A newly developed XRF-Sensor with high sensitivity for increased sorting efficiency.

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Abstract

X-Ray Fluorescence spectroscopy (XRF) is an element sensitive detection method and all kinds of materials can be separated as long as they are different in at least one element with an atomic number of Calcium or higher. Due to this capability XRF-Sensors can amongst other things be used to separate different kinds of glass (lead-glass, ceramics…), different metals (e.g. “meatballs” in scrap preparation) or in mining plants to separate metal rich from dead rocks.

Due to the increased use of alloying metals as well as composite constructions of metals with other materials, detailed information about the composition of a single piece of material becomes more and more important for the recycling process. The United Nations Environment Programme (UNEP) stated in their report on metal recycling from 2013, that the main reason for the low End-of-Life recycling rates of alloys is the loss of resources due to non-functional recycling and draw the conclusion: *“A far more sophisticated approach is urgently needed to address the challenges of recycling complex products, which contain a broad variety of interlinked metals and materials.”* [1]

With this newly developed XRF-Sensor, LLA Instruments GmbH addresses this problem. For this belt system sensor more sophisticated technology and task specific detection is used to provide more detailed information on the composition in shorter time than currently available technology. Due to this higher sensitivity, the separation efficiency is enhanced, and for the cases where the efficiency of currently available systems is already good enough, the throughput can be increased.

We present results of our 3 track test setup having a field of view of 3x (25 mm x 25mm) showing very good limits of detection (LOD) as a function of conveyor belt velocity, sample size and clearance. Major elements are still detected at belt velocities of 4 m/s (=> 5 ms measurement time), a 100 mm clearance and samples as small as 2 mm² Cu wires.

Introduction

The increasing demand for metals over the last decades has put permanent pressure on the natural resources and has lead to raising costs for raw metals. The global demand will keep rising especially in developing countries due to rapid industrialization but also in developed countries due to modern metal intensive technologies.

To ensure an appropriate supply while reducing the exploitation of our natural resources, secondary resources temporarily locked up in so called “urban-mines” have to be used. With the existing infrastructure common metals like steel, copper and aluminum can be recovered relatively easily as they are often used in simple parts. For example the recycling rate of steel can be greater than 90% for certain input streams while other metals like e.g. Ni and Cr are often lost in big amounts. Reck et.al.[2] have quantified the global amount of recycled Ni with 103 Gg/a (2005), which corresponds to only 13 % of the mined Ni quantity. Also big amounts of Cr are lost due to difficulties in separating ferritic stainless steel, with Cr concentrations between 10 % and 27 %, from unalloyed steel.

Modern technology systems are getting more and more complex with small amounts of ‘critical’ metals (Rare Earth Elements (REE), Platinum Group Metals (PGM),…) in electrical and electronic components (electrical and electronic waste (WEEE)) and non-traditional mixtures of elements as e.g. in aluminum-alloys or superalloys. As an example, a modern car contains next to main components as plastic and steel nearly all metals available since it integrates a broad range of metal containing products. The recycling rate of critical metals, as e.g. Nd, Pr… from magnets, Sn, Au… from circuit boards or Pt, Rh, Pd… from catalyzers, is low and often only possible by means of manual separation. [3,4]

A sustainable metal management therefore requires next to an efficient EoL collection of products a much more effective sorting, optimized physical separation and metallurgical technologies so that an economically viable recovery of metals from sorted recyclates can be achieved. This only works if the recycling approach moves away from a Material-Centric towards a Product-Centric approach. From a metallurgical point of view this means that the sorting has to be alloy specific which with the existing infrastructure for metal sorting is only partially possible. Metal sorting relied mainly on different magnetic and inductive properties of metals which is not sufficient anymore due to the use of more complex material mixtures and the development of new materials with non-traditional properties. Therefore, as stated in the UNEP report: *“Recycling systems need to adjust to the fact that recycling has become increasingly difficult due to the rising complexity of products.”*

State of the art technology for metal sorting is using X-ray transmission (XRT) to measure differences in the density of the materials (Al-alloys and steel) and X-ray fluorescence (XRF) to directly detect elements. A common application for XRF-sorting technology is the

removal of “meatballs” (Cu-coils of electro motors) from the ferrous steel fraction in car shredder plants.

Even though XRF-technology is capable to distinguish between different alloys, with the state of the art XRF-sorters this is only partially possible. For the newly developed XRF belt system sensor LLA Instruments GmbH uses more sophisticated technology and detection algorithms to provide this more detailed information in shorter time.

Goals and approach

The goal was to configure a sensor which is able to distinguish between different alloys or increase the content of a certain element (e.g. REE, PGM...) within a sorted fraction. Therefore the detection limits (LOD) have to be lowered to be able to detect the desired metals within the matrix.

The best way to lower the LOD is to increase the measurement time, giving better peak to background ratios (P/B) resulting in better LOD. Since long measuring times are economically unviable, the intensity of the fluorescence signal and the detection efficiency have to be increased.

