

# Interference-Free Determination of Rare Earth Elements in Electronic Waste Using ICP-OES Spectroscopy <sup>[1]</sup>

Jan Knoop<sup>a</sup>, Uwe Oppermann<sup>a</sup>, Jürgen Schram<sup>b</sup>

<sup>a</sup>Shimadzu Europa GmbH, Duisburg, Germany

<sup>b</sup>Niederrhein University of Applied Sciences, Faculty of Chemistry, Krefeld, Germany

## Background

### Rare Earth Elements (REEs): Yttrium, Scandium & Lanthanide Group

The demand on REEs is heavily increasing, as they are used in many high-tech products, e.g. in wind generators or hard disc drives due to their specific magnetic behaviour. The supply situation for REEs is getting worse, as the world market is depending on Chinese exports, that's why it may be worthwhile to recycle electronic waste in European countries.

## Analytical Task

The aim is to optimise a method for analysing REEs in different kinds of electronic waste (e-waste) with a simultaneous ICP optical emission spectrometer (ICPE-9000, SHIMADZU, fig. 1).



FIG 1 ICPE-9000, SHIMADZU.

Depending on the field of application the level of matrix elements and target elements will be completely different, resulting in a wide variety of spectral interferences, which have to be identified.

Thus, also some other elements of economic interest (bulk-, minor-, trace- and ultratrace-amounts) should be analysed in the same way.

## Sample Preparation

At first the homogenization of the samples consisting of electronic boards, mobile phones and LCD displays (see fig. 2 for examples) has to be done, using laboratory mills. Each sample is handled separately. A cutting mill is applied for rough-crushing and a vibrating disc mill for fine grinding.

The resulting particles should have an equivalent diameter of less than 50 µm, which is ensured by SHIMADZU's Particle Size Analyser SALD 2201. With the use of Methanol as grinding aid in the vibrating disc mill, the best results were obtained.

The 2<sup>nd</sup> step is to transfer the solid state particles into a liquid status for ICPE 9000-Measurement. For this step microwave digestion is recommended, using 10 mL nitric acid and 150 mg of sample. For digestion program see tab. 1

## System Configuration & Parameters

- ICPE-9000 (Axial and radial view can be performed in one run.)
- Minitorch for aqueous solutions
- Cyclone spray chamber
- Coaxial nebulizer, sampling rate = 1 mL/min
- Autosampler ASC-6100 (up to 60 Samples)

For instrumental parameters see tab 2.

