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X-Ray fluorescence determination of impurity traces using a secondary emitter and a solid-state detector

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The possibility of trace impurity determination in a light material by XFA method using an X-ray optical scheme with a secondary emitter has been studied. At 0.01 kW tube power, the line contrast is practically similar to that in the focusing crystal-diffraction scheme with a high-power 1.2 kW source. The 100-fold gain in the contrast comparing to the standard XFA scheme provides the Cr and Pb determination in aqueous solutions using experimental calibration plots from 0.05 ppm, while the detectability threshold for Ti, V, Cr, and Mn in aluminium alloys being lowered to 0.1–0.2 ppm. The scheme compactness allows the light element lines registration without the sample evacuation.

Исследованы возможности определения "следов" примесей в легком материале методом РФА в рентгенооптической схеме с вторичным излучателем. При мощности трубки 0,01 кВт обеспечивается практически такая же контрастность линий, как и в фокусирующей кристалл-дифракционной схеме с мощным источником 1,2 кВт. Стократный выигрыш в контрастности по сравнению со стандартной схемой РФА обеспечивает определение хрома и свинца в водных растворах по экспериментальным градуировочным функциям, начиная с 0,05 ppm, а предел обнаружения примесей Ti, V, Cr и Mn в алюминиевых сплавах снижен до 0,1÷0,2 ppm. Компактность схемы позволяет регистрировать линии легких элементов без вакуумирования пробы.

1. Introduction

The X-ray fluorescence method for determination of material composition is applied widely in different scientific and engineering areas due to its rapidity, high automatization level, and non-destructive measurement procedure. The main limitation of the method is its low sensitivity (~5–10 ppm) [1] when measuring the trace chemical elements, at least comparing with optical methods, atomic absorption spectroscopy, mass-spectroscopy, etc. The low sensitivity is due to the background continuous spectrum of the X-ray tube scattered by the sample that overlaps the sample fluorescence lines to be measured. The known way to lower the background is to monochromatize the primary radiation. However, this results in a drastic intensity drop, hence, in poor detectability of the low impurity concentrations.

In [2], a monochromatization scheme is described including the focusing both of the tube primary radiation and the sample fluorescence emission. This scheme has provided two orders increased line contrast without substantial intensity loss. Consequently, the analysis sensitivity is increased by hundred times comparing to the standard scheme and achieved the sensitivity of above-mentioned optical spectral analysis. However, the schemes with focusing are extremely complex and expensive, and demand high-power sources of primary X-ray emission.

The aim of this work was to consider the possibility to determine the impurity traces

using X-ray optical scheme where the primary radiation monochromatization is provided not by the reflection from a crystal but by fluorescence excitation in the secondary emitter being a fluorescent anode.

2. X-Ray optical scheme

In the scheme designed (Fig. 1), the tube with shoot-through anode is attached to the removable secondary emitter which intersects the whole directional diagram of the tube radiation. The sample is mounted in front of the secondary emitter with the angles of incidence onto the secondary emitter (φ_1), and onto the sample (φ_2) being optimized for the emitter and sample materials. Directly behind the emitter, the input slit of the solid-state detector is positioned. The scheme provides a high usage efficiency both for the tube radiation (as the aperture is $\varepsilon_1 \approx 0.12$ for primary radiation) and for the sample fluorescence. Indeed, with $\approx$7 mm distance between the sample and the detector slit and 2×2 mm^2 detector slit, the aperture $\varepsilon_2 \approx 0.08$ is provided for registration of the sample output fluorescence. The fraction of the primary radiation used to excite the sample fluorescence in the crystal-diffraction scheme [2] is 20 to 40 times lower than in our scheme with the secondary emitter (Fig. 1). That is why our results obtained with the tube power 0.01 kW can be compared with the results from [1] where the tube of 1.2 kW power was used.

3. Spectral line contrast and detectability threshold

The primary spectrum monochromatization both in [2] and in our work has allowed to eliminate the background of the scattered continuous spectrum. The main background source in both cases is the tail of Compton band appearing from scattering the monochromatized radiation at the sample material. This tail is the more intense, the lower is the average atomic number of the sample. So, it is the most difficult to provide high contrast of the lines of impurity traces in a light material, for example, water.

