

Robust analysis of REE in electronic waste

High sample throughput with analysis times of less than 2 minutes per sample with the iCAP PRO Series ICP-OES

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Goal

To demonstrate the capability of the Thermo Scientific™ iCAP™ PRO Series ICP-OES in axial viewing mode for high throughput, robustness, and highly sensitive analysis of trace and ultra-trace amounts of rare earth elements (REE) and metals in electronic waste such as mobile phones.

Introduction

Rare earth elements (REEs) are 17 elements in the periodic table, out of which 15 belong to the lanthanide series, found in the second last row of the periodic table – lanthanum (La) to lutecium (Lu). The remaining two elements are scandium (Sc) and yttrium (Y), commonly included in REEs because of their close geological occurrence in ores along with the lanthanides. In nature, REEs can often also be found associated with thorium (Th), an element commonly included and reported in



REE studies. REEs, unlike their name might suggest, are not rare in nature but the ores from which they can be mined in an economically viable fashion are often hard to find. Nevertheless, REEs have important industrial applications: Ce, La, and Y in glass and metallurgy industries, Nd in permanent magnets, and Gd in medical image visualization, to name a just few, and this contributes to their high market demand and price. REEs are also used in various components of electronic devices such as in magnets, screens, etc.

High demand and limited resources of REEs in the world and the environmental impact of electronic waste (e-waste) enforce the development of sensitive, selective, and robust

analytical technology to detect and characterize these elements from e-waste and environmental samples, such as wastewaters. The amount of electronics production as well as generation of e-waste has increased significantly in the last decades due to accelerating technological advances. Thus, the recycling and management of waste electrical and electronic equipment (WEEE) is a growing problem. Old and discarded electronic waste is emerging as an important source for recovery of valuable REEs and other metals like Fe, Ni, Ag, and Au.

REEs are analyzed using techniques like inductively coupled plasma mass spectrometry (ICP-MS), ICP optical emission spectrometry (ICP-OES) and X-ray fluorescence.¹ ICP-MS is often the technique of choice for such analyses because of the high sensitivity and dynamic range of linearity achievable. ICP-OES is a suitable, low initial cost alternative for this kind of analyses. ICP-OES instruments are easy to operate, require low maintenance, and can provide high sample throughputs. With new age technology it is possible for ICP-OES techniques to deliver similar detection limits, high linearity range, and very good spectral resolution for REEs at much lower investments.

In the current application note, WEEEs in the form of mobile phone wastes have been inspected and analyzed for REEs and other metals using the robust and highly sensitive iCAP PRO series ICP-OES system, demonstrating the analytical capabilities of the instrument for this kind of important application.

Experimental conditions

A Thermo Scientific™ iCAP™ PRO XP ICP-OES Duo instrument in axial mode was used for the analyses of REEs and other recoverable metals in electronic waste in the current study. A standard sample introduction kit suitable for aqueous samples, consisting of a glass cyclonic spraychamber, standard glass nebulizer, quartz glass duo torch, and other components listed in Table 1, was used. Sample introduction was automated using a Teledyne™ CETAC™ Technologies ASX-560 Autosampler. The instrument parameters used during analysis are provided in Table 1.

Table 1. Instrument configuration and operating parameters

iCAP PRO XP Duo parameters	
Pump tubing	Sample Tygon™ orange/white Drain Tygon white/white
Spraychamber	Glass cyclonic
Nebulizer	Standard glass nebulizer
Center tube	1.5 mm (quartz)
Torch	Quartz Duo torch
Pump speed	45 rpm
Flush pump speed	100 rpm
Pump stabilization time	10 s
Wash time	20 s
Nebulizer gas flow	0.65 L·min ⁻¹
Auxiliary gas flow	0.5 L·min ⁻¹
Coolant gas flow	14.0 L·min ⁻¹
RF power	1300 W

Data acquisition and data processing

The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS™) Software was used to create LabBooks for sample analysis and to acquire, process, and report data.

Sample preparation

Thin-film transistor (TFT) screens, printed circuit boards (PCBs), and magnets in speakers and two mobile phones were selected as samples representing electronic mobile phone waste (Figure 1). Sample powders were prepared using a grinder; magnets were left whole. 1 to 2 g of sample material was digested overnight in concentrated acids (HCl:HNO₃ = 1:1); magnets were digested in aqua regia. Samples were filtered and final solutions contained 10% TraceMetal™ grade HCl and HNO₃ mixture. A solution mimicking the real samples was prepared for long term analysis experiments.

