

# Non-Destructive Process Control during Recycling of Spent Photovoltaic Modules

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**Abstract:** With the progressive shortage of fossile energy carriers the search for renewable sources is increasingly urgent. National regulations as well as international agreements (e.g., the Kyoto Protocol) require future energy sources with long – term availability at moderate costs. Furthermore, no environmental pollutants shall be emitted during production, operation and waste treatment. One of the most promising techniques is the production of electrical energy by photovoltaic modules. In order to save material resources and avoid environmental pollution through undesirable landfill the recycling of waste modules is necessary. Both the glass carrier material and the photoactive converting layer (CdTe in this study) shall be re-used. Different techniques for separation of the components are currently under study. At different phases of these processes analyses for process surveillance and control have to be carried out, primarily to obtain information about the separation efficiency and the enrichment level of CdTe being the most valuable one of the materials involved.

Two methods were applied. First, energy-dispersive X-ray fluorescence spectrometry using a small and mobile device later to be used for on-site measurement and process control. Second, instrumental photon activation analysis using an electron linear accelerator as activating bremsstrahlung source. This method is intended to be used later for iterative intermediate characterisation of random samples for quality control. In this work, the feasibility of both methods for this task was studied.

Key words: Process control, X-ray fluorescence, radioactivation, radiation measurement

## Introduction

According to the EU Directives WEEE<sup>2</sup> and RoHS<sup>3</sup> the use of hazardous substances in electric/electronic devices has to be reduced stepwise to approximately zero level. Furthermore, a total recycling of nearly all materials involved is aimed. Thus, major attention is directed to avoidance of environmental pollution through combustion or landfill, to regain valuable material, to promote the development and use of renewable energy sources.

As compared to other energy producing techniques, photovoltaics (PV) is one of the most promising options:

- No emission of any matter into the environment during operation
- Extremely long operation period (estimated average: 25 years)
- Minimum maintenance, robust technique
- Aesthetic aspects

Drawbacks are:

- High energy consumption during production
- in some cases use of costly (e.g., indium) or hazardous (e.g., cadmium) materials

Nonetheless, the use of photovoltaics is rapidly increasing, and the respective market is developing accordingly.

Currently, two basically different converter materials of photovoltaic (PV) modules are in use, namely semiconductor silicon (to a greater extent) and thin-film compound semiconductors like CIS (copper, indium, sulfur) and CdTe. This work will focus on CdTe.

Preliminary studies were made regarding recycling techniques of these PV module types<sup>4,5</sup> and analysis of large amounts of electronic wastes<sup>6</sup> in the Federal Institute for Materials' Research and Testing in Berlin, Germany. The recovery strategy of valuable materials from spent PV modules is based upon well-established wet mechanical separation techniques such as floatation. Hence, large energy consumption and undesirable use of aggressive chemicals are avoided. One point of major importance within a sustainable recycling process is the environmental compatibility. In accordance to the agreements and directives mentioned above this means: Avoidance of use and, consequently, no emission of contaminants and reduction of energy consumption during production.

## Experimental

### *Separation techniques*

As yet, two different separation techniques are under consideration, namely first:

- Opening the spent module
- Separation of CdTe from the glass carrier by sand blasting
- Separation of CdTe from blast sand, glass cuttings etc. by floatation,

second:

- Crushing of the spent module with a hammer mill
- Separating CdTe from the fragments by abrasion in a gyro-wheel mixer using abrasive agents, e.g. silicon carbide
- Separation of CdTe from the tailings (glass carrier fragments, cuttings, abrasives etc.) by sieving. The material was divided into several grain size range fractions by stepwise sequential sieving so as to obtain separation efficiency values as a function of the grain size of the crushed material.

The separation efficiencies of both approaches were determined using radioanalytical methods.

### **Characterisation methods**

Two different methods were applied for the analytical investigations, namely energy-dispersive X-ray fluorescence spectroscopy (EDXRS) and instrumental photon activation analysis (IPAA). Later, EDXRS will be applied for continuous on-site process control since the hardware is handy, easy to use and easy to move to different locations of operation. In this work, however, the application of EDXRS for the determination of the separation efficiency of the preliminary laboratory-scale floatation experiments will be described. IPAA was applied in both separation approaches.

