

Report

Identifying rare and precious metals in EE-waste with X-Ray Fluorescence

Test analysis of selected recycled mobile phones and batteries in a prototype x-ray fluorescence measurement station

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KEYWORDS:

Metrology
X-ray
Fluorescence
Recycling
Rare Earth Elements
Precious Metals

VERSION
0.2

DATE
2012-08-30

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CLIENT(S)
Elretur

CLIENT'S REF.
Guro Kjørsvik Husby

PROJECT NO.
P 90J369

NUMBER OF PAGES/APPENDICES:
9 + Appendices

ABSTRACT

XRF may be used for on-line detection of critical elements

To investigate the feasibility of using X-Ray Fluorescence (XRF) to identify objects containing Indium and other critical material on-line in a waste stream a series of tests were performed on e.g. mobile screen and batteries. Due to the extensive time needed to record the full XRF spectrum of each item and of reference samples of the critical elements to be identified only a small number of samples could be measured. In an on-line situation, however, only a few, narrow, spectral bands needs to be recorded reducing the measurement time to an estimated 10 to 100 milliseconds. Element like In could be detected on mobile phone screens in the low concentration represented by the ITO electrode layer. In the tested batteries Co gave very strong signals.

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REPORT NO.
A23575

ISBN
978-82-14-05306-7

CLASSIFICATION
Unrestricted

CLASSIFICATION THIS PAGE
Unrestricted

Document history

VERSION	DATE	VERSION DESCRIPTION
0.1	2012-06-27	Assembled from memos etc.

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APPENDICES

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1 Summary and conclusions

The purpose of the Elretur project is to identify possible recycling strategies of EEE using spectroscopy. This report summarizes the results of measurements done on some electronic equipment samples using X-ray and optical spectroscopy. Electronic equipment may have quite complex chemical composition. X-ray fluorescence (XRF) technique has been chosen because in principle it allows to uniquely identify and possibly quantify chemical elements present in a material. We have picked ITO (Indium Tin Oxide) as a test compound for this study both because it is present in a lot of modern screen (mobile phone, computer) and because of its scarcity. Other interesting metals are the lanthanide, rare earth metal (Re), precious metal (Au, Ag, Pt) and hazardous one (Hg, Pb, As). The electronic equipment tested comprises mobile phones and battery. For the mobile phone, the measurement focus on the screen part of the phone, because even a for a simple mobile phone, the number of compounds that can give a response in the measured signal is very high and because it is there that ITO is present as a very thin (100 nm) transparent and conductive electrode. Some mobile have been measured both before and after dismantlement.

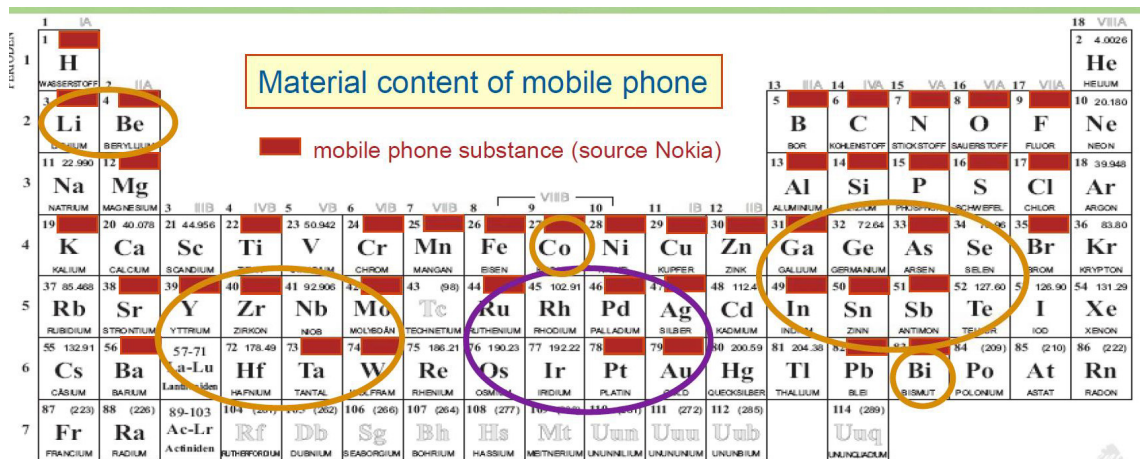


Figure 1. Material content of a mobile phone.¹

The measurements have been performed using high energy resolution but slow detectors from Amptek. The geometry of the measurement influences the ratio XRF signal/scattering signal (Compton and Rayleigh scattering) measured by the detector. The geometry that has been used for the measurement was not optimal and can be further optimized.

