

Determination of Rare Earth Elements in electronic waste using ICP-OES

To analyze ultra-trace-amounts in samples containing different matrix-elements in unknown concentration-areas (varying from sample to sample) is a challenge, the ICPE-9000 (Inductively Coupled Plasma Emission spectrometer) completes successes. This application segment describes how to analyse Rare Earth Elements (REE) in electronic waste samples like mobile phones, notebooks, electronic boards and more (cf. fig. 1). Keywords such as sample preparation, system parameters and spectral interferences outline user expectations in this application segment. For more Background information on REEs in electronic waste (e-waste) please order Shimadzu News 3/2012.

■ Sample preparation

At first the homogenization of the samples consisting of many different components has to be done, using laboratory mills. The rough-crushing is done with a cutting mill and the fine grinding by a vibrating disc mill. The resulting equivalent diameter of the sample particles should be less than 50 μm . To ensure the grinding-results, Shimadzu's Particle size analyser SALD 2201 can be used. With the use of Methanol as grinding aid in the vibrating disc mill, the best results were obtained.

The 2nd step is to transfer the solid state particles into a liquid status for ICPE 9000-Measurement. Microwave digestion is recommended for this working step. 10 mL nitric acid is used to digest a particle-samples weighing 150 mg.



Figure 1: Electronic waste samples

■ Instrumental parameters

To ensure the sample introduction system is completely conditioned with the sample, the rinse times have to be set above the normaly range. For this and more System Parameters see table 1.

Parameter	Settings
RF generator power	1.2 kW
Cooling gas	10 L/min
Plasma gas	0.6 L/min
Carrier gas	0.7 L/min
Plasma torch	Mini torch
Observation	Axial
Sensitivity	Wide range
Exposure time	20 sec.
Solvent rinse time	35 sec.*
Sample rinse time	50 sec.*
*sample introduction tube length \approx 40 cm	

Table 1: System Parameters

■ Standard system Configuration

- ICPE-9000 (axial view)
- Mini torch for aqueous solutions
- Cyclone spray chamber
- Coaxial nebulizer with sampling rate of 1 mL/min
- Autosampler ASC-6100

■ Identification of Spectral interferences

At first the spectral interferences between the analytes themselves are considered. This can be easily done by using the external-permuting-calibration-model, which means to calibrate not with an equal rising concentration for all elements, but rather mixing the analyte amounts for each REE. The example in table 2 intimates, for which standard the interferences can get obvious. In standard 3 there should be no higher emission signal for Cer than in the blank (standard 1). If there is a higher emission, this is caused by one of the other elements. The resulting calibration would be non-linear.

REE	Concentration [$\mu\text{g/L}$]					
	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6
Dy	0	80	160	120	40	0
Er	0	150	100	0	50	200
Gd	0	20	10	30	40	0
La	0	0	80	40	120	160
Nd	0	3600	900	2700	1800	0
Ce	0	200	0	50	150	100

Table 2: Permuting calibration

Additionally matrix-interferences have to be checked. Therefore each expected element is measured as unknown sample. Here the same aspect as for the permuting calibration is valid: If the matrix element causes an emission signal for REE, interferences exist for this emission line.

■ Limit of detection (LOD)

All emission lines with spectral interferences mustn't be considered. For all remaining lines the LOD can be determined, regarded to the solid sample. Some examples are given in table 3.

REE	LOD [$\text{mg(REE)/kg(sample)}$]
Dysprosium	0,397
Erbium	0,147
Lanthanum	0,262
Praseodymium	0,450
Yttrium	0,034

Table 3: LOD for Rare Earth Elements (REE)

■ Results and Conclusion

Using the ICPE-9000 to analyze Rare Earth Elements in electronic waste without sample-preconcentration or matrix-depletion was possible in a direct method, even tough to the effect that such sample preparation steps get more and more focused for spectroscopic methods^[1].

Especially Yttrium is present in many samples and for mobiles there was a match for the combination of Nd/Pr/Dy, which is typically for strong magnets e.g. used in modern speakers. The analysis shows, for which sample-type the recovering of the extreme expensive REEs can be done.

Additionally it was successful to transfer the questioning to automobile catalysts samples. Here also the determination of REEs was possible

[1] Zawisza, Pytlakowska, Feist, Polowniak, Kita, Sitko, (08/2011): Determination of rare earth elements by spectroscopic techniques: a re-view; J. Anal. At. Spectrom 26 (12), page 2373-2390