*EDXRS* Samples from the floatation experiments lay before as fine powder batches. These were brought into cylindrical PE vessels of 2 cm inner diameter which were equipped with thin (ca. 20  $\mu\text{m}$ ) PE-foil windows to allow soft X-rays to escape. Both a radionuclide source (<sup>241</sup>Am) and an X-ray tube (HVmax: 140 kV; 50 kV at minimum current was selected for the XRF experiments) were sequentially used for excitation. A small, Peltier-element

cooled CdTe detector connected with a miniature pulse processing system was used for spectrum collection. This spectrometer was small and mobile, and it could be operated without external power supply, controlled by a small notebook computer. See Ref<sup>7,8</sup> for more details. At radionuclide excitation, the exposure periods ranged from 5 min to 20 min. Using the X-ray tube a standard exposure period of 30 s was sufficient (Fig. 1)

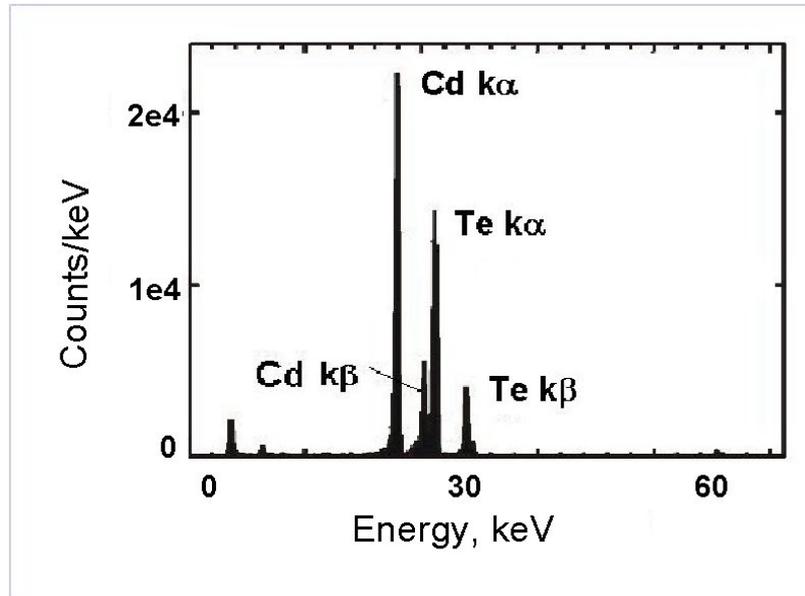


Fig. 1: XRF spectrum of CdTe-containing blast sand

*IPAA* During the separation experiments, the yields of the grain size fractions were largely different. Thus, respectively different amounts of sample material were available for analysis. The IPAA procedure of small samples will not be discussed here. A detailed description can be taken out of Ref.<sup>8</sup>. This paper will focus on IPAA of the large sample batches.

In contrast to XRF, IPAA will be applied for intermediate quality control analysing random samples. The mechanism of this method is similar to that of the more widely propagated reactor neutron activation analysis (INAA). The sample is exposed to high energy bremsstrahlung of an electron linear accelerator. 30 MeV bremsstrahlung of the accelerator of the Federal Institute of Materials' Research and Testing in Berlin, Germany (BAM LINAC) was used. Atoms of the respective analytes undergo photonuclear reactions during photon bombardment whereby normally neutron-deficient radionuclides are produced.

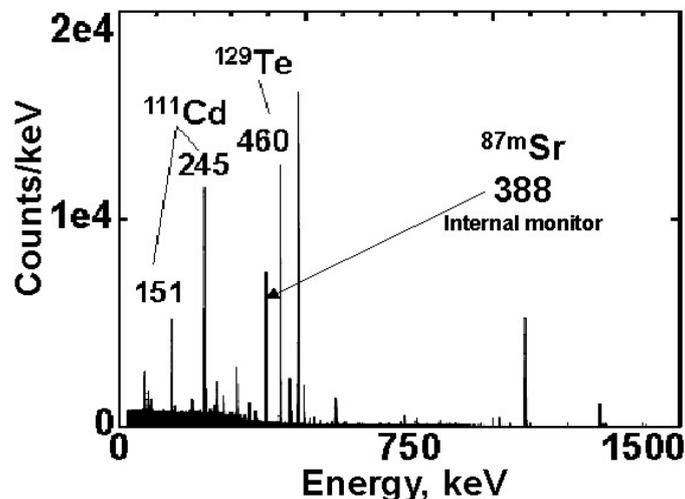


Fig. 2: Photon activation analysis of blast sand –  $\gamma$ -spectrum of product nuclides

After bremsstrahlung exposure, the characteristic  $\gamma$ -radiation of the product nuclides is measured (see Fig. 2) with a high resolution photon spectrometer equipped with a large volume germanium diode. For more details of this method the reader might refer to Ref.<sup>9</sup>. In Tab. 1, the nuclear reactions and the respective nuclear data are given. There are two spectroscopical options to select from: One can use either the short-lived ( $^{111}\text{Cd}$  and  $^{129}\text{Te}$ , respectively) or the long-lived ( $^{115}\text{Cd}/^{115\text{m}}\text{In}$  and  $^{121}\text{Te}$ , respectively) product nuclides for evaluation.