A set of calibration and linearity standards were prepared in 10% acid, using certified reference material (CRM) “Multi-element Solution 1” (Sigma-Aldrich, Sigma-Aldrich Co., UK) and single element solutions (1000 mg·L⁻¹, SPEX CertiPrep Group, Metuchen, NJ, US) of individual analytes. Part of the magnet sample and laboratory prepared sample solution was spiked with 1 and 0.8 ppm REEs, respectively, to demonstrate analytical accuracy.

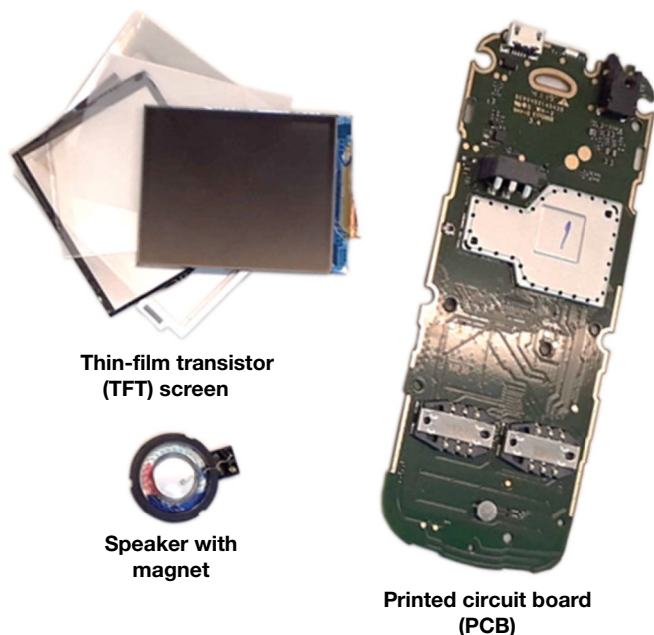


Figure 1. Disassembled components of mobile phones that were selected for analysis: TFT screens, magnets from within speakers, and PCBs. The magnet was digested whole; the other two samples were ground down using a kitchen grinder.

Results and discussion

The correlation coefficient R^2 , the limit of detection (LOD) or instrumental detection limits (IDL), and the method detection limits (MDL) for the different elements along with the corresponding wavelengths are seen in Table 2 (REEs and Th) and Table 3 (base, precious, and other metals). MDLs reported are only of analytes detected in the samples.

The intuitive wavelength selection tool of the Qtegra ISDS Software, along with inspection of subarray plots and Fullframe images, was carried out to select interference-free wavelengths in standard solutions. Since REEs emit spectral lines in similar regions of the spectrum, inter-element spectral interferences are a challenge. The Qtegra ISDS Software features simplify this task. An example of an interference-free spectrum of the REE Nd with background correction points set appropriately is seen in Figure 2.

With a complicated sample matrix, as is the case for electronics, enriched not only in REEs but also other elements (mainly base metals like Fe, Ni, etc. and precious

Table 2. Analyte wavelengths, correlation coefficient R^2 (over a calibration range of 1–10,000 $\mu\text{g}\cdot\text{L}^{-1}$), instrumental detection limits (IDL, calculated by Qtegra ISDS Software) and method detection limits for the rare earth elements and Th for the axial mode of the iCAP PRO XP Duo instrument. The MDLs of the elements seen in the real samples have been reported.