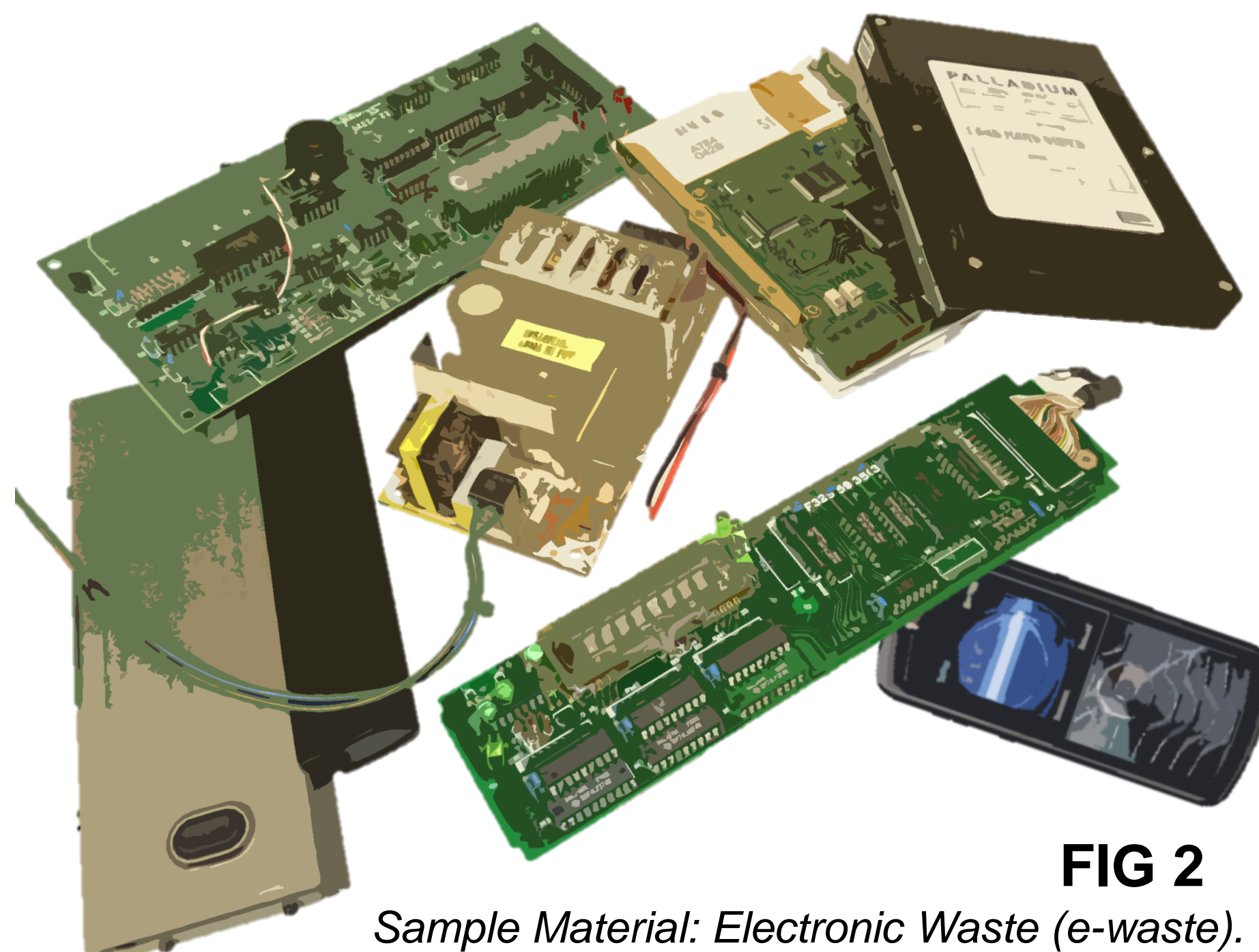


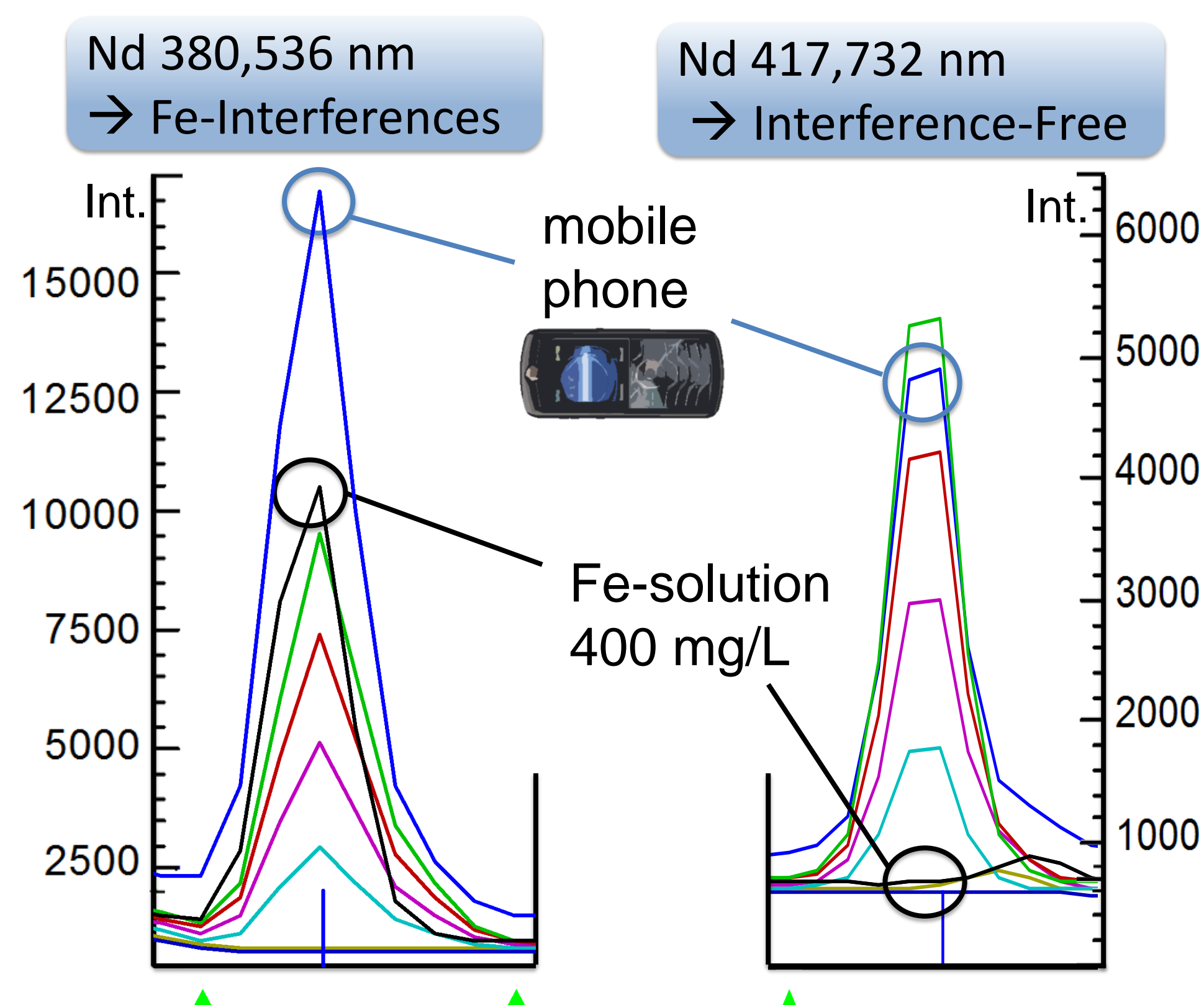
FIG 2 Sample Material: Electronic Waste (e-waste).

