X-ray absorption spectral analysis of heavy metals with Si-PIN detectors

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Abstract. An X-ray absorption spectroscopy method for the detection of heavy metals at the \(K\)-absorption edges is implemented using the designed Si-PIN detector. The limits of detection of heavy metals and uncertainty of measurement are estimated by the results of measurements of the thickness of gold and lead foil.

1. Introduction
In many technological operations, such as baggage check, ore dressing, sorting of scrap or waste electronic products, there is a need to detect certain chemical elements. Despite the abundance of tools and methods for elemental analysis, there are very few real devices that can be built into existing conveyor systems and possess the necessary performance to detect certain chemical elements in objects on a conveyor. X-ray Absorption spectroscopy analysis (XASA), which uses the attenuation of the flow of X-ray quanta at the \(K\)-absorption edges. In this work, the possibility of using the XASA method with the designed Si-PIN detector for the express determination of heavy metals in conveyor systems is considered and the resolution of the method is estimated. To determine heavy metals by the XASA method, a device with a detector possessing the necessary response rate when the analyzed material moves along a conveyor, operating at room temperature without additional cooling, and having sufficient resolution and an upper limit of the operating range of about 100 keV is required. Due to the fact that silicon detectors are widely used in X-ray scanners and the technology of their manufacture is well-established, this study considers the possibility of using Si-PIN detectors for the XASA of heavy metals at lines of the \(K\) series in a special configuration when X-ray radiation is directed along a layer, i.e., along the long side of the detector. The peculiarity of using Si-PIN detectors is that the analysis was carried out in the range covering the characteristic lines of the \(K\) series of heavy metals. To do this, the detector is oriented so that the radiation is directed along the PIN structure, i.e. along the long side of the detector. The detector used in the measurements was developed for X-ray diffraction analysis [1] and then modified for use in XASA in the framework of this study. Detector dimensions are as follows: width 1.5 mm, length 12 mm, and thickness of silicon wafer 0.5 mm. The spatial resolution in this geometry, when the radiation is directed along the layer, is quite acceptable for scanners and can be about 0.5-1.5 mm. The lack of forced cooling eliminates problems with evacuating the detector and substantially simplifies its design. The resolution rating of the detector gives an energy resolution of 1.65 Kev on the 59.5 Kev line of the \(^{241}\)Am source in non-
forced cooling mode at room temperature of 22 °C. Detailed specifications of the detector are given in [2].

In this study, the efficiency of the XASA method using the developed detector is experimentally evaluated. In the considered cases, a small amount of a heavy-metal element is located behind a screen made of a metal with a lower atomic number. For example, a microcircuit with gold-plated contacts is mounted in a device case with steel walls or a device electronic board made with the use of copper contacts coated with lead solder is mounted into an aluminum case. For these cases, the detection limits are experimentally determined and the error in measuring the thickness of the gold coating and the lead layer is estimated.

2. Experimental setup
The scheme of the experimental setup is shown in figure 1. The silicon detector is oriented with the end face toward the received radiation. The area of the end of the Si-PIN detector is 0.75 mm². A RAPAN X-ray radiation source and an X-ray tube with a tungsten anode were used in the setup. The voltage in the tube was $U = 150$ kV. The detector was located at a distance of 820 mm from the X-ray tube, so that an extended object could be placed in the illuminated volume, as in a typical X-ray scanner window with a size of 60 x 80 cm. The intensity of tube radiation is very high on tungsten K-lines and at lower values of energy, which causes a large detector load. To eliminate this problem, a filter made of materials with small atomic numbers was used to correct the spectrum and ensure normal operation of the detector, which was located behind the collimator of the tube. The detector was placed in a lead case with a wall thickness of 2 mm. The thickness of the lead collimator of the detector was 10 mm, and the aperture diameter in the collimator was 3.5 mm.

![Figure 1. Scheme of the experiment: 1 is an X-ray tube; 2 is a lead collimator; 3 is a low energy filter; 4 is a screen; 5 is a sample; 6 is a lead collimator of the detector; 7 is a detector in a lead case.](image)

The relationship between the incident radiation intensity $I_0$, transmitted radiation intensity $I$, and coordinate $x$ along the beam-propagation direction is determined by the following formula:

$$x \mu_{h,l} = -\ln(I/I_0)_{h,l}$$  \hspace{1cm} (1)

where $\mu_{h,l}$ is the linear absorption coefficient, and the $h$ and $l$ indices refer to the energy windows above and below the absorption edge, respectively.

The $x$ coordinate in Eq. (1) is measured in length units, and $\mu$ is measured in inverse length units. $x \mu$ can be expressed as $x \rho_n \mu_n$, where $\rho_n$ is the reference value of the density and $\rho$ is the density of the used material. In the limit of narrow windows near the absorption edge, the following formula is obtained:
\[ x_a = \frac{\ln(I_h/I_l)}{\mu_l(s - 1)} \]  

where \( s \) is the absorption jump.

Formula (2) assumes a linear dependence of \( x_a \) on the real thickness \( l_m \), measured mechanically. Factors affecting linearity and measurement error \( x_a \) are thin absorption edge structure, detector noise and collimator fluorescence.

In case of wide windows analyzed in [3], in addition to the above factors affecting the linearity and measurement error, the dependence of the detector sensitivity coefficient on the energy and the unevenness of the X-ray tube radiation spectrum will be manifested.