Elements and wavelengths (nm)	R^2	IDL ($\mu\text{g}\cdot\text{L}^{-1}$)	MDL for TFT screens ($\mu\text{g}\cdot\text{L}^{-1}$)	MDL for PCBs ($\mu\text{g}\cdot\text{L}^{-1}$)	MDL for speaker magnets ($\mu\text{g}\cdot\text{L}^{-1}$)
Ce 404.076	1.0000	1.3	16.6	13.3	34.0
Ce 535.353	1.0000	1.4	-	-	-
Dy 353.170	1.0000	0.3	-	-	-
Dy 400.045	0.9998	1.2	-	-	-
Er 337.271	1.0000	0.4	-	-	-
Eu 412.970	1.0000	0.1	1.2	1.0	2.5
Eu 420.505	1.0000	0.1	1.7	1.4	3.6
Gd 335.047	1.0000	0.8	10.9	8.7	22.3
La 412.323	1.0000	0.3	-	-	-
Lu 261.542	0.9999	0.1	0.8	0.7	1.7
Nd 406.109	1.0000	1.3	-	-	-
Nd 430.358	1.0000	1.6	21.4	17.1	43.7
Pr 422.535	1.0000	0.6	7.1	5.7	14.5
Pr 390.844	1.0000	1.6	-	-	-
Pr 417.939	0.9999	2.1	27.3	21.8	55.9
Sc 357.253	1.0000	0.2	-	-	-
Tb 367.635	1.0000	1.4	-	-	-
Th 318.019	1.0000	4.1	-	-	-
Tm 313.126	1.0000	0.3	-	-	-
Y 371.030	0.9999	0.1	4.9	3.9	10.0
Yb 289.138	1.0000	0.4	-	-	-

metals like Au, Ag, etc.), interference-free wavelength selection becomes more challenging. An example is shown in Figure 3 where Tb is interfering on the analyte of interest Gd at the wavelength 336.223 nm. The Qtegra ISDS Software helps predict an interference from Tb (seen in the right panel in Figure 3). Upon running a single element solution of Tb, a false positive signal is obtained on this Gd wavelength. Interference correction in Qtegra ISDS Software can be enabled for such a wavelength, provided the interfering analyte, in this case Tb, has at least one wavelength itself that is clean and free of interferences.

Linearity

The calibration curves for the different wavelengths have R^2 values greater than 0.9999 in the axial plasma view, over the calibration ranges 1 to 10,000 $\mu\text{g}\cdot\text{L}^{-1}$ for REEs and 1 to 100,000 $\mu\text{g}\cdot\text{L}^{-1}$ for the metals (Tables 2 and 3).

Sensitivity

The IDLs are all in the single digit $\mu\text{g}\cdot\text{L}^{-1}$ (ppb) range (Tables 2 and 3). The IDL is calculated directly by Qtegra ISDS Software based on three times the standard deviation of a ten-replicate measurement of the calibration blank. The R^2 values are also computed in Qtegra ISDS Software and displayed below the individual calibration curves in the "Concentration" tab. These values can additionally be exported using the "Query" option in Qtegra ISDS Software (Figure 4).

The analyte MDLs are sample specific and depend upon sample preparation steps and are relevant only for elements detected in the samples (Tables 2 and 3). MDLs are calculated by multiplying the IDLs with dilution factors for each sample. Samples like speaker magnets have much higher concentrations of analytes and require greater dilution factors, thereby yielding higher MDLs.

Table 3. Analyte wavelength, correlation coefficient R^2 (over a calibration range of 1–100,000 $\mu\text{g}\cdot\text{L}^{-1}$), IDLs and method detection limits (MDL) for base, precious and other metals for the axial mode of the iCAP PRO XP Duo instrument

Elements and wavelengths (nm)	R^2	LOD or IDL ($\mu\text{g}\cdot\text{L}^{-1}$)	MDL for TFT screens ($\mu\text{g}\cdot\text{L}^{-1}$)	MDL for PCBs ($\mu\text{g}\cdot\text{L}^{-1}$)	MDL for speaker magnets ($\mu\text{g}\cdot\text{L}^{-1}$)
Ag 328.068	1.0000	0.4	5.6	4.5	11.4
Al 167.079	1.0000	2.1	27.3	21.8	55.9
Au 242.795	1.0000	1.0	13.5	10.8	27.6
Cr 205.560	1.0000	0.8	10.5	8.4	21.4
Cu 324.754	1.0000	3.1	40.3	32.2	82.5
Fe 259.940	1.0000	0.6	7.3	5.8	14.8
Ni 231.604	1.0000	1.4	18.7	15.0	38.4
Pb 220.353	1.0000	5.9	76.4	61.0	156.4
Pd 340.458	1.0000	1.3	-	-	-
Pt 265.945	0.9999	2.5	-	-	-
Sc 357.253	1.0000	0.2	-	-	-
Sn 189.989	1.0000	2.5	-	-	-
Zn 213.856	1.0000	1.3	16.9	13.5	34.58