## Spectral Interferences

At first the spectral interferences between the analytes themselves are considered. This can easily be done by using an *external-permuting-calibration-model*, which means not to calibrate with an equal rising concentration for all elements, but rather mixing the concentration as implied by tab. 3. The arrows should indicate, for which standard the interferences can get obvious and how the identification works:

By this calibration strategy there should be no higher emission signal for cerium in standard 2 than in the blank. If there is a higher emission, this is caused by one of the other elements. The resulting calibration will be non-linear.

Other interferences are identified by measuring the matrix elements as standard solution in the concentrations expected in the digested samples. From matrix element solutions no emission should be caused at the analyte-line. For neodymium an example shows matrix interference caused by iron in fig. 3 and in addition the interference-free line. Besides iron, the other regarded matrix elements are: Al, Ti, Cr, Mn, Co, Ni, Cu, Zn, Zr, Nb, Ag, Sn, Sb, Au, Pb.



Emission of Nd-Calibration, Fe-Solution and Sample "Mobile Phone": Identification of Matrix Interferences.

FIG 3

## Results (I) – Application Work

The final method allows both, the accurate quantitation of REEs in e-waste and a high sample throughput because of simultaneous measurement, which is a perfect combination. Because many matrix elements are present, from over 200 investigated lines only 10 lines remain to determine 7 REEs. For LODs see tab. 4.

SHIMADZU Europa GmbH

Albert-Hahn-Str. 6-10,

D-47269 Duisburg

+49(0)203/7687-0

www.shimadzu.eu

shimadzu@shimadzu.eu

TAB 1 Temperature Program for Microwave Digestion.

Step	Ramp [min]	Temp. [°C]	Heat Mode
1.	25	220	RAMP
2.	20	220	HOLD

TAB 2 Instrumental Parameters, ICPE-9000.

Parameter	Setting
RF generator power	1.2 kW
Cooling gas	10 L/min
Plasma gas	0.6 L/min
Carrier gas	0.7 L/min
Plasma observation	Axial (for traces)
Sensitivity	Wide range
Exposure time	20 sec.
Solvent rinse time	35 sec.*
Sample rinse time	50 sec.*
RF generator power	1.2 kW

\*sample introduction tube length ≈ 40 cm

TAB 3 Calibration to Identify Spectral Interferences.

REE	Concentration [µg/L]	blank	std 1	std 2	std 3	std 4	std 5
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	

TAB 4 Interference-Free Wavelengths to Determine REEs.