3. Measuring the thickness of metal films by the XASA method

The effectiveness of the proposed method for analyzing heavy metals was experimentally verified using a setup whose diagram is shown in Figure 1. Experiments were conducted, in which the element to be analyzed was lead and the material behind which it is located was a 6-mm-thick steel sheet in one case, and 16-mm-thick aluminum and 1.2-mm-thick copper sheets in the other case. Figure 2 illustrates the comparison of the lead-foil thicknesses measured by the XASA method and with a micrometer gauge (\( l_m \)).

Since the sample under study consisted of several layers of technical foil, the exact calculation of the absolute thicknesses is impeded by a lack of accurate values of the density. Therefore, calibration by means of a reference sample with the maximum thickness was performed after measurements. The B type uncertainty was assumed zero for this thickness.

The value linearly depends on the value in the range from 0.02 to 0.4 mm. When the sample thickness is more than 2 mm, the dependence becomes nonlinear. This is because the intensity \( I \) decreases and the noise level of the detector begins to have an effect. The detection limits of an element depend on the measurement error. If calibration and measurements were carried out with the same steel screen, the measurement error is about 5 μm. If screens made of different materials are used (a steel screen for calibration, and copper and aluminum screens for measurements), then the assessment gives a resolution of 18 μm in the case of measuring the lead-foil thickness. Replacing the screen material (steel, copper, and aluminum) affects both the change in the intensity of the X-ray quanta flux from the X-ray tube and the change in the spectrum. Both factors lead to an increase in the measurement error.

**Figure 2.** Alignment of the lead-foil thicknesses measured by the XASA method (\( l_a \)) and with a micrometer gauge (\( l_m \)); rhombs correspond to the first series of measurements with a 6-mm-thick steel screen; triangles correspond to the second series of a 6-mm-thick steel screen; squares correspond to the measurements of a 0.2-mm-thick lead foil behind a two-layer screen comprised of 1.2-mm-thick copper and 16-mm-thick aluminum sheets; \( l_a = x_a k \), where \( k \) is the calibration coefficient determined from the equality \( l_a = l_m \) at \( l_m = 0.4 \) mm.
Figure 3. Absorption spectra near the absorption edge ($E = 80.725$ keV) of gold foils with thicknesses of (1) 12, (2) 24, and (3) 36 μm. The energy windows selected (4) below the absorption edge and (5) above the absorption edge; $N$ is the spectrometer-channel number; $\Delta n$ is the number of counts in the channel minus the average number of counts over all channels.

Experiments on measurements of the thickness by the XASA method were carried out, in which gold foil samples with thicknesses of 6 to 36 μm were placed behind a steel screen with a thickness of 6 mm. Figure 3 shows the deviations of the intensity from the average value near the absorption edge for various gold-foil thicknesses.

For comparison, the gold-foil thicknesses measured by the XASA method and with a micrometer gauge are shown in figure 4. In contrast to the previous experiment, the spectrum was measured 10 times, and ten thickness values and then their mean, as well as the A and B type uncertainties, were calculated. The measurement uncertainties calculated for each series is given in Table 1. In further calculations, an expanded uncertainty averaged over six series was used, which is 2.7 μm. Energy windows with a width of about 3.5 keV were chosen, and the interval between them was about 3 keV.

Table 1. Uncertainty in measuring the gold-foil thickness by the XASA method

| Thickness, μm | 6   | 12  | 18  | 24  | 30  | 36  |
|--------------|-----|-----|-----|-----|-----|-----|
| Uncertainty of type A, μm | 1.5 | 2.3 | 3.2 | 2.1 | 3.1 | 2.4 |
| Uncertainty of type B, μm | 1.1 | 2.0 | 1.1 | 0.1 | 0.8 | 0   |
| Total standard uncertainty, μm | 1.9 | 3.1 | 3.4 | 2.1 | 3.2 | 2.4 |

Figure 4 demonstrates that the dependence of the value on the value is close to a linear dependence in the range from 0.006 to 0.036 mm under the selected experimental conditions. With a distance of 820 mm between the X-ray tube and the detector, the relative standard uncertainty of the weight
measurement, i.e., the ratio of the minimum weight of the sample per unit area to the weight of the shield per unit area, is 0.1%; the minimum weight of the detected metal gold is 0.15 mg. Similar estimates for the heavy metal thallium show that such indicators are sufficient to detect microdoses from 0.1 mg of thallium in a steel cell with a wall thickness of up to 3 mm.

To simplify the spectrum-analyzer scheme and reduce the acquisition time, a two-channel analyzer with fixed windows can be implemented using the example of the detector described in [1]. By changing the threshold levels of the detector, one can retune the analyzer for the required metal. By expanding the windows to the level of currently used scintillators, it is possible to obtain a distribution over atomic number groups and an object image that are standard for scanners.

Additional ways to reduce the measurement time are as follows: an increase in the current of the X-ray tube, transition to a pulsed mode of synchronous detection, and a decrease in the distance between the X-ray tube and the detector.

4. Conclusion

The performed studies show the possibility of using the ARSA method with Si-PIN detector in sorters, X-ray scanners and inspection equipment to search for objects containing heavy metals, as well as for the enrichment of ores containing heavy metals and the determination of precious metals in waste products of electronic technology.

One of the proposed options for scanners: at first, all objects are analyzed in the normal mode, and then selected objects with large atomic numbers, which are darkened in the picture, are analyzed further by scanners with the option of controlling certain elements.

To extend the functionality, two detectors tuned to different metals can be used in the same scanner.

References.

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