards were used for each element, as described in Table 1. Selected calibration curves are shown in Figure 1.

Calibration standards were prepared from the same acid mixture and robustness was tested from multiple emission lines per element and a spike recovery test. Contents of about 1200 (Ag), 80 (Au), 10 (Pd) and 1 mg/kg (Pt) were consistently found from two lines per element and matrix-specific detection limits of 14 µg/kg (Ag), 60 µg/kg (Au), 100 µg/kg (Pd) and 140 µg/kg (Pt) were achieved.

Table 1: Concentration of calibration standards

Element	Unit	Cal. 0	Std. 1	Std. 2	Std. 3
Ag, Au, Pd, Pt	mg/L	0	0.1	1	10

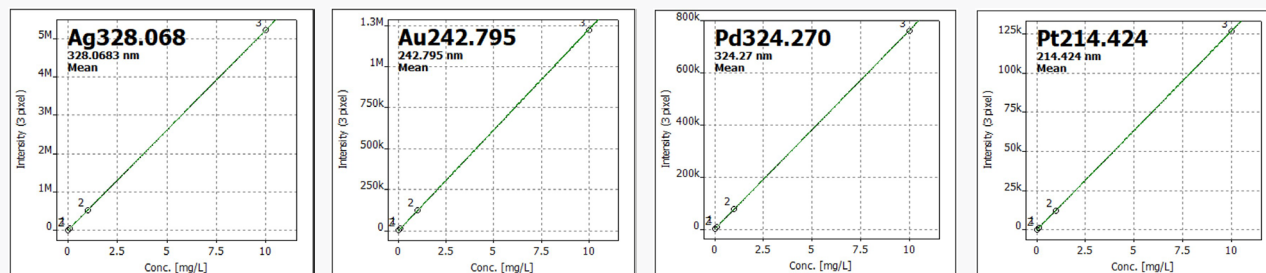


Figure 1: Selected calibration curves

Instrument settings

The analysis was performed on a PlasmaQuant 9100 Elite ICP-OES, equipped with the HF-kit. The sample introduction components were selected to achieve a high level of sensitivity for trace elements in high matrix samples while being resistant to hydrofluoric acid. In conjunction with this instrument, a Teledyne CETAC ASX-560 Autosampler was used. A summary of individual settings and components is given in Table 2.

Table 2: Instrument settings

Parameter	Specification
Plasma power	1,200 W
Plasma gas flow	12 L/min
Auxiliary gas flow	0.5 L/min
Nebulizer gas flow	0.7 L/min
Nebulizer	Parallel path nebulizer, 1.0 mL/min, PFA
Spray chamber	Cyclonic spray chamber, 50 mL, PTFE
Outer tube/Inner tube	Syalon/Alumina
Injector	Alumina, ID: 2 mm
Sample tubing	PVC (black/black)
Pump rate	1.00 mL/min
Fast pump	4.00 mL/min
Measuring delay/Rinse time	45 s/45 s
Torch position	0 mm

Method and evaluation parameters

Method parameters are shown in Table 3.

Table 3: Method parameters

Element	Line [nm]	Plasma view	Integration	Read time [s]	Evaluation		
					Pixel	Baseline fit	Correction
Ag	328.0683	axial	Peak	10	3	ABC ¹	-
Ag	338.2891	axial	Peak	10	3	ABC	-
Au	197.7440	axial	Peak	10	3	ABC	-
Au	242.7950	axial	Peak	10	3	static	CSI ²
Pd	324.2700	axial	Peak	10	3	static	-
Pd	360.9550	axial	Peak	10	3	static	-
Pt	214.4240	axial	Peak	10	3	static	-
Pt	265.9450	axial	Peak	10	3	static	-

1 ... Automated Baseline Correction

2 ... Software tool for the correction of spectral interferences (see Figure 2 and 3)

Results and Discussion

It is well known that emission lines of copper, iron, and other metals and transition metals interfere with the analytical lines of certain elements. Especially, the determination of precious metals and PGMs (platinum group metals) is hampered in such matrices. Usually, matrix matching is recommended for the calibration to overcome these issues. For this purpose, pure standards or reference materials are needed that show minimum contamination for the elements to be determined. One possibility to overcome the application issues is to use high resolution instruments with the capability of separating spectral interferences from the desired analytical line. The here presented results clearly demonstrate the enormous application advantages originating from the high resolution (2 pm @ 200 nm) of the PlasmaQuant 9100 Elite system in comparison to instruments with lower resolution allowing for choosing appropriate and sensitive analysis lines for most of the elements. The plasma geometry and the efficient removal of the plasma tail using argon (recycled from optical system purge) as counter gas leads to the high sensitivity of the instrument.