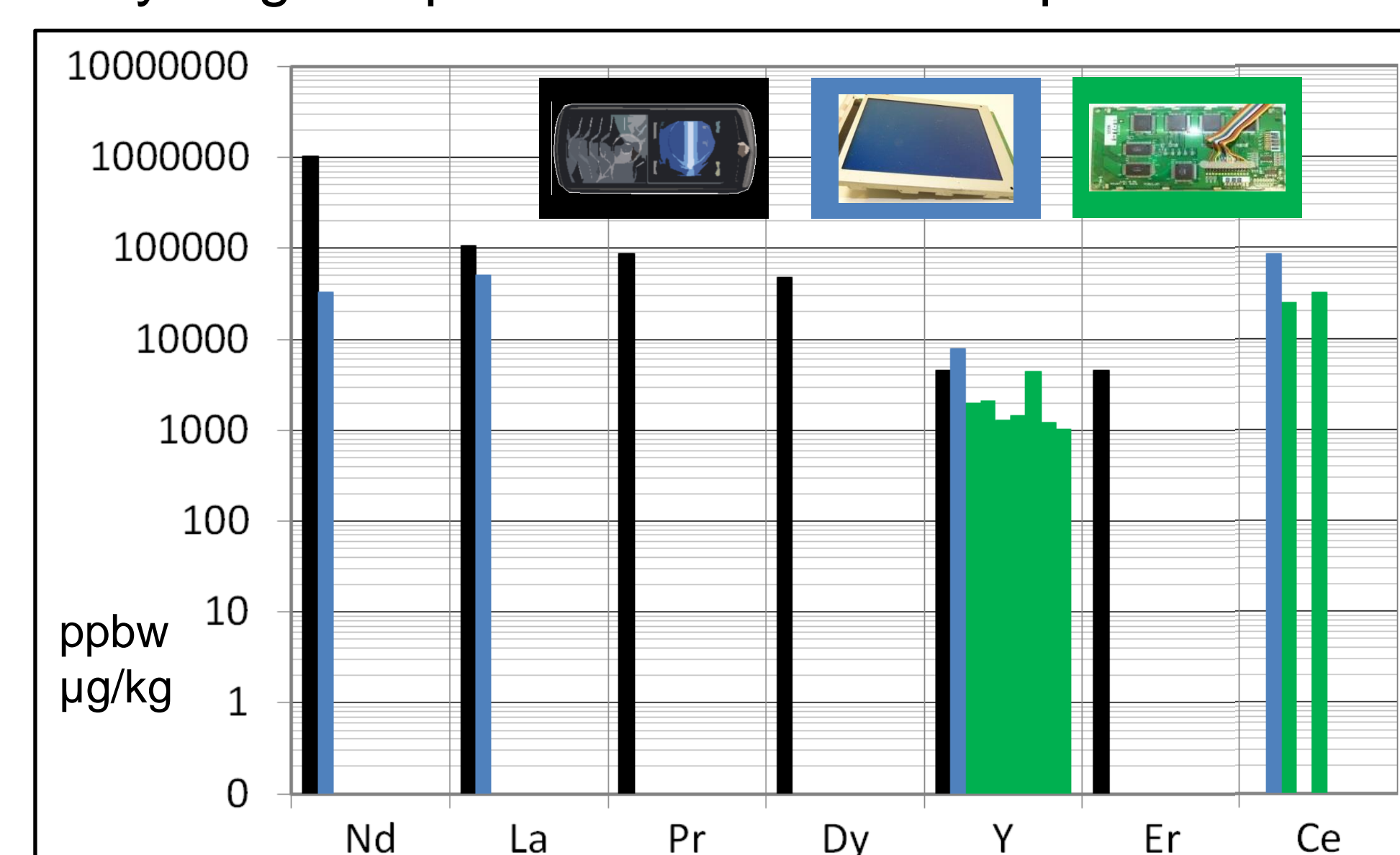
REE	Wavelength [nm]	Intensity <sup>[2]</sup> [-]	LOD [mg analyte / kg sample]
Ce	446,021	2400	1,230
Dy	353,602	5500	0,397
Er	349,910	6700	0,169
Er	369,265	7900	0,147
La	398,852	4400	0,262
La	399,575	3600	0,277
Nd	417,732	2400	1,670*
Pr	418,948	2500	0,450
Y	371,030	13000	0,024
Y	377,433	10000	0,034

\*Can be optimised by use of lower conc. for calibration (cf. Tab 3)

## Results (II) – Sample Measurement

As it is shown in fig. 4, different REEs have been quantified in different kind of sample material (1x mobile, 1x LCD (screen only), 7 x circuit boards). While there is a variation of REEs in high end products, the variation in circuit boards is much less, only Y and Ce are present (>LOD).

If e-waste is taken into consideration to recover REEs, the consequence is, that high-order e-waste like mobiles seems to be the best material for recycling. To decide if recovery regarding REEs e.g. from a special sample type is reasonable, the developed method can help recycling companies to answer this question.



REEs in Different Kind of Samples, Sorted by Sample-Type. FIG 4

[1] Knoop, Oppermann, Schram, J. Chem. Chem. Eng. 8 (2014) 635-640

[2] CRC Handbook of chemistry and physics