We have compared the contrast of analytic lines obtained in [2] for the aqueous solutions of Co, Fe, and Cr impurities and similar solutions of Cr and Pb in our work. At $C \approx 5$ ppm impurity content, the contrast $K = 3.15$ was obtained in [2], which corresponds to the detectability limit $C_L = 0.02 \cdot C/K = 0.032$ ppm, while in our work, the contrast $K = 2.23$ corresponds to $C_L = 0.045$ ppm. A slight loss in the analytical line contrast is caused by the larger scattering angle ($2\varphi = 138°$) in our scheme comparing to $2\varphi = 108°$ in [2]. The result is the increased background observed, as the Compton scattering intensity increases with scattering angle.

Thus, our simple and high-aperture scheme with the secondary emitter to monochromatize the primary radiation provides a

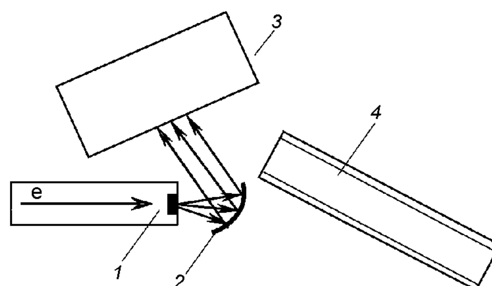

Fig. 1. X-ray optical scheme with the secondary emitter: *1*, X-ray tube anode; *2*, secondary emitter; *3*, sample under study; *4*, solid-state detector.

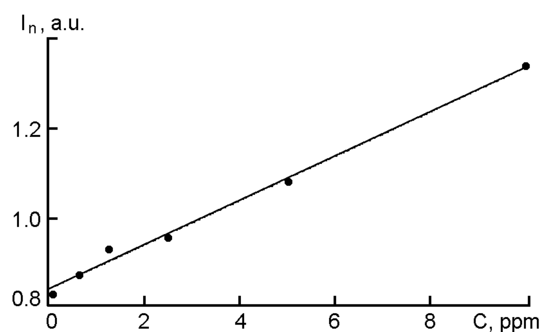

Fig. 2. The calibration function for Cr determination in aqueous solution for the concentration range 0.08 to 10 ppm.

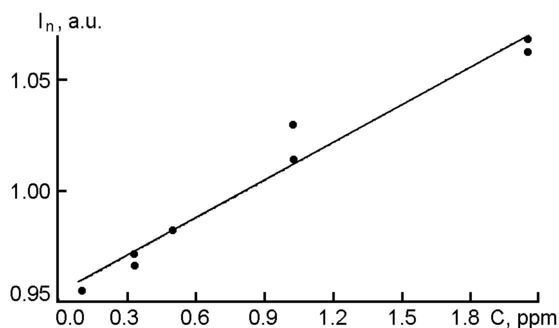

Fig. 3. The calibration function for Pb determination in aqueous solution for the concentration range 0.1 to 2 ppm.

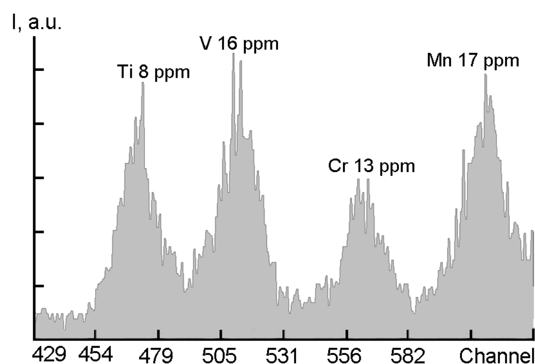

Fig. 4. The spectrum fragment of standard reference material CO aluminium alloy. The detectability threshold for Ti, V, Cr and Mn is from 0.1 to 0.2 ppm for 100 s.

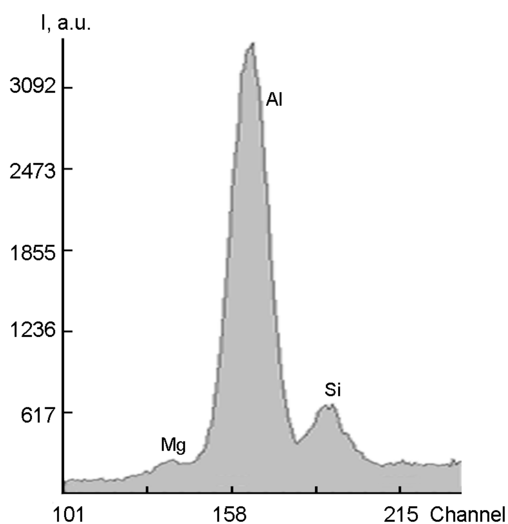

Fig. