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THICKNESS DETERMINATION OF COATINGS BY X-RAY FLUORESCENT ANALYSIS USING A CALIBRATION CURVE OBTAINED BY CALCULATIONS

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Abstract. When measuring a coating thickness by X-ray fluorescent analysis, the preliminary calibration of the detection system is required using reference samples with a known coating thickness. This operation is quite time-consuming and gives results only for a certain detection system and a pair of elements (the base material and coating). In our study, the calibration curve has been obtained by the Monte Carlo calculation method using the MCC 3D software. In so doing, we calculated the dependences of the ratios of peak intensities of fluorescence lines from Fe K_α (substrate) and Zn K_α (coating), as well as Cu K_α (substrate) and Au L_α (coating) on the values of coating thickness. Moreover, the coating thickness determination errors were obtained. A conclusion was made about the possibility of using the Monte Carlo method to determine the coating thickness without preliminary calibration.

Keywords: X-ray fluorescence analysis, thickness, substrate, thin film, simulation, Monte Carlo method

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ОПРЕДЕЛЕНИЕ ТОЛЩИНЫ ПОКРЫТИЙ МЕТОДОМ РЕНТГЕНОФЛУОРЕСЦЕНТНОГО АНАЛИЗА С ИСПОЛЬЗОВАНИЕМ ГРАДУИРОВОЧНОЙ ЗАВИСИМОСТИ, ПОЛУЧЕННОЙ РАСЧЕТНЫМ ПУТЕМ

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Аннотация. При измерении толщины покрытия методом рентгенофлуоресцентного анализа (РФА) требуется провести предварительную калибровку системы регистрации на эталонных образцах с известной толщиной покрытия. Такая операция занимает довольно много времени и дает результат лишь для определенной системы регистрации и пары элементов (базового материала и его покрытия). В настоящей работе калибровочная кривая определена расчетным методом Монте-Карло с использованием программы MCC 3D. Так были получены зависимости отношения интенсивностей линий флуоресценции Fe K_α (подложка) и Zn K_α (покрытие), а также Cu K_α (подложка) и Au L_α (покрытие) от значений толщины покрытий. Кроме того, рассчитаны погрешности определения толщины покрытий и сделан вывод о возможности применения метода Монте-Карло для расчета толщины покрытия без предварительной градуировки. Помимо этого, были рассчитаны оптимальные углы установки детекторов относительно нормали для расчета толщины покрытия методом РФА.

Ключевые слова: рентгенофлуоресцентный анализ, покрытие, подложка, тонкая пленка, симуляция Монте-Карло, градуировочная зависимость

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Introduction

Applying coatings to various surfaces and controlling their thickness are important challenges for many industries. The composition and thickness of coatings are determined using ultrasonic testing, eddy-current testing, X-ray fluorescence analysis (XRF), and electron microscopy. Each of the methods has its own advantages and disadvantages [1]. For XRF analysis of coating thickness, the layer order must be known and a calibration sample must be available.

The goal of this study is to develop a method for determining the coating thickness by the Monte Carlo method [2]. Using this method, we established the exposure time required for X-ray irradiation of the sample to determine the coating thickness with the required accuracy.

Zinc coatings on iron and gold coatings on copper were chosen as test pairs because they are the most common. Galvanizing steel, i.e., coating the metal with a layer of zinc that blocks

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moisture and oxygen, protects steel from corrosion and is widely used to rust-proof steel products. Gold plating is most often applied to copper products in the jewelry industry, as well as for decorative design and for creating and restoring works of art [3]. Although alloys rather than pure metals are used in practice, we considered the simplest systems: Zn–Fe and Au–Cu.

Experimental samples and procedures

The key dependences and exposure times were determined using Monte Carlo simulations performed with the certified MCC 3D software [4–6]. This software has passed metrological certification, so the results obtained with it should be considered reliable.