Experimental setup

For test purposes a three track XRF detection system was build, consisting of three energy dispersive X-ray detectors and a high power X-ray source.

To increase the intensity of the fluorescence signal a water cooled high power X-ray tube was chosen as excitation source. This tube has a more than 10 times higher flux than air-cooled sources which are usually used in this sensor systems leading to a significant increase of the fluorescence signal. To handle the high countrate state of the art Silicon Drift Detectors (SDD) are used, which have an energy resolution around 200 eV even at countrates as high as 1 Mcps (Mega counts per second).

Figure 1 shows a picture of the three track setup including X-ray tube, detector array and the rotary table which was used to simulate different conveyor belt velocities. All tests shown in the following sections were carried out with this setup.

Figure 2 shows a bottom view of the detector array holding a slit mask. The broad slit in the back defines the area illuminated by the primary radiation which is 25 mm x 75 mm at a distance of 100 mm from the mask (100 mm clearance). The field of view of the detectors is restricted by three small slits to 25 mm (100 mm from the mask) not overlapping stripes (tracks) which together with the width of the illumination defines the resolution of 25 mm x 25 mm.

Figure 3 shows a sketch of the setup together with two objects and the paths of primary and fluorescence radiation.

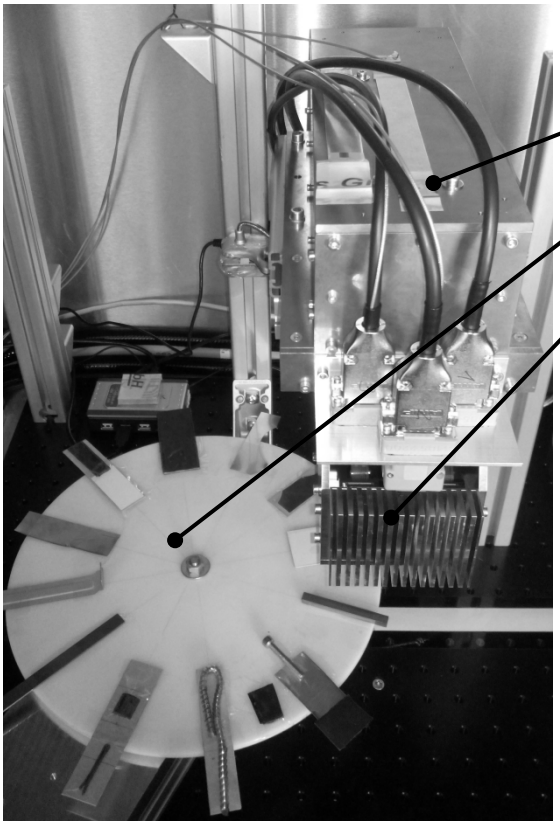


Figure 1 - Test setup with rotary table

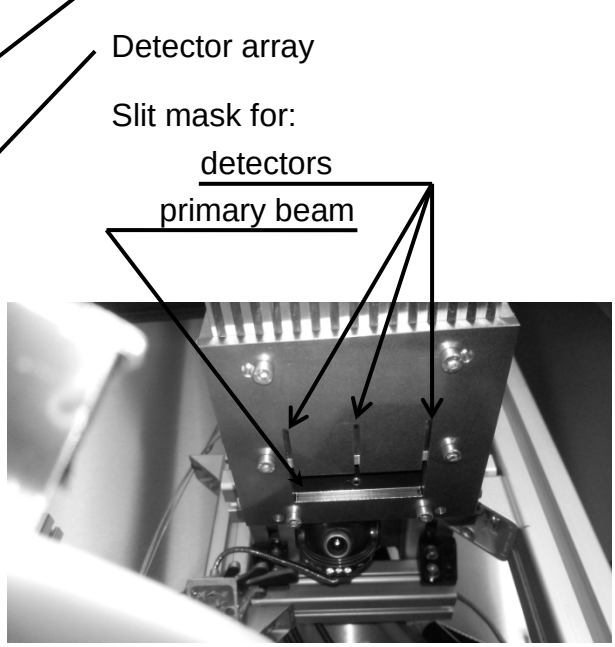


Figure 2 - Slit mask defining the field of view

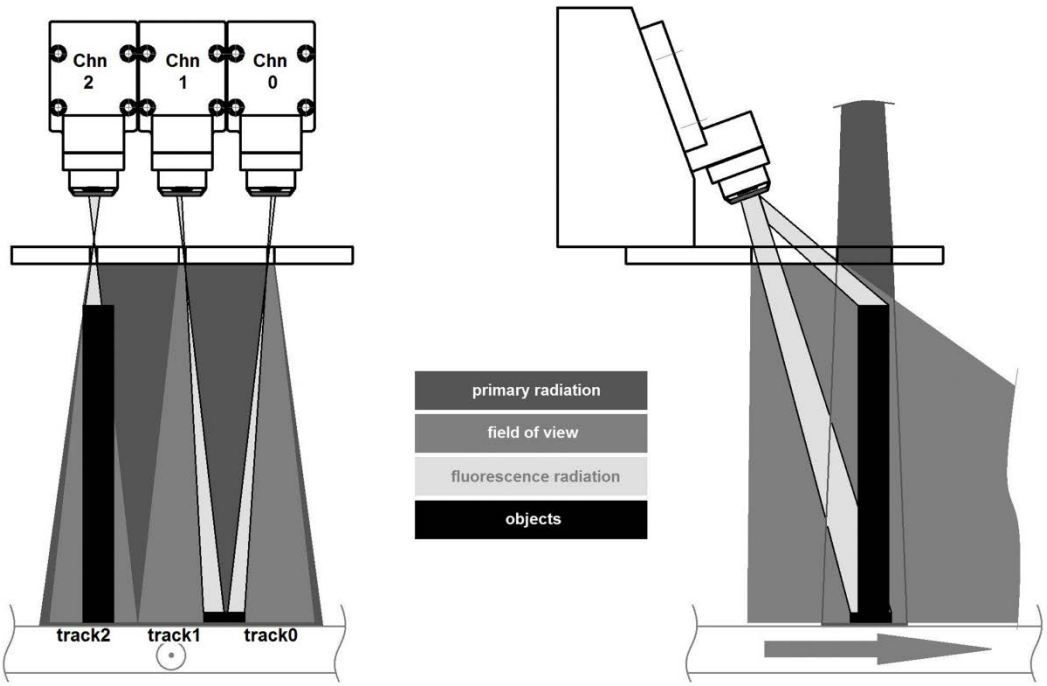
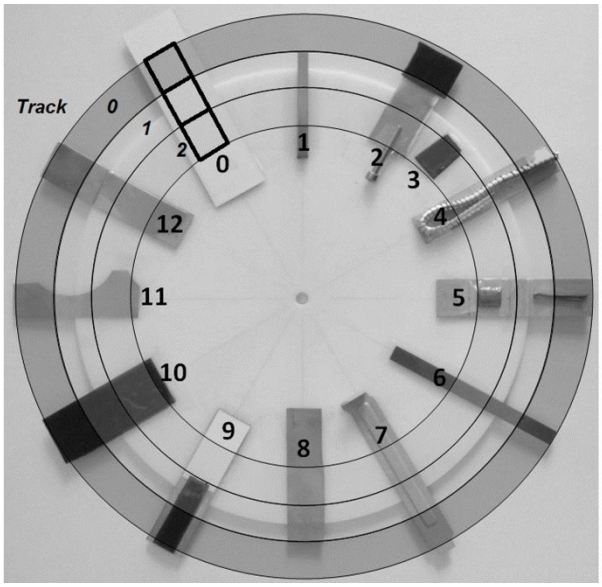


Figure 3 - Sketch of the setup showing the field of view and two extreme cases of samples