**Tab. 1:** Photoreactions of the elements under study

Element	Reaction	Half-life	$\gamma$ -Energy, keV
Cd	$^{112}\text{Cd}(\gamma, n)^{111\text{m}}\text{Cd}$	49 m	245
	$^{116}\text{Cd}(\gamma, n)^{115}\text{Cd}$	53,38 h	527
	$^{115}\text{Cd}(\beta)^{115\text{m}}\text{In}$	53,38 h	336
Te	$^{130}\text{Te}(\gamma, n)^{129}\text{Te}$	69,6 m	460
	$^{122}\text{Te}(\gamma, n)^{121}\text{Te}$	16,8 d	574
Sr	$^{88}\text{Sr}(\gamma, n)^{87\text{m}}\text{Sr}$	2,81 h	388

During preliminary experiments it turned out that the short-lived product nuclides offer more advantage; due to their half-lives and the extremely high respective photonuclear cross-sections high specific activities are induced, hence exposure and counting periods could be kept short. Thus, a high throughput can be achieved in the routine case. Moreover, by short exposure times no long-lived radioactivity at significant level is produced in the material; after several days, samples can either be treated as non-active waste or undergo further experiments.

In activation analysis, IPAA in particular, the uniformity of the activating dose received by the sample and the calibration material is crucial. The activating bremsstrahlung beam exhibits a pronounced radial flux and energy gradient and a slight but significant flux gradient. Therefore, careful monitoring of the activating radiation dose is necessary. This can be done by metal foils inserted in front and behind each material sample in the stack<sup>9</sup> or with the help of an internal monitor. This might be an inherent (a component of the matrix with well-known content) or an additive one (an element that is added to both the sample and the calibration material). In this work, a matrix-inherent internal monitor was applied in the analysis of the material from the hammer mill approach, namely the glass carrier-inherent strontium. Scandium was used as an additive monitor in the analysis in the floatation experiments. The  $\gamma$ -signals emitted by the product nuclides of the internal monitor can be used for corrections of systematic errors due to activating photon flux gradients. These corrective measures are required in particular when analysing large sample volumes. For more details about internal monitors in IPAA the reader might refer to Ref.<sup>10</sup>.

*The study of large samples* The operation procedure of both methods needed to be modified as compared to the classical application modes since large volumes of sample material had to be analysed. This was necessary because of the pronounced inhomogeneity of the sample material. To avoid processing of excessively large numbers of samples the representativeness of the analytical results had to be achieved through analysis of large sample masses. In case of EDXRS this was realised by opening the spatial angle of the exciting beam so as to

comprise a larger sample area. In IPAA, a broad activating radiation field was produced. The BAM LINAC is equipped with an electron beam scanner which guides the electron beam meander-shaped over the bremsstrahlung converter (“TV-screen principle”), thus producing a large-volume bremsstrahlung field. By this means it is possible to activate large samples with volumes up to several litres<sup>9</sup>. In the second phase separation approach (“Hammer mill experiment”) the typical single sample mass was ca. 100 g -150 g; the masses of the entire sample stacks ranged between 1 kg and 1.5 kg.

*Procedure* The calibration material was synthesised from glass powder matrix doped with ultrapure CdTe to make a concentration of 0.5 mass-% CdTe. Samples of the different grain size fractions and a batch of the calibration material were brought into cylindrical PE vessels of 10 cm in diameter allowing 100 ml volume for each sample respectively 10 ml for the calibration material. Several sample batches (up to five) were stacked to a cylinder package of up to 25 cm height. This was irradiated in coaxial geometry with 30 MeV bremsstrahlung. The exposure period was 10 min. After a cooling period of one hour the samples were measured with standard high-resolution photon spectrometers. Spectra were collected for 15 min. Following this procedure, up to ten samples per day could be analysed, the sample preparation not included.