Short summary of the measurements:

- Indium and Tin fluorescent lines were measured on the entire screen, meaning that with a large probability Indium Tin oxide can be detected using XRF.
- The measured signal is very weak, of the order of the scattered signal strength from the phone, and, in comparison with other fluorescing compounds like Sr, it is several order of magnitude lower in signal strength. It may be very challenging to detect and quantify of ITO in small glass pieces in an on-line setting.
- Other metals like Ag, Sb (weak signal), Zr (weak) and Sr (very strong) have been also measured on some screen. The presence of Strontium in some glass screen was surprising. Strontium Oxide was used in older TVs with picture tube screen as a way to absorb X-ray generated by the electron beam knocking

¹ :”Mining our computer”, Christian Hagelüken, UMICORE presentation

the screen² (see also ³). Zr could be of interest to recycle, but Sr?. Co, Ti, Fe (all of them with very strong signal) have been measured easily in the mobile batteries. Co is also a metal of interest for recycling.

- The presence of other metals, like the lanthanide, was difficult to detect, because their K line lie too high in the energy spectrum to be measurable using our conventional Si detector (> 30 keV). Lanthanide L lines lie at very low energies and are very close to each other and difficult to separate from other strong K lines of Ti, Cr, Cu etc.... CdTe detectors or the SINTEF prototype Si detector can be used to detect K lines on interesting EE known to contain lanthanide or rare earth metal.
- Cu and Br were also detected.

Optical measurements were also tried using Infrared spectroscopy and LIBS (Laser Induced Breakdown Spectroscopy). These tests gave no conclusive results, partly because we wanted to detect bulk properties of the material and optical methods only will analyse the surface, and partly because we wanted to do analysis of the whole detection area of the object. The consequence is that small details of material of interest will only give rise to a signal at the detector below the noise level.

2 X-ray measurement

2.1 Setup for the measurement

The measurement setup is illustrated in

Figure 2. A 160 kV x-ray source irradiates a sample. Either of two energy dispersive detectors from Amptek is used to measure the X-ray fluorescence from the sample, one with a Si and one with a CdTe photodiode. CdTe based detectors are more expensive and usually more sensitive to vibration than Si one. The first one allows measuring X-ray fluorescence in the 5-50 keV with a very good energy resolution, while the second offers good sensitivity over the 5-200 keV range, but with lower energy resolution.

² http://www.boston.com/business/articles/2010/05/24/what_is_strontium_and_its_connection_to_tv/

³ <http://en.wikipedia.org/wiki/Strontium>

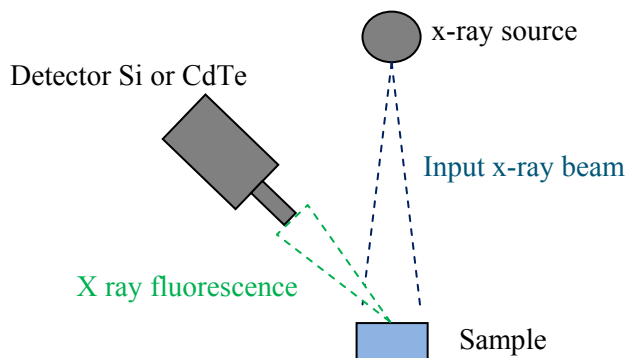


Figure 2. Set up and geometry for the measurement of X-ray fluorescence

2.2 X-ray voltage requirements

For measuring X-ray fluorescence, the incoming x-ray photon must have a higher energy than the so-called K-edges or L-edges energies of the elements present in the materials. These are the energies value necessary to expel an electron from one of the atomic shell of the atom being irradiated. Typical XRF spectrums are composed of line at energies approximately equals to the K or L edge energy value. The identification of the energies of the line allows to uniquely identifying the elements present in the material. This K and L edges extends from a few keV to approximately 60 keV for elements like Copper, Iron or the Lanthanides. XRF lines coming from K-edges excited level have typically higher intensity than the L-edges excited and are easily measured. Typical metals like copper, iron have K-edges in the 5-10 keV making XRF "easy" to detect them using silicon photodiode. Other metals like the lanthanides have K-edges lying over 30 keV and are more difficult to detect using conventional silicon photodiode, but can be detected using CdTe or the energy dispersive silicon detector being developed by SINTEF.

A broad and sometimes rather intense background coming from Rayleigh and Compton scattering usually accompanies the XRF line and will interfere with the measurements. The background contribution thus has to be minimized to correctly identify element and quantify their concentrations. The measurements were performed varying the voltage source and optimizing roughly the set up geometry of the setup. Additional "physical" filter, made of thin aluminum and copper plates, were also used to increase the contrast of the XRF signal.

2.3 Elements detected

The elements detected are summarized in Table 1 for each electronic component. A brief estimate is given on the relative strength of the signal. Most of the elements detected in the EE have been identified by comparing the XRF spectrum of EE with the spectrum of reference samples containing almost pure element.

EEE type	Element detected	Signal strength
Screen NOKIA	Sr	Very strong
	Zr	Weak
	Ag	Very weak
	In	Very Weak

	Sn	Very Weak
	Sb	Very weak
Screen Siemens	Ag	Very weak
	In	Very Weak
	Sn	Very Weak
	Sb	Very Weak
Screen "Creative"	Ag?	Very weak
	Sn	Very weak
	In	Very weak
	Sr, Y, Zr	Weak, overlapping lines
Screen Ipod	Sr	Very strong
	Sn	Very weak
	In?	Very weak
Battery NOKIA E51	Ti	Strong
	Mn	Strong
	Fe?	Strong
	Co	Strong
Battery Siemens	Ti	Strong
	Mn	Strong
	Fe?	Strong
	Co	Strong

Table 1. Relative fluorescence response for different elements in selected components

2.4 Example of SRF spectrum

Some XRF spectrums are given in the following for some of the samples.. For Figure 3, Figure 4 and Figure 5, showing the ITO lines, the received spectrum was filtered with a 1 mm aluminium sheet to reduce the contribution from the Sr lines, and a long integration time was used. For these measurements, 1024 channels are filled for each integration time of 1 s, giving a spectrum with high resolution but at a slow rate. For an online application, a reduced number of channels will be used (< 10), giving a greatly reduced integration time. Figure 6 show the spectrum with some identified element for three different mobile phone batteries.

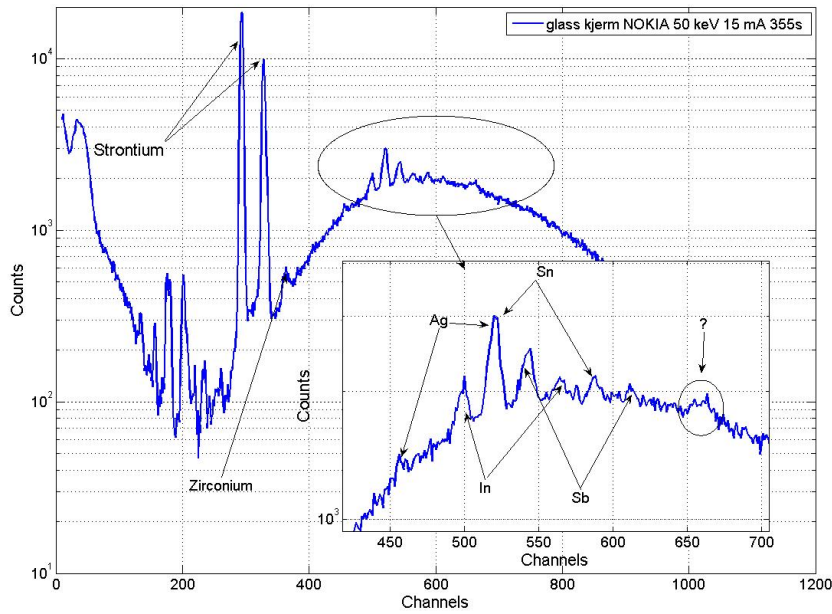


Figure 3. NOKIA screen (liquid crystal sandwiched between two glass sheets), “glassy” part only. The ITO seems to be present as very small and thin stripes deposited on the glass, that are easily scraped away using a scalpel

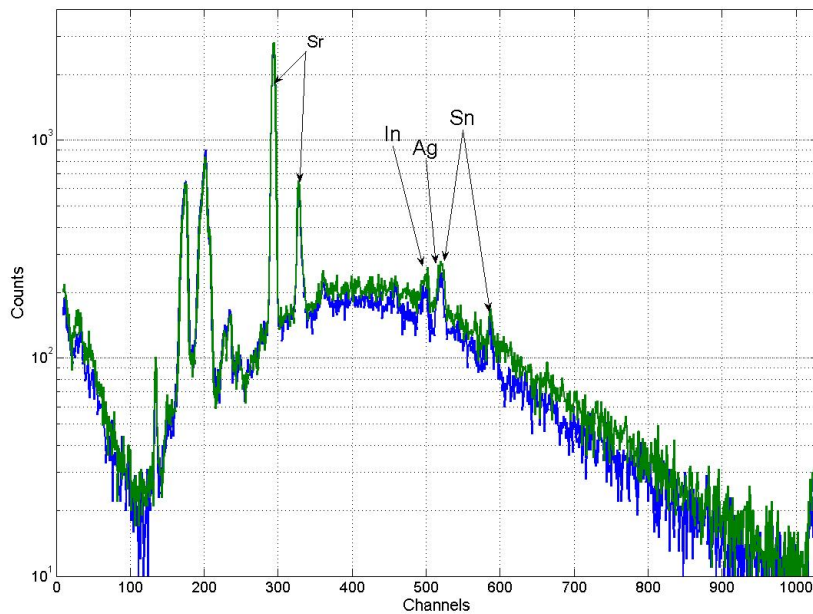


Figure 4. Element identified by XRF in an iPod screen.

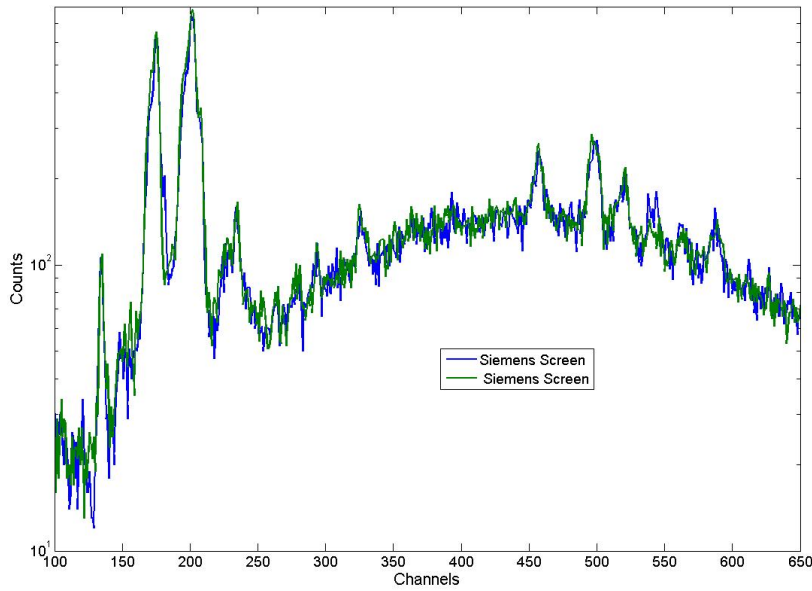


Figure 5. Element identified by XRF in a Siemens mobile phone screen

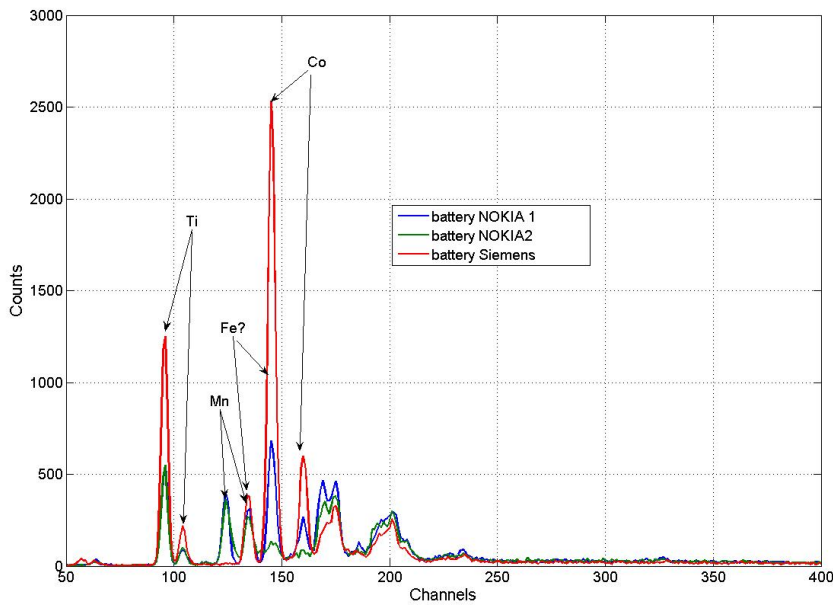


Figure 6. Element identified by XRF in NOKIA and Siemens mobile phone batteries



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