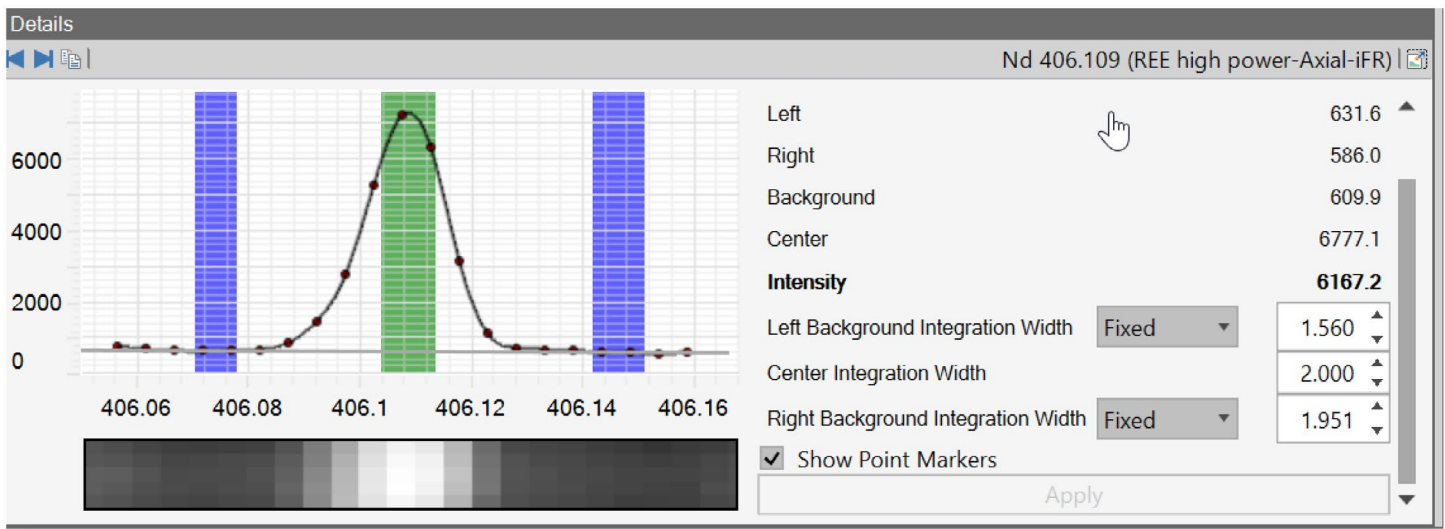


Figure 2. Clean interference free spectrum of REE- Nd at 406.109 nm in axial mode