## Results and discussion

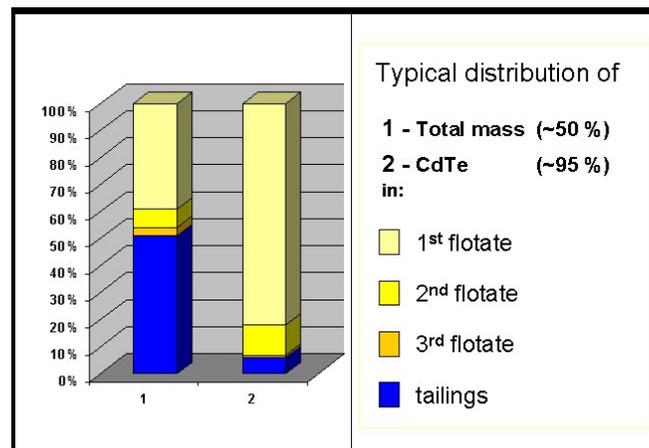
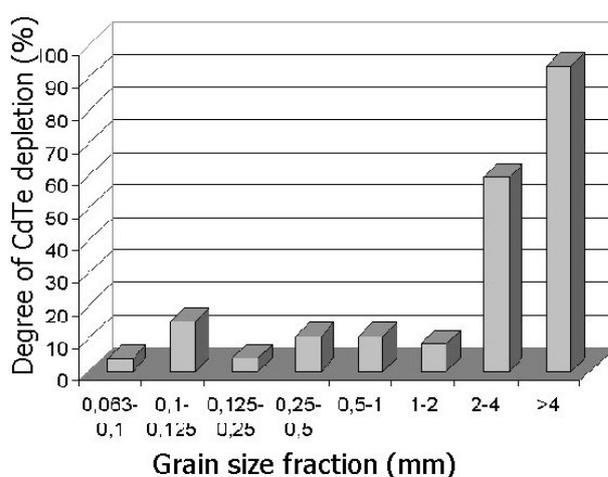


Fig. 3: Separation efficiency of floatation

1 – The potential of a three-step floatation process to separate CdTe from the other material components is presented in Fig. 3. In the right hand column the distribution of CdTe between the floatate and the tailings is displayed. Ca. 95 % transfer of CdTe from the initial mixture (CdTe, blast sand, glass cuttings etc.) into the floatate indicates, regarding CdTe only, a quite good separation efficiency of the floatation process. The left column, however, dulls this impression significantly; it shows the distribution of the total initial mass between floatate and tailings. About 50 % of the total mass is transferred into the floatate, and the content of CdTe, depending upon the different operation parameters of the Floatation process, amounts up to several tens of per cent. Thus, the enrichment factor:

$$F_e = \frac{\text{Mass fraction of CdTe in the floatate}}{\text{Mass fraction of CdTe in the original material}}$$

is by far insufficient; for re-use a purity level of at least 5N is required.



**Fig. 4:** Separation efficiency of gyrowheel treatment

2 – In Fig.4, the result of the “Hammer mill experiment” including gyrowheel treatment is displayed. CdTe was separated quite efficiently from the large grains of the glass carrier material; the fraction >4 mm was depleted from CdTe to nearly 100 %. However, the depletion rate dramatically decreases at smaller grains. All in all, more than 60 % of the total mass is transferred into the concentrate which contains about 10 % of CdTe. Thus the result of this separation experiment is even poorer than that of the floatation procedure. Moreover, the concentrate also contains the total batch of the fine-grain SiC added to serve as an abrasive.

### Analytical quality control

Since no certified reference material whose complies with the composition of the material under investigation has been available the quality control had to be performed by comparative analysis of selected and well-prepared material batches from the process studied. The analytical methods applied were: IPAA, XRF and ICP-OES. The results are compiled in Tab. 2. Most of the values stand in satisfactory agreement.

**Tab. 2:** Comparison of results; values in mass-%

Sample	PAA	EDXRS	ICP-OES	expected
Std1	0.99 (0.05)*	1.03 (0.07)	1.01 (0.04)	0.995**
Std3	1.97 (0.09)	2.01 (0.12)	2.04 (0.07)	2.08
Std4	2.45 (0.11)	2.39 (0.10)	2.30 (0.08)	2.38
Std6	3.91 (0.18)	4.00 (0.23)	3.79 (0.21)	3.88
Dust1	3.97 (0.22)	3.99 (0.20)	3.94 (0.23)	---
Conc1	10.42 (0.36)	9.78 (0.49)	9.85 (0.31)	---

\*from preparation (Std 1...6: synthetic calibration samples for EDXRS

\*\*Values in brackets:  $1\sigma$  S.D. of the single value from at least 6 determinations

## Conclusions and outlook

A two-fold conclusion can be drawn from this study and its respective results. First, it was shown that both analytical methods applied are well suitable for the analytical tasks within the process described. Second, the results of both separation experiment procedures are poor. However, recently another approach was started, namely “non-destructive” both in opening the glass carrier and separating of the CdTe layer using special microemulsions. The first preliminary experiments were performed, and their results give rise to optimism.

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