The samples mounted on the rotary table where chosen to represent a variety of different materials, shapes and sizes to give an overview for possible applications.



	track 0	track 1	track 2
0	fluor. screen	fluor. screen	fluor. screen
1	---	brass bar	brass bar
2	lead	Al-sheet	screw
3	---	lead	lead
4	brass swarf	brass swarf	brass swarf
5	Nd-magnet	Cu-wire	Cu-wire
6	Cu-bar	Cu-bar	Cu-bar
7	galv. steel	galv. steel	galv. steel
8	---	Cu-sheet	Cu-sheet
9	lead	lead	fluor. screen
10	lead	lead	lead
11	steel-sheet	steel-sheet	steel-sheet
12	Cu-sheet	Cu and steel	steel-sheet

fluor. - fluorescent screen contains tungsten
galv. - galvanized ... zinc coated

Elements: Cr, Mn, Fe, Co, Ni, Cu, Zn, Nd, W, Pb

Figure 4 - Rotary table with samples and sample description

Results and discussion

Long time measurements

Since the samples had an unknown composition, every sample of the rotary table was measured at first during 60 s to make an elemental qualitative analysis..

Figures 5 and 6 show spectra of the samples mounted on the rotary table. For each sample position the spectra for all three tracks and the regions of interest (ROI´s) for the strongest lines (Kα or Lα) of each element with a width of 200 eV are shown. The width was chosen taking in to account the energy resolution of the system at high countrates and avoiding as much as possible overlaps in the ROI´s of different elements as e.g. between Nd and Cr or W and Zn.Attention has to be paid to the fact that there are overlapping fluorescence lines as e.g. the fluorescent screen in pos0 contains just tungsten, but a sloppy detection might interpret other W-L-lines as Ni, Cu, Zn. Also the W-Lβ peaks at 9.67keV and 9.95keV could be misinterpreted as Ge (9.88keV), Au (9.71keV) and Hg (9.99keV).

The stainless steel screw in pos2 of track2 consists of Cr (16-19%), Mn (~6.5%), Ni (5-10%), Cu (1.7-2.2%) and Fe and even though Mn is present the concentration might be overestimated due to the overlap of the Cr-Kβ-line.

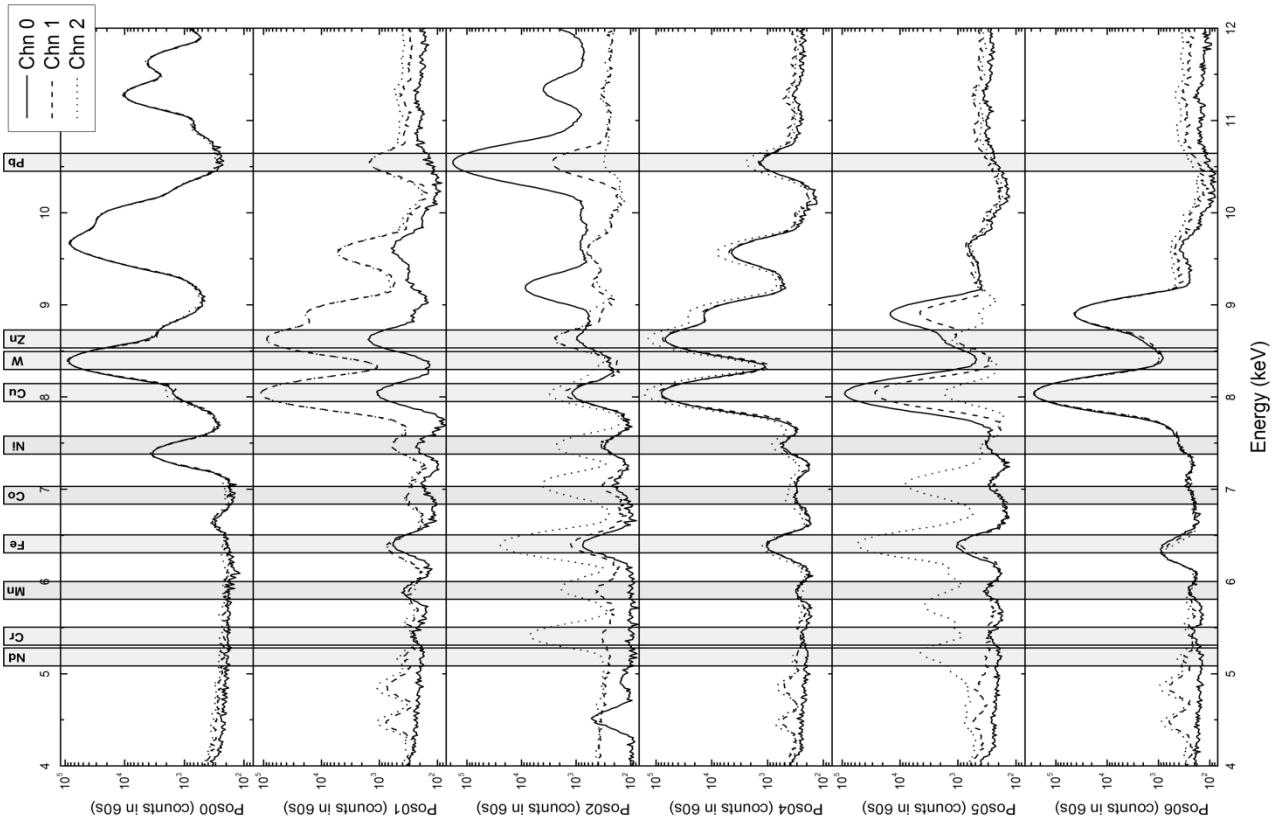


Figure 5 - Spectra of 60 s measurements of positions 0-2 and 4-6 including ROI´s for the main fluorescence lines of the present elements. (note the log-scale for the y-axis)

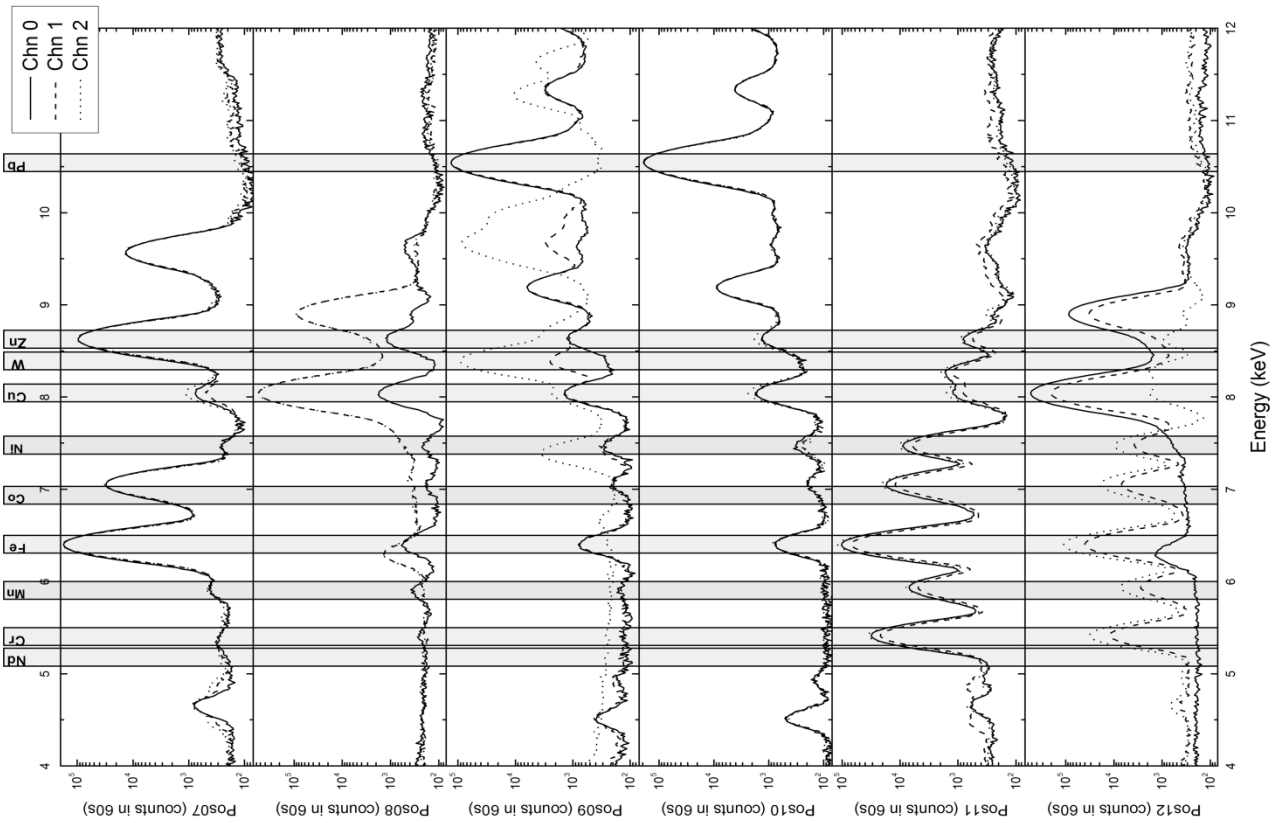


Figure 6 - Spectra of 60 s measurements of positions 7-12 including ROI´s for the main fluorescence lines of the present elements. (note the log-scale for the y-axis)

Simulation of different belt velocities

The measurements were conducted at different velocities with measurement times adapted to keep a resolution of 25 mm. Table 1 shows the simulated velocities for different rotating speeds, the middle track (#1) was designed to have a circumference of 1m, therefore all measurement results presented where taken from this track.

Table 1 – Circumferences and corresponding velocities

	Ø in mm	Circumference	0.5 rpm	1 rpm	2 rpm	3 rpm	4 rpm
Track0	368	1.16 m	0.58 m/s	1.16 m/s	2.32 m/s	3.48 m/s	4.64 m/s
Track1	318	1.00 m	0.5 m/s	1.0 m/s	2.0 m/s	3.0 m/s	4.0 m/s
Track2	268	0.84 m	0.42 m/s	0.84 m/s	1.68 m/s	2.52 m/s	3.36 m/s

The resolution was tested using the signal of a 3 mm thick Cu-wire. Spectra were acquiring continuously with a measument time of 10 ms while the Cu-wire was rotated at different velocities passing the sensor with 0.5, 1 and 2 m/s. Figure 7 shows the normalized Cu-signal

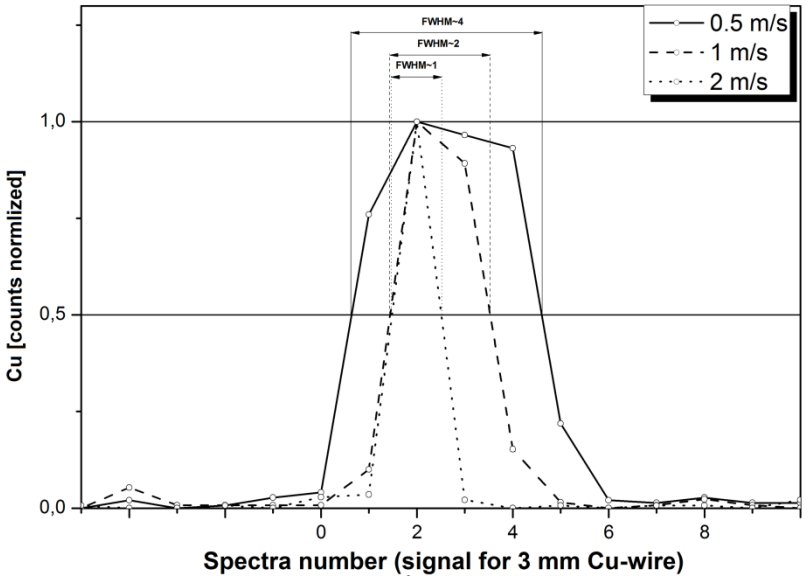


Figure 7 - Cu-signal from consecutive spektra at different velocities. 3 mm Cu-wire; measurment time 10 ms.

From the FWHM (Full Width Half Maximum) a resolution of:

5 mm for 0.5 m/s, 10 mm for 1 m/s and 20 mm for 2m/s

can be calculated.

The following figures show measurements of the full set of samples on the rotary table. For the characteristic elements of the samples the ROI data is plotted over time. The range of the x-axis is chosen to show 2 rotations of the table which for track1 represents a distance of 2 m.

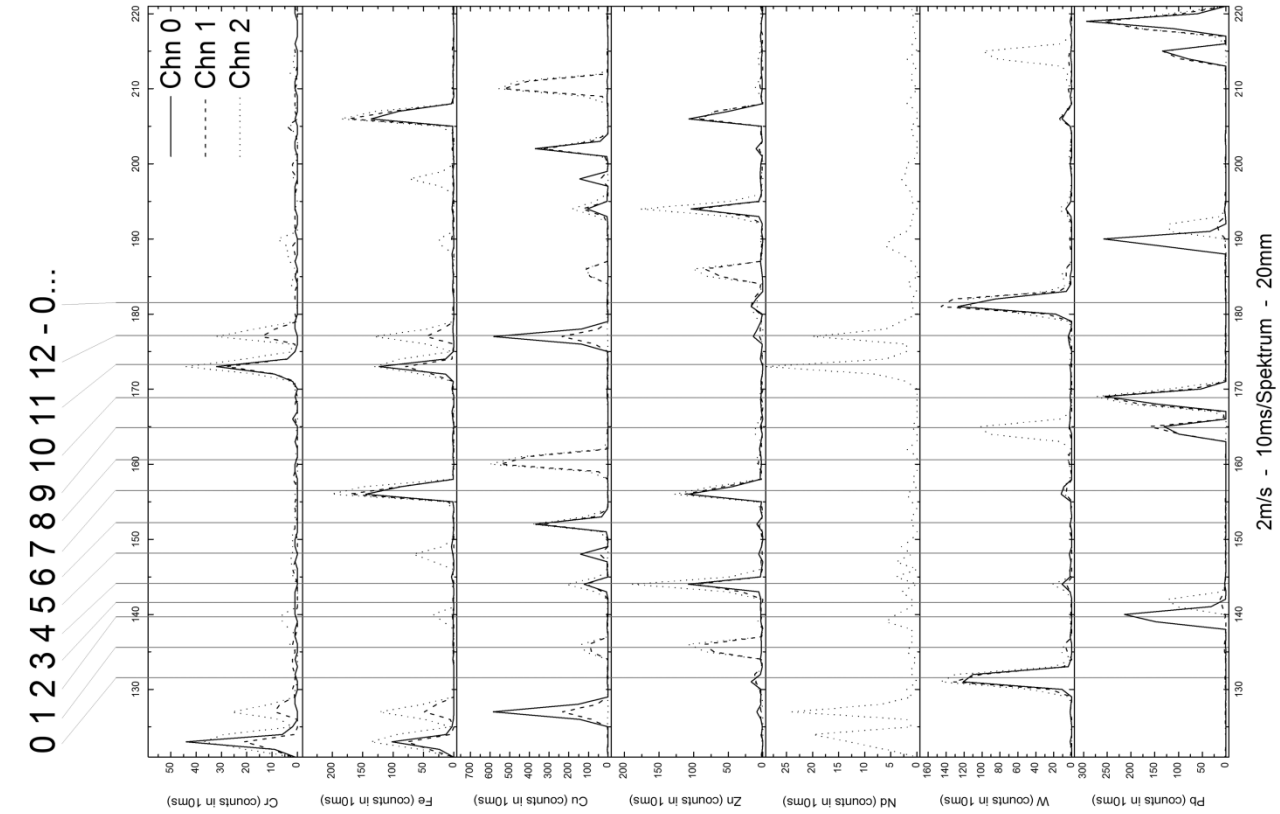


Figure 8 - ROI data of the present elements for 2 rotations with 10 ms measuring time per spectra and 2 m/s simulated belt velocity (total = 1 s).

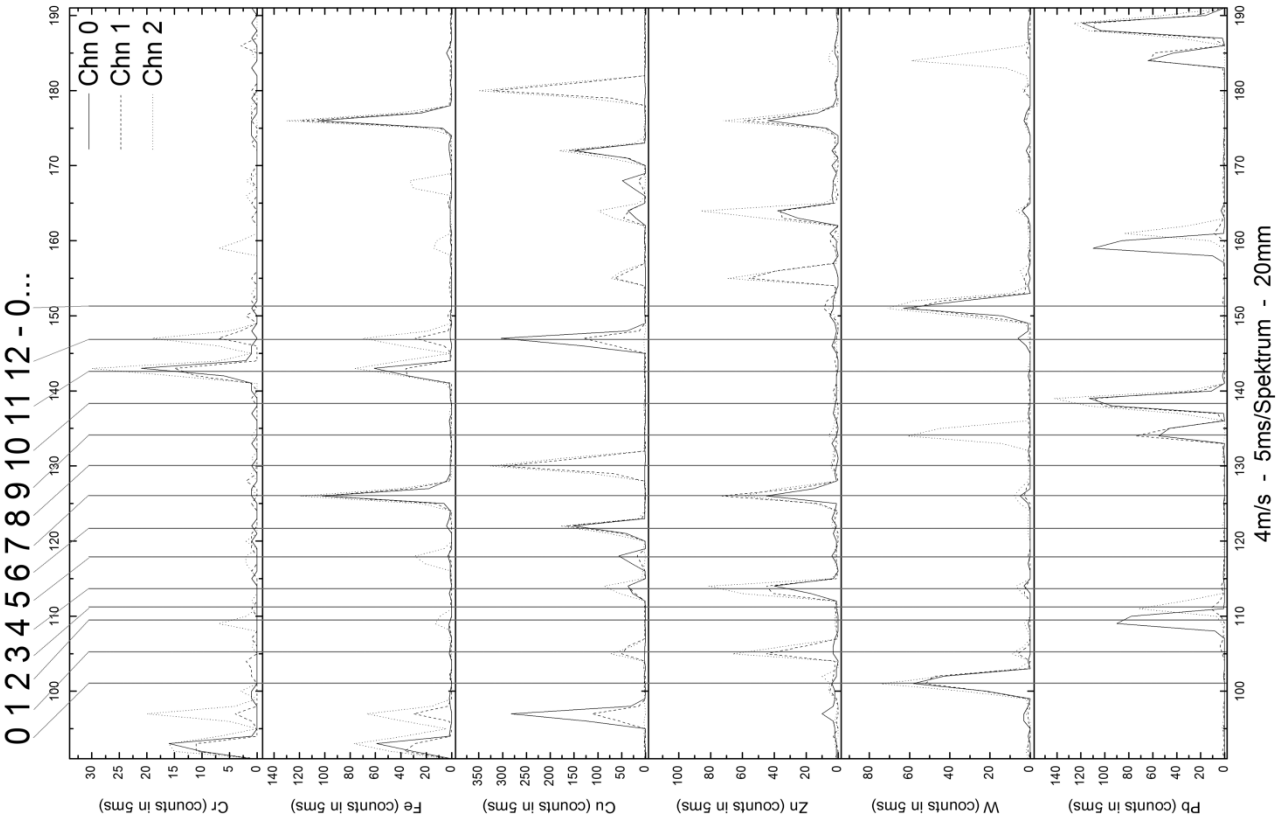


Figure 9 - ROI data of the present elements for 2 rotations with 5 ms measuring time per spectra and 4 m/s simulated belt velocity (total = 0.5 s).

Six different stainless steel samples were measured with the new sensor to test the sensitivity for different alloys. Figure 10 shows the spectra of the samples acquired with a measuring time of 10 ms and the ROI´s for the detectable elements. The first 5 samples were of known composition, which was measured with different independent methods. Table 2 shows the mean values of these measurements.

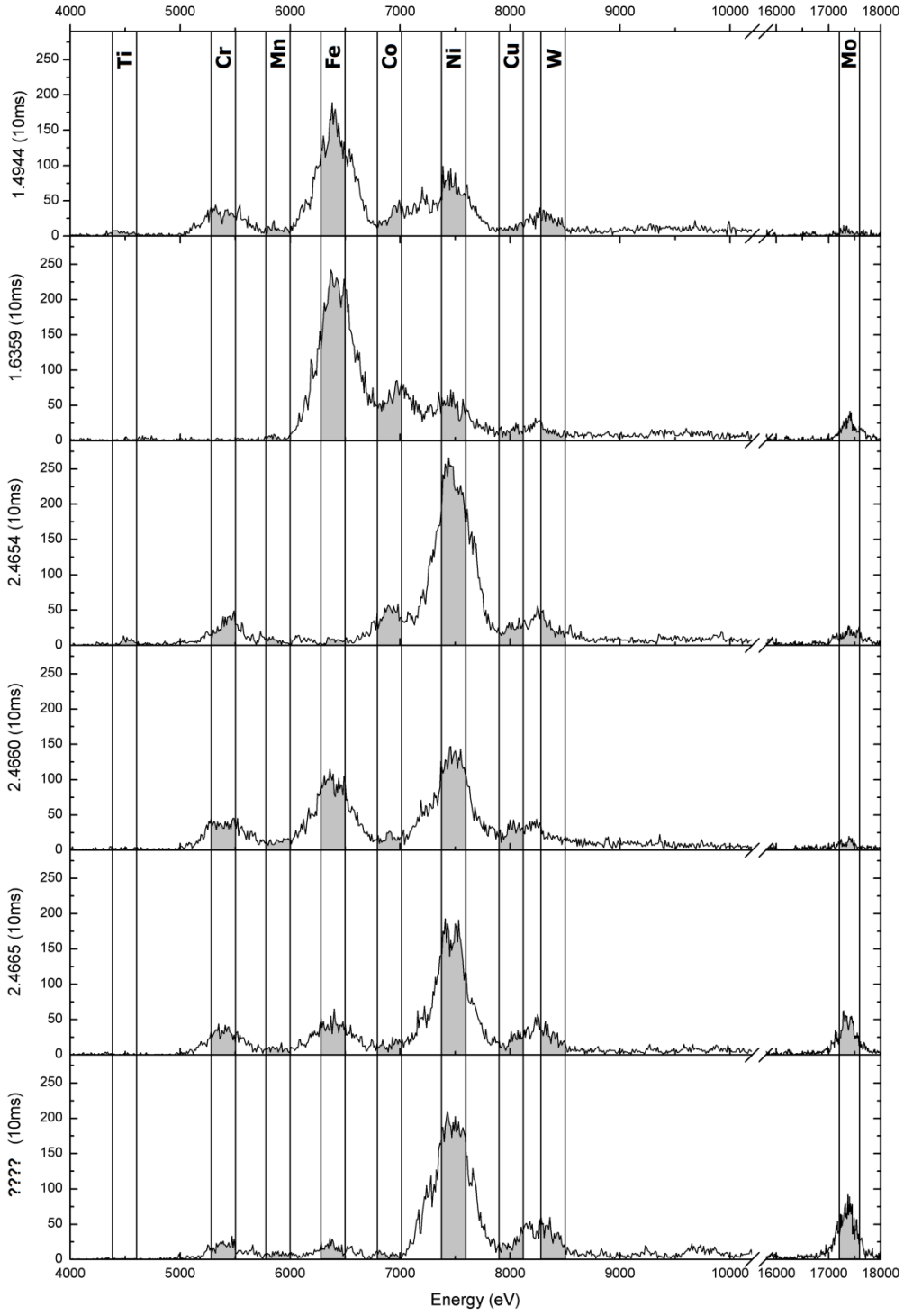


Figure 10 - Spectra from the steel samples acquired in 10 ms for 5 steel samples with known and one with unknown composition.

The values for the steel with the unknown composition (sample 6) are calculated values using the countrates from the samples with known concentrations as reference. Due to the low statistic the values have a big uncertainty, anyway a possible match was found with the stainless steel 2.4819.

Table 2 - Elemental composition of six different steel samples (values in weight-%)

sample\element	Si	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Nb	Mo	W
1.4944	0.20	2.06	0.24	15.07	1.91	53.93	0.16	25.10	0.01	0.04	1.26	0.01
1.6359	0.04	0.50	0.01	0.06	0.03	68.19	8.07	18.04	0.02	0.01	5.02	0.01
2.4654	0.04	3.06	0.03	19.37	0.02	1.13	14.01	57.71	0.01	0.05	4.47	0.1
2.4660	0.29	-	-	19.65	1.51	34.79	0.34	37.55	3.25	0.18	2.29	0.15
2.4665	0.21	-	-	21.55	0.43	17.66	0.90	49.25	0.10	0.03	9.10	0.77
more than ??? less than	**-**	**-**	**-**	***14 - 19***	**-**	***4 - 9***	**-**	***54 - 59***	**-**	**-**	***13 - 18***	***2 - 7***
?? 2.4819 ??	0.05	-	0.20	***15.90***	0.33	***5.87***	0.13	***57.85***	0.08	0.02	***16.20***	***3.37***

Conclusions

It was shown that the newly developed XRF belt system sensor using more sophisticated technology and detection algorithms is able to provide a more detailed information than currently available systems. Furhermore it was proven that even with measurment times of only 10 ms, which with 25 mm resolution corresponds to 2.5 m/s belt velocity, different steel alloys can be distinguished. The detection limits for the system are in the range of a few weight-% which given the short measurement times is a quite good value.

References

[1] Global Metal Flows Working Group of the International Resource Panel of UNEP.: *Metal Recycling - Opportunities, Limits, Infrastructure.* (http://www.unep.org/resourcepanel-old/Portals/24102/PDFs/Metal_Recycling-Full_Report_150dpi_130919.pdf)

[2] Reck, B. K. and Rotter V.S.: *Comparing growth rates of nickel and stainless steel use in the early 2000s.* In: *Journal of Industrial Ecology*. DOI 10.1111/j.1530-9290.2012.00499.x.

[3] Chancerel, P., Meskers, C.E.M., et.al.: *Assessment of precious metal flows during pre-processing of waste electrical and electronic equipment.* In: *Journal of Industrial Ecology*, 13 (5), 2009, pp. 791-810

[4] Hagelüken, C.; Meskers, C.E.M.: *Mining our computers - Opportunities and challenges to recover scarce and valuable metals from end-of-life electronic devices.* In: *Proceedings of Electronics Goes Green 2008*, Berlin, 7-10 September 2008, pp. 585-591