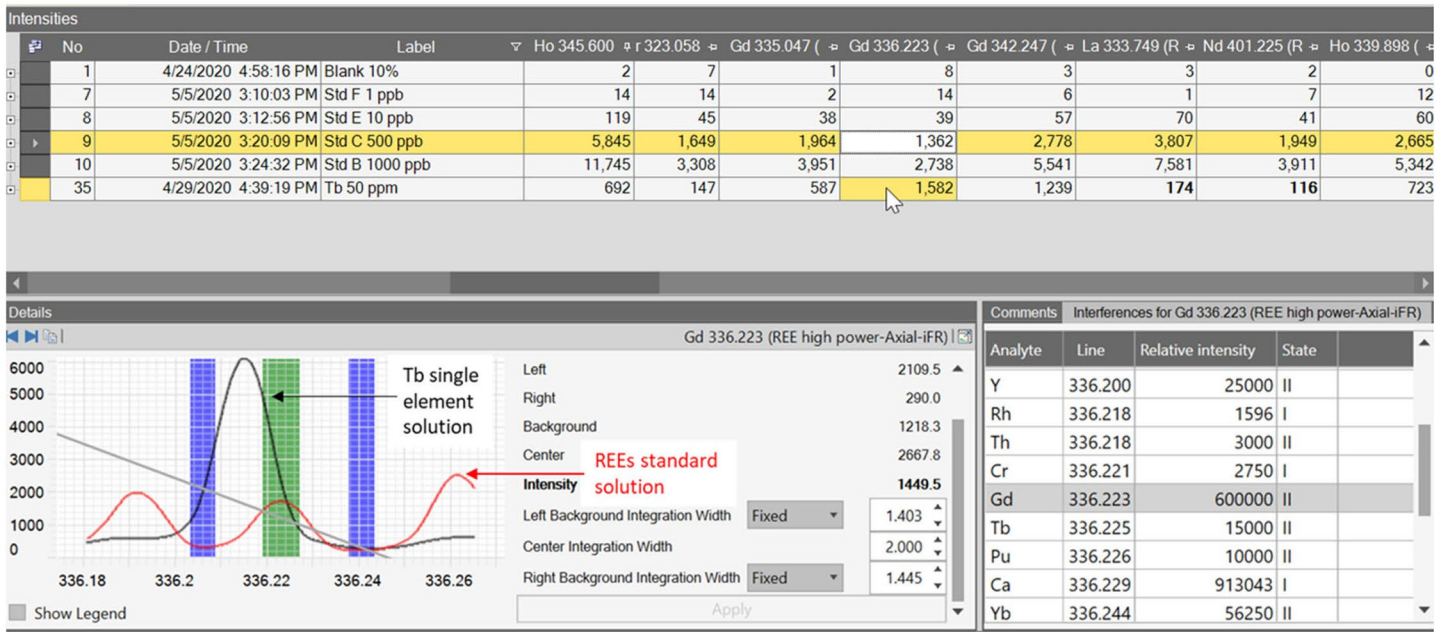


Figure 3. Interference of Tb on Gd at 336.223 nm. Qtegra ISDS Software interference correction can be applied to correct for this.