Despite the high resolution of the system, the most sensitive emission line of gold at 242.795 nm cannot be sufficiently separated in the complex matrix of electronic waste. By superimposing the spectra of gold standard and sample, it becomes clear that the two spectra are not exactly at the same wavelength and that the shape of the emission spectra differs. This suggests that the sample spectrum is not just gold alone (see Figure 2). With the help of the software implemented spectra library, Mn at 242.794 nm could be identified as the interfering element.

High-resolution optics and a charge-coupled device (CCD) detector offer excellent spectral resolution, which permits interference-free measurement by well-separated lines. The CCD detector depicts emission line and background intensities concurrently; allowing an automatic background correction. Apart from Au 242, all emission lines used were interference-free thanks to the High-Resolution Optics of the PlasmaQuant 9100 Elite. Direct line overlap of Au 242 by manganese was corrected by the CSI software tool. Recovery rates for all metals were in the range between 95% and 110% and may be further improved by the use of an internal standard.

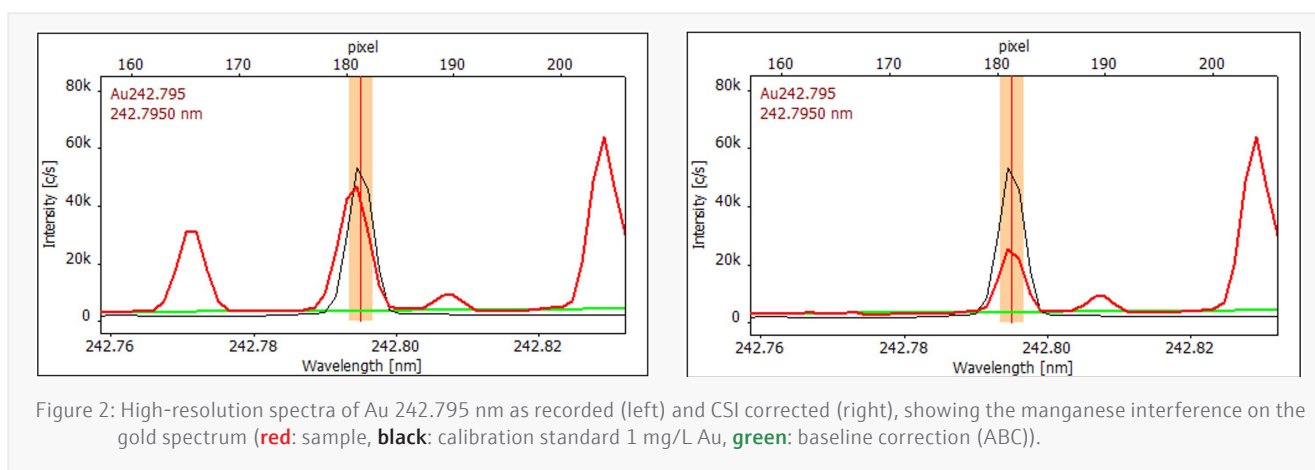


Figure 2: High-resolution spectra of Au 242.795 nm as recorded (left) and CSI corrected (right), showing the manganese interference on the gold spectrum (red: sample, black: calibration standard 1 mg/L Au, green: baseline correction (ABC)).

A spectral correction was performed with a spectrum of the pure interferent. The correction spectrum was obtained by measuring a diluted single-element manganese standard (e.g. 100 mg/L Mn) at the specific analytical line to be corrected. Figure 3 shows the correction spectrum and the correction model at 242.795 nm. By applying the CSI algorithm of spectral correction, this highly sensitive gold line becomes accessible for quantification.