The source used to irradiate the sample was modeled using the spectrum of an X-ray tube with a transmission rhodium anode and a 127 μm beryllium window operating at 30 kV (an equivalent of the Moxtek Magnum). In contrast to [7–10], where an experimental spectrum of the X-ray tube was used as the irradiation source, we simulated the X-ray spectrum by the Monte Carlo method.

The X-ray tube model used is shown in Fig. 1. The simulation was performed for a tube with a collimator; the diameter of the generated photon beam at the sample was 2 mm, the radiation intensity was $I = 1.26 \cdot 10^7$ photons/(s·μA).

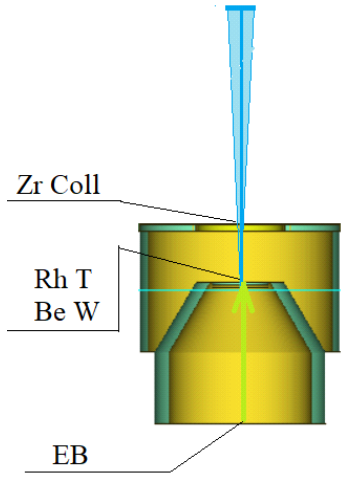


Fig. 1. Model of collimated X-ray tube used in the simulations:
zirconium collimator Zr Coll, rhodium target Rh T, beryllium window Be W, electron beam EB; the generated photon beam is shown as a blue cone

The detector in the study was a simulation model of an Amptek detector with a 500 μm crystal and a 12.7 μm beryllium window.

Determination of optimal detector angle relative to the normal for calculating the coating thickness

To find the optimal detector angle, we considered a system with the following arrangement: X-rays from the source struck the sample at a right angle, and the flux of fluorescence photons was recorded by ring detectors (to accelerate the simulations) positioned at different angles 3 cm from the sample surface. Five positions of the detector were selected. The detectors were positioned at the following angles relative to the sample normal (degrees): 15, 30, 45, 60 and 75. An iron disk with a diameter of 0.5 cm and a thickness of 1 cm was used as a sample. A Zn layer with thickness s (ranging from 0 to 50 μm) was deposited on the sample. The simulation setup is shown in Fig. 2.

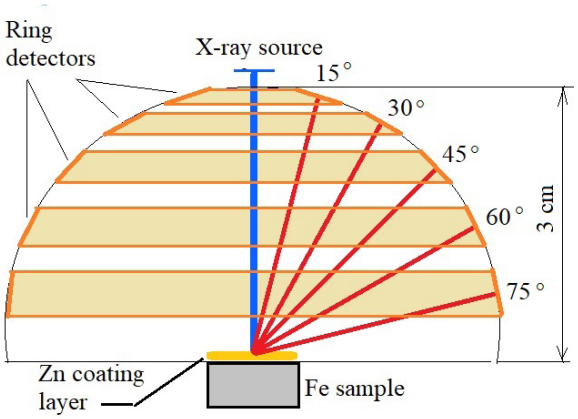


Fig. 2. Simulation model for the Zn–Fe pair:
Fe sample, Zn coating layer; Ring detectors, X-ray source. The incident X-rays are shown as a blue line; fluorescence emitted from the sample at different angles is shown as red rays

The simulations yielded the fluorescence spectra from samples with different Zn coating thicknesses and at different angles. First, the Fe K_α and Zn K_α peak intensities were plotted as a function of coating thickness s for different detector angles. A similar dependence was obtained for gold on copper.

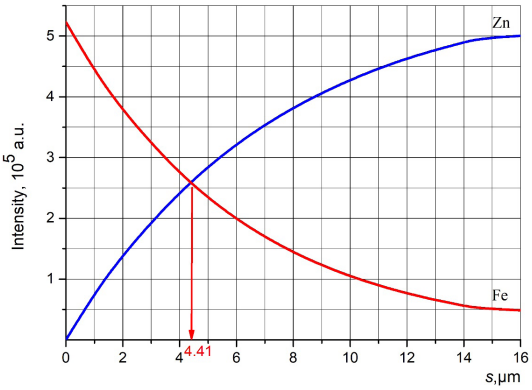


Fig. 3. Calculated Fe K_α and Zn K_α peak intensities versus coating thickness for detector angle of 45°

