

# Analysis of Coatings and Layers using the ARL QUANT'X EDXRF Spectrometer

Pascal Lemberge, Thermo Fisher Scientific  
Ecublens, Switzerland

## Introduction

XRF is probably best known and most appreciated for the fast, precise and accurate elemental analysis in industrial production control of building materials, slags, metals and petrochemical products. For all these applications, samples are expected to be homogeneous, flat and usually infinitely thick with respect to the penetration depth of X-rays.

Homogeneity is crucial because the detected X-rays typically originate from the first few microns below the surface of the material.

However, being in essence a surface analysis technique XRF is also used for the analysis of coatings, layers or thin films on a substrate; samples which are – by definition – not homogenous. In this case, the characteristic line intensity changes with thickness of the layer containing the element. This principle is illustrated in figure 1.

## Instrumentation

The ARL QUANT'X EDXRF spectrometer used for this application is a compact benchtop analyzer with a spacious sample chamber allowing the analysis of larger and irregular samples. It's equipped with the latest generation of Silicon Drift Detector (SDD) and a 50 kV, 50 W rhodium or silver target X-ray tube. The peak-to-background for elements from F to Am is optimized by a set of nine specially designed filters and ensures that the ARL QUANT'X spectrometer can be easily adapted per application or element range.

The instrument can also be equipped with a camera to assist in positioning the sample as well as a range of collimators to adjust the beam diameter.

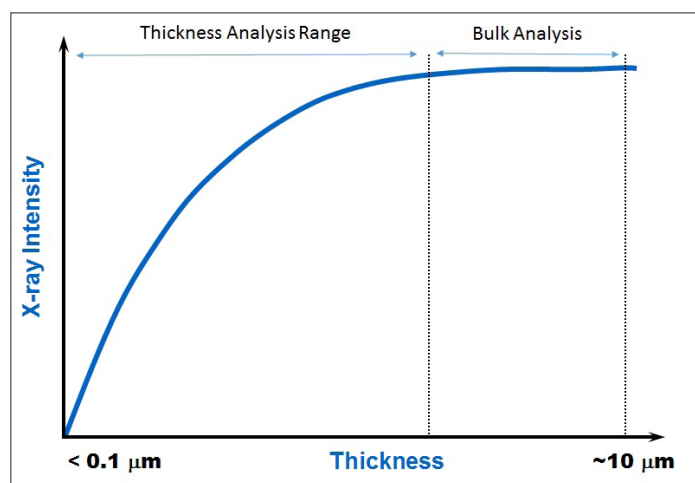
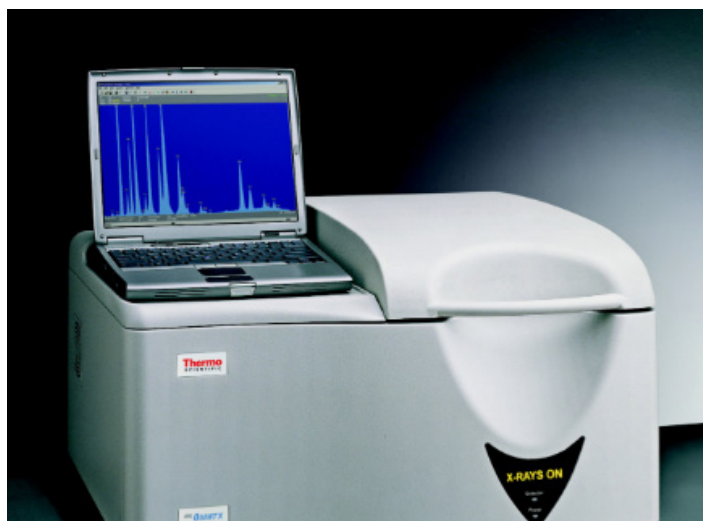


Figure 1: Thickness and bulk analysis with XRF

Applications

Coatings are used in manufacturing to improve product characteristics achieving a better performance, often combined with a reduction in cost. Coatings are mainly applied to improve corrosion and wear resistance. Examples are coatings on metal substrates such as a zirconium (Zr) on aluminium (Al) or zinc (Zn) and tin (Sn) coatings on steel. A protective coating on a metal can also be an oxide or nitride such as TiN. In such cases it is important that at least one element in the coating is detectable with XRF. In a Tin coating this would be Ti and the thickness of the coating is determined by measuring titanium. The substrate doesn't have to be a metal. Coatings can also be applied on glass. Another common example would be the application of a silicon (Si) coating on paper or plastic.