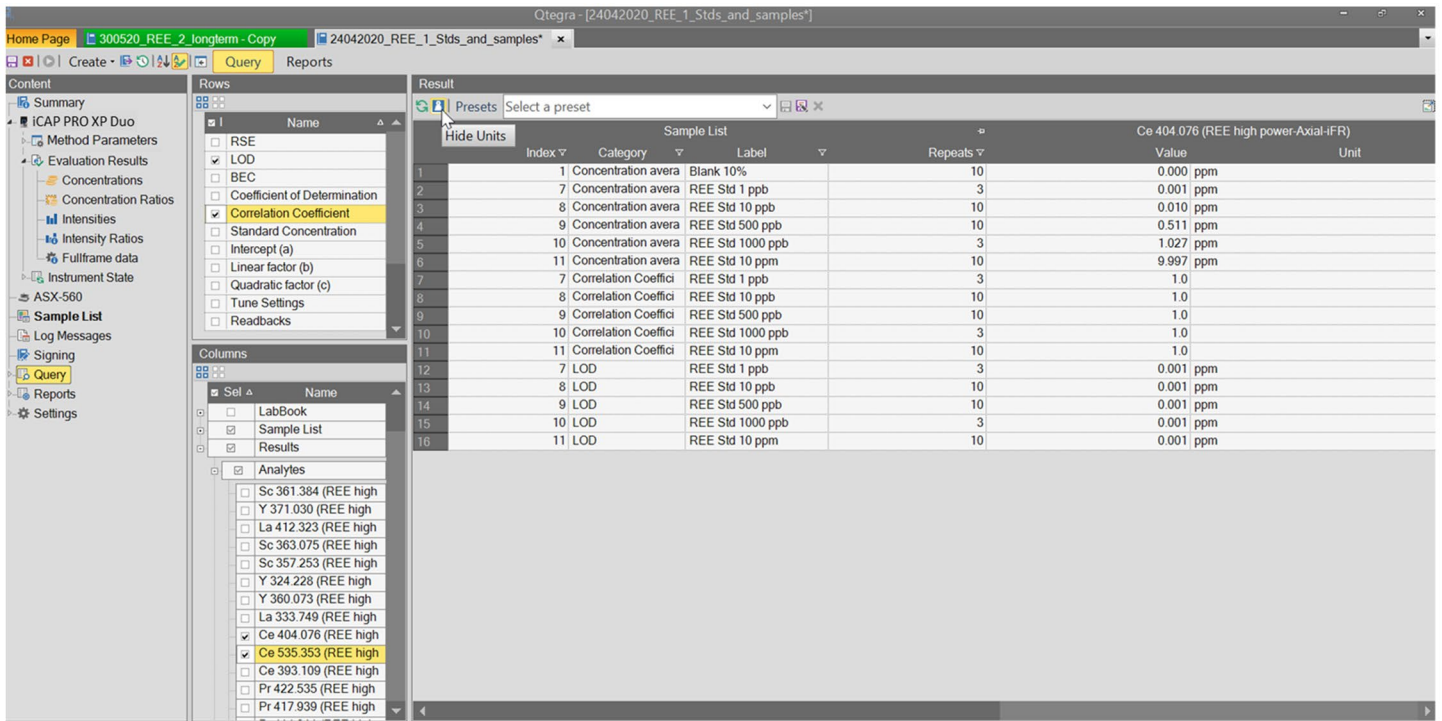


Figure 4. Query function in Qtegra ISDS Software offers export of all measured and calculated parameters, e.g., concentrations, IDL/LODs, etc.

Precision/spike recovery

The spike recoveries of a 0.8 ppm spike on a simulated sample and 1 ppm spike on magnet speaker samples (run intermittently during the long-term tests) are shown in

Figure 5 and Figure 6, respectively. Spike recoveries in the $\pm 15\%$ range are obtained for most analytes.

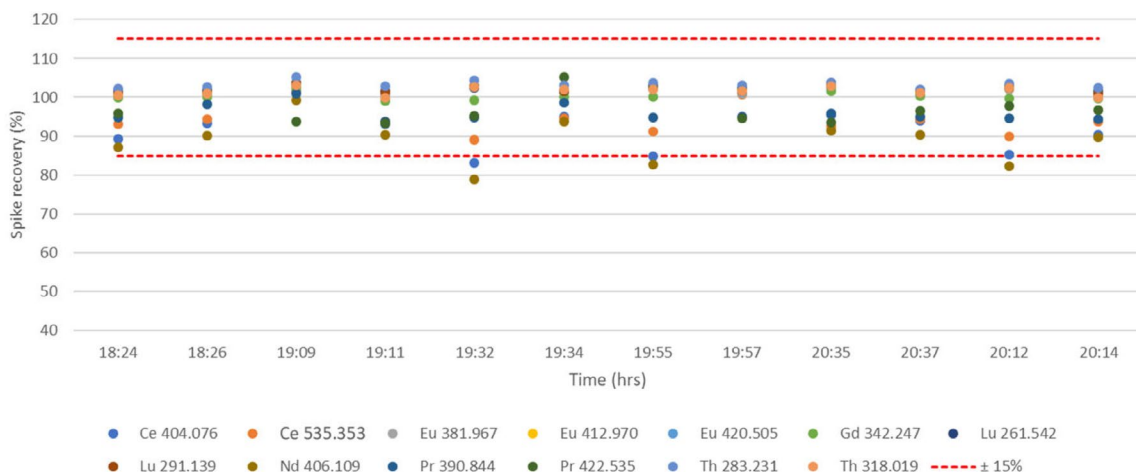


Figure 5. Spike recoveries in spiked laboratory simulated solution run intermittently over a couple of hours

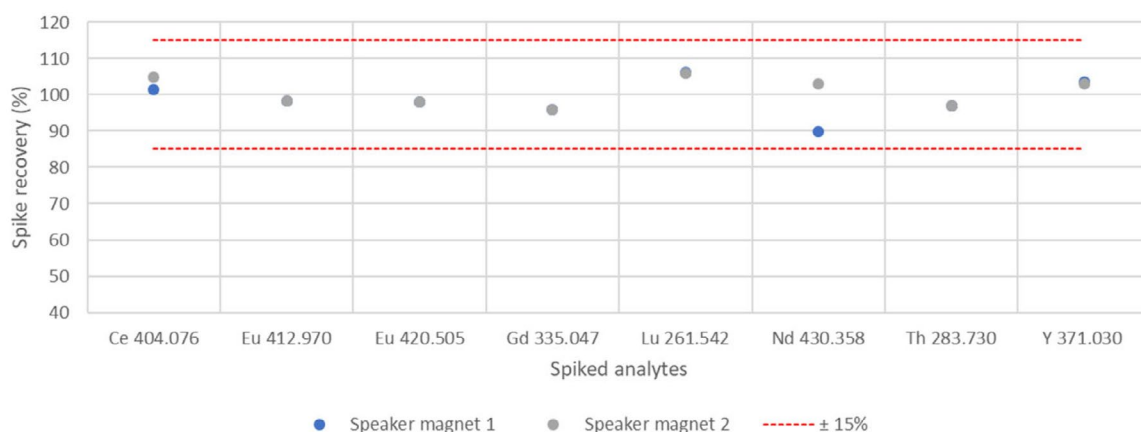


Figure 6. Spike recovery in speaker magnet samples, 1 ppm spike

Method performance and quantification of REEs and other metals in real samples

The REEs and metals found in the samples and their final recalculated concentrations are shown in Table 4. Sample solutions were diluted as necessary. Dilution factors or sample weights and final volumes can be specified in the respective Qtegra ISDS Software LabBooks and final dilution factors, and final analyte concentrations will be automatically calculated by the software.

Robustness

The two long-term stability tests show the relative concentration of analytes is between 80 and 120% over ~ 6 hours of analyses (including samples, standards, blanks, and washes), which might be a typical working day in the laboratory (Figure 7, panels A and B). A short exposure time of 5 s was used, resulting in analysis time for a single sample of < 2 min, including uptake time, 3 repeats, and rinse times.

Table 4. Final calculated concentrations ($\mu\text{g}\cdot\text{g}^{-1}$) of REEs and metals in undiluted samples of mobile phone components – TFT screen, PCB, and magnets from the speakers

Element and wavelength (nm)	TFT screen 1 ($\mu\text{g}\cdot\text{g}^{-1}$)	TFT screen 2 ($\mu\text{g}\cdot\text{g}^{-1}$)	PCB 1 ($\mu\text{g}\cdot\text{g}^{-1}$)	PCB 2 ($\mu\text{g}\cdot\text{g}^{-1}$)	Speaker magnet 1 ($\mu\text{g}\cdot\text{g}^{-1}$)	Speaker magnet 2 ($\mu\text{g}\cdot\text{g}^{-1}$)
Rare earth elements (REE)						
Ce 404.076	<DL	<DL	1.025	1.016	28,678.856	27,907.174
Eu 412.970	<DL	0.768	<DL	<DL	<DL	<DL
Eu 420.505	<DL	0.765	<DL	<DL	<DL	<DL
Gd 335.047	0.079	0.141	3.598	3.959	4047.393	5930.288
Lu 261.542	0.022	0.017	1.947	1.633	17.255	16.207
Pr 417.939	<DL	<DL	<DL	<DL	12,802.391	14,267.827
Nd 430.358	<DL	<DL	<DL	<DL	37,392.193	40,643.866
Y 371.030	0.015	0.020	0.833	1.132	<DL	<DL
Metals						
Ag 328.068	13.599	41.205	289.296	496.581	<DL	<DL
Al 167.079	1085.738	1322.702	475.877	486.056	22,820.756	28,300.425
Au 242.795	5.404	1.686	2.604	0.989	29.942	31.624
Cr 205.560	252.225	183.967	1057.523	945.728	3036.511	3549.902
Cu 324.754	1364.658	5841.867	189,027.425	164,140.575	-	-
Fe 259.940	877.812	677.548	2406.179	2130.731	803,015.933	840,304.409
Ni 231.604	189.522	218.559	1663.002	1647.645	1107.861	1091.483
Pb 220.353	0.074	0.171	5.111	4.025	235.458	254.557
Zn 213.856	47.018	56.269	699.394	704.884	31,947.532	35,770.742

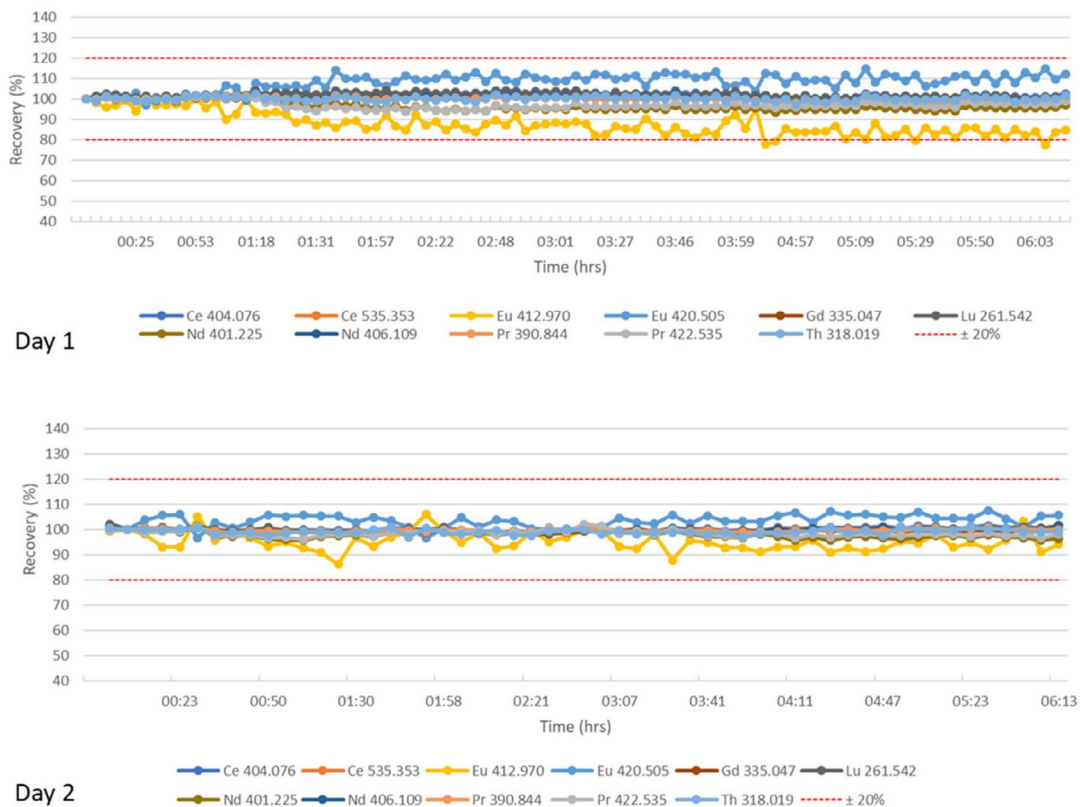


Figure 7. Recoveries of analytes, displaying instrument stability during long-term experiments run on two days. Each experiment constitutes at least 6 hours of continuous analysis in axial mode of the iCAP PRO XP Duo instrument.

Conclusions

This application note describes an analytical solution that can be used for the determination of REEs, precious metals, and toxic elements in electronic waste using the iCAP PRO XP ICP-OES Duo system. The analytical procedure outlined in this note includes a simplified sample preparation technique to handle mobile phone waste and ensure that such complex samples are suitably prepared for analysis using ICP-OES.

The highlights are summarized below:

- Various REEs and other valuable or toxic metals were found in the analyzed e-waste samples, displaying both the potential value for such samples in the recycling industry as well as the need for responsible waste management.
- Excellent large linear dynamic range was obtained for REE (1 to 10,000 $\mu\text{g}\cdot\text{L}^{-1}$) and basic metals (1 to 100,000 $\mu\text{g}\cdot\text{L}^{-1}$), making the iCAP PRO XP ICP-OES Duo system an ideal analytical tool for multi-elemental analysis of samples such as e-waste, which have large variations in concentrations of constituent elements. The large dynamic range enables users to reliably analyze trace to ultra-trace levels at low concentration (Eu, Pb, etc.) as well as accurately quantify elements like Fe, Cu, etc. present in very high concentration.
- Highest sensitivity (in the low ppb range) was achieved for all targeted analytes in the Axial viewing mode. This is essential for detecting REEs, precious and poisonous elements, which often are present in very small amounts in e-waste samples.
- Recovery values within the expected ($\pm 15\%$) range were obtained for both real as well as laboratory simulated samples, demonstrating the accuracy of the technique.
- Excellent system robustness was demonstrated with no significant bias in the analytical results as observed for two consecutive days of continuous data acquisition. The vertical torch design in the Duo instruments enables plasma stability even with complicated samples matrices.
- Fast analysis time with less than 2 min/sample allows for high sample throughput and minimal downtime, making it ideal for contract testing laboratories or for users engaged with analyzing a high number of samples daily.
- For applications where sample throughput is not critical, the iCAP PRO XP ICP-OES Duo system with slightly longer integration times, translated to more time per sample, can be used without compromising on analytical performance.
- Using analytical advances available on the iCAP PRO XP ICP-OES system, in combination with the Qtegra ISDS Software tools, suitable wavelength selection and effective interference removal of target elements in e-waste sample matrix is obtained with ease.

Reference

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