The value s = 4.41 μm corresponds to equal heights of the fluorescence maxima from the substrate and coating

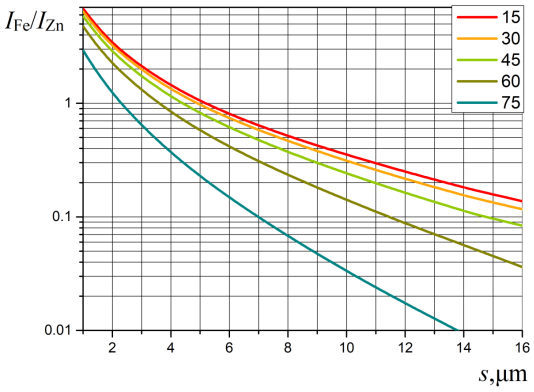


Fig. 4. Calculated Fe K_α/Zn K_α peak intensity ratios versus coating thickness for different detector angles (in degrees)

As an example, Fig. 3 shows the Fe K_α and Zn K_α peak intensities as a function of coating thickness s for a detector angle of 45°. The other dependences have a similar shape, but as the detector angle increases, the intersection point of the curves shifts toward smaller thicknesses. This is because the information depth decreases as the detector angle increases.

The intersection of the curves corresponds to the coating thickness at which the heights of the peaks associated with Fe K_α (substrate) and Zn K_α (coating) are equal.

Fig. 4 shows the Fe K_α/Zn K_α peak intensity ratio as a function of coating thickness for different detector angles.

A family of curves was plotted based on the simulation results, reflecting the dependence of the peak intensity ratio on the coating thickness for various angles. We can conclude from the data in Fig. 4 that the dependences of the Fe K_α/Zn K_α peak intensity ratio on the coating thickness are close for detector angles up to 45°. The behavior of the curves changes above this value: the ratio drops more sharply, and the range of measurable thicknesses narrows considerably. This result indicates that the geometric parameters of the instrument must be precisely known and controlled.

The simulation model of the X-ray fluorescence analyzer is shown in Fig. 5. Fig. 5,*a* shows the model, including the radiation source, the sample, and the detectors. Fig. 5,*b* shows the simulated trajectories of the incident X-ray photons and of the fluorescence photons emitted by the sample.

The simulation setup in Fig. 5 comprises four identical Amptek detectors arranged symmetrically about the vertical axis at 45° to the normal to speed up statistics accumulation.

As a result of the calculations, we obtained a calibration curve for the Fe K_α/Zn K_α peak intensity ratio as a function of coating thickness for a 45° detector angle at a tube voltage of 30 kV and a current of 1 mA. The same dependence was obtained for a Cu substrate coated with Au. The results are shown in Fig. 6. A similar dependence was described in [2].

The accuracy of the thickness measurement based on a calibration curve depends on the number of detected signals used to construct that curve.

The relative uncertainty δ in measuring the n_1/n_2 count ratio, assuming a Poisson distribution for counts n_1 and n_2, is given by the formula:

$$\delta = \sqrt{1/n_1 + 1/n_2}. \qquad (1)$$

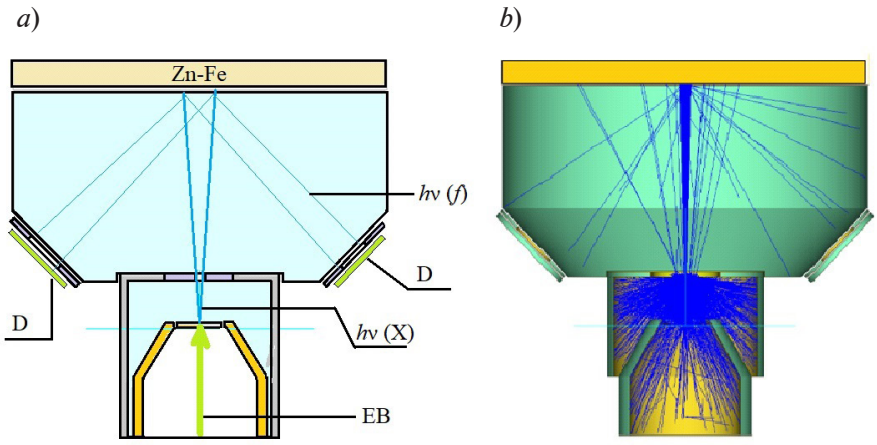


Fig. 5. Simulation model of the X-ray fluorescence analyzer (*a*) and the corresponding simulated photon trajectories (*b*); electron beam EB, generated X-ray photons *hν* (X), Zn-Fe sample, fluorescence photons *hν* (*f*), detectors D

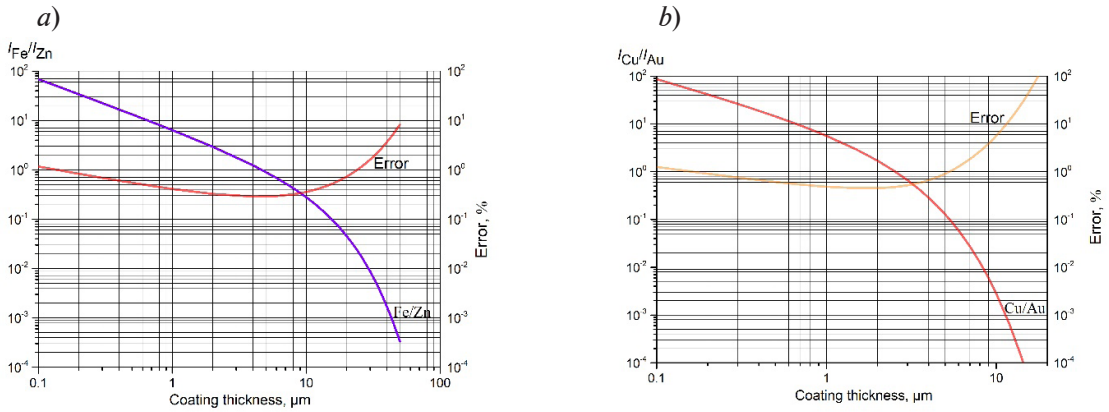


Fig. 6. Fe K_α/Zn K_α (*a*) and Cu K_α/Au L_α (*b*) peak intensity ratios as functions of coating thickness; corresponding uncertainty of coating thickness measurement for the chosen tube radiation intensity ($U = 30$ kV, $I = 1$ mA); the detector angle is 45° in both cases

Fig. 6 shows the substrate-to-coating peak intensity ratios as functions of coating thickness, along with the corresponding thickness measurement uncertainties.

The thickness measurement uncertainty we obtained is comparable to the values reported in [2, 9].

Conclusion

The results presented in this work show that Monte Carlo simulations in X-ray fluorescence analysis of coating thickness make it possible to determine coating thickness without prior calibration and to optimize the measurement process to achieve the required accuracy. However, this naturally requires experimental verification. In this work, we considered the simplest case, where the coating thickness was calculated for a pure element deposited on a pure substrate. Nevertheless, the Monte Carlo method can be used to calculate the thickness of coatings consisting of an arbitrary set of elements.

Once the relationship between coating thickness and the substrate-to-coating peak intensity ratio is known, the exposure time required to measure that thickness with the required accuracy can be found easily. Note that long exposure times are needed to measure gold coatings thicker than 10 μm on copper and zinc coatings thicker than 40 μm on iron with acceptable accuracy. For a practical instrument designed to measure coating thickness by the method described here, the optimal detector angle relative to the normal should not exceed 45°. At larger angles, the range of measurable thicknesses narrows substantially, and the measurement uncertainty increases.

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