Layer analysis isn't restricted to one layer only. A stack of layers on a substrate can also be analyzed as long as there's one unique element per layer. Applications can be found in the electronics and semiconductor industries.

In this application note, we show two applications: zirconium on aluminium and the analysis of CIGS solar cells.

1. Zirconium on aluminium

Zirconium conversion coatings are applied on aluminium to improve corrosion resistance and is preferred over chromate. The latter posing health and environmental issues.

A calibration is set up using a total of 20 standards with Zr coating thicknesses covering a range from 2 to 20 mg/m². The Zr Kα line is used allowing for an analysis in air. The measurement time equals 60s live time. To improve the signal-to-background ratio a thick palladium (Pd) primary beam filter is used.

2. CIGS solar cells

Copper Indium Gallium Selenide (CIGS) is a direct bandgap semiconductor used in the manufacturing of solar cells. Because CIGS strongly absorbs sunlight, less material is required than for other semiconductor materials and this has led to the production of thin-film photovoltaics. The structure of a CIGS thin film solar cell is shown in figure 3.

CIGS solar cells are analyzed as such without any sample preparation other than – when necessary - cleaning the surface of the cell. Table 1 shows the excitation conditions used for this application. As light elements are not present all measurements can be run in air. A measurement time of 30s per condition will generate element characteristic peak intensities of several thousand counts.

For the determination of both thickness and elemental composition of each layer we used the thin film quantification method based on fundamental parameters (FP) included with the Thermo Scientific WinTrace QUANT'X EDXRF software. This package only requires input about the number of layers and the elements present in each layer. Any information about thickness or concentration is not required.

The calibration curve is shown in figure 2. An excellent correlation coefficient of 0.993 is obtained. The average error (RMSE) over the entire thickness range is around 0.3 mg/m².

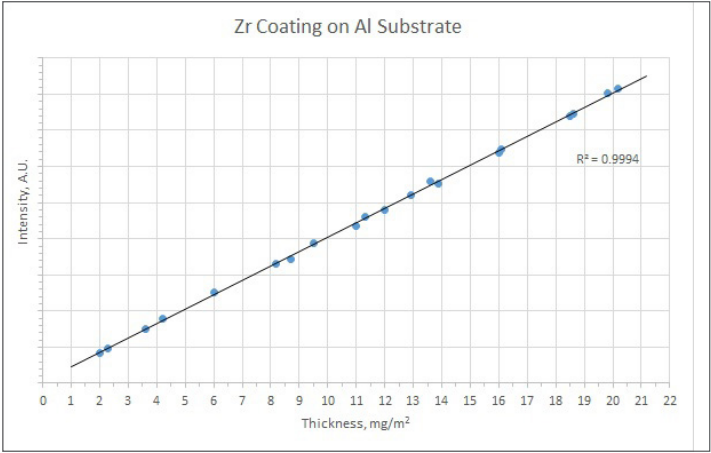


Figure 2: Calibration curve for Zr coating thickness on Al



Figure 3: Typical CIGS multilayer

Table 1 – EDXRF excitation conditions for CIGS analysis

| Voltage [kV] | Filter   | Atmos-phere | Live time [s] | Elements of Interest |
|--------------|----------|-------------|---------------|----------------------|
| 30           | Pd Thick | Air         | 120           | Cu, Ga, Se           |
| 50           | Cu Think | Air         | 120           | In, Mo               |

Calibration is done using bulk samples of Cu, Ga<sub>2</sub>O<sub>3</sub>, SeO<sub>2</sub>, Mo and In as well as thin film standards for each element at a concentration of ~50 µg/cm<sup>2</sup> each. Table 2 shows the analysis and repeatability results of a typical CIGS solar cell. This particular cell was not covered with a transparent front contact explaining the absence of any Cd and Zn (see also figure 3).