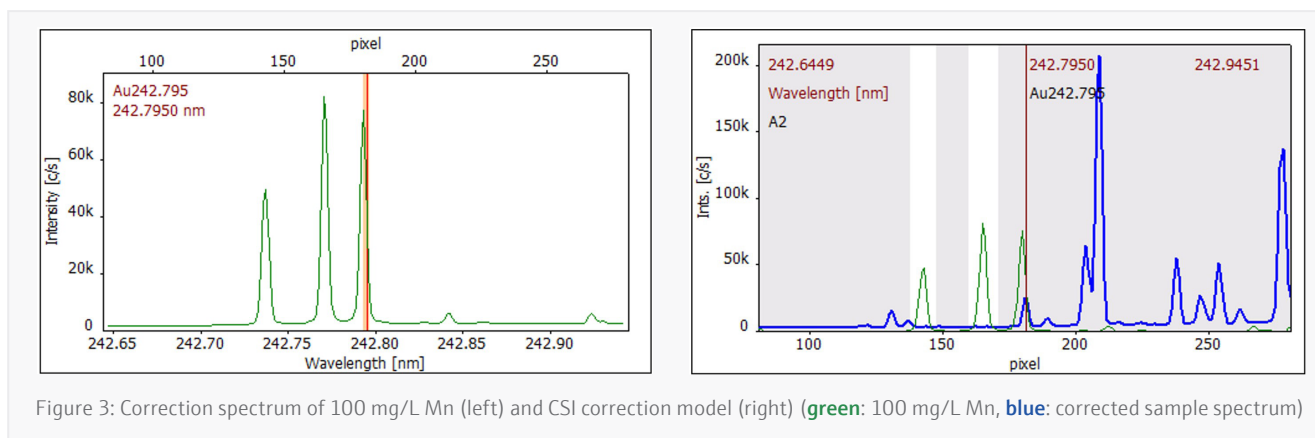


Figure 3: Correction spectrum of 100 mg/L Mn (left) and CSI correction model (right) (green: 100 mg/L Mn, blue: corrected sample spectrum)

All results are shown in Table 4. The detectability of low to sub $\mu\text{g/L}$ concentrations in the measurement solutions correspond to method limits of detection in the sub mg/kg range for all investigated elements. The accuracy of the method was verified by recovery measurements of 1 mg/L spikes in the measurement solution. As shown in the result table, all investigated elements show recovery values of 95 to 110%.

Table 4: Electronic waste sample

Element	Line [nm]	Mass fraction [mg/kg]	RSD ¹ [%]	LOD _{inst} ² [$\mu\text{g/L}$]	LOD _{meth} ³ [mg/kg]	Spike recovery [%]
Ag	328.068	1200	2	0.07	0.014	110
Ag	338.289	1250	1	0.08	0.016	110
Au	197.744	82.6	1	2.0	0.4	101
Au	242.795	84.3	0.8	0.3	0.06	104
Pd	324.270	9.5	0.7	0.8	0.16	102
Pd	360.955	7.6	1.5	0.5	0.10	103
Pt	214.424	1	6	0.7	0.14	96
Pt	265.945	(0.6) ⁴	(14) ⁴	1.2	0.24	95

1 ... Relative Standard Deviation values obtained from 3 replicate measurements per sample

2 ... instrumental limits of detection determined in the calibration blank

3 ... method limits of detection refers to 0.25 g sample in 50 mL

4 ... value is below limit of quantification of this emission line (LOQ = 3 x LOD), thus RSD value is affected by noise

Summary

In summary, the PlasmaQuant 9100 Elite is well suited for electronic waste applications. With its high resolution, high sensitivity, and advanced software-tools the determination of precious metals can be easily performed in such materials. The suitability of the system was demonstrated by using two different wavelengths per element and spike recovery tests.

Recommended device configuration

Table 5: Overview of devices, accessories, and consumables

Article	Article number	Description
PlasmaQuant 9100 Elite	818-09101-2	High resolution ICP-OES
speedwave XPERT	819-5005000-2	Microwave Pressure Digestion System



Figure 6: PlasmaQuant 9100 Elite

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