The repeatability of the instrument was tested by analyzing both samples 10 times in a row. At a relative error of 0.5% or less, the repeatability of the layer thickness determination is excellent. Relative errors on the concentrations are below 1% for all elements (when present) except for Ga (1.5%).

**Table 2: CIGS analysis results**

| Sample Run Nr | CIGS layer |        |        |        |        | Mo layer |        |
|---------------|------------|--------|--------|--------|--------|----------|--------|
|               | CIGS (µm)  | Cu (%) | Ga (%) | Se (%) | In (%) | Mo (µm)  | Mo (%) |
| CIGS A 01     | 1.292      | 16.26  | 5.90   | 49.91  | 27.92  | 0.925    | 100.00 |
| CIGS A 02     | 1.303      | 16.42  | 5.74   | 49.92  | 27.92  | 0.922    | 100.00 |
| CIGS A 03     | 1.289      | 16.17  | 5.82   | 49.70  | 28.31  | 0.922    | 100.00 |
| CIGS A 04     | 1.294      | 16.22  | 5.91   | 49.60  | 28.28  | 0.922    | 100.00 |
| CIGS A 05     | 1.293      | 16.26  | 5.79   | 50.10  | 27.86  | 0.934    | 100.00 |
| CIGS A 06     | 1.295      | 16.38  | 5.90   | 49.76  | 27.96  | 0.924    | 100.00 |
| CIGS A 07     | 1.298      | 16.31  | 5.91   | 49.66  | 28.12  | 0.927    | 100.00 |
| CIGS A 08     | 1.301      | 16.04  | 5.71   | 49.72  | 28.54  | 0.926    | 100.00 |
| CIGS A 09     | 1.290      | 16.24  | 5.84   | 49.71  | 28.22  | 0.934    | 100.00 |
| CIGS A 10     | 1.294      | 16.29  | 6.02   | 49.98  | 27.71  | 0.931    | 100.00 |
| Average       | 1.295      | 16.26  | 5.85   | 49.81  | 28.08  | 0.927    | 100.00 |
| 1-Sigma       | 0.005      | 0.11   | 0.09   | 0.16   | 0.25   | 0.005    | 0.00   |

## Conclusion

A benchtop EDXRF analyzer such as the ARL QUANT'X combines flexibility in sample presentation with reliable and precise performance. Both straightforward coating applications as well as complex multilayer stacks can be handled.

Find out more at [thermofisher.com/xrf](https://thermofisher.com/xrf)

For Research Use Only. Not for use in diagnostic procedures. © 2018 Thermo Fisher Scientific Inc. All rights reserved. All trademarks are the property of Thermo Fisher Scientific and its subsidiaries unless otherwise specified. **XRAN41918 1018**

**ThermoFisher**  
SCIENTIFIC

**Africa-Other** +27 11 570 1840  
**Australia** +61 3 9757 4300  
**Austria** +43 1 333 50 34 0  
**Belgium** +32 53 73 42 41  
**Canada** +1 800 530 8447  
**China** +86 10 8419 3588  
**Denmark** +45 70 23 62 60

**Europe-Other** +43 1 333 50 34 0  
**Finland/Norway/Sweden**  
+46 8 556 468 00  
**France** +33 1 60 92 48 00  
**Germany** +49 6103 408 1014  
**India** +91 22 6742 9434  
**Italy** +39 02 950 591

**Japan** +81 45 453 9100  
**Korea** +82 2 3420 8600  
**Latin America** +1 561 688 8700  
**Middle East** +43 1 333 50 34 0  
**Netherlands** +31 76 579 55 55  
**New Zealand** +64 9 980 6700  
**Russia/CIS** +43 1 333 50 34 0

**South Africa** +27 11 570 1840  
**Spain** +34 914 845 965  
**Switzerland** +41 21 694 71 11  
**UK** +44 1442 233555  
**USA** +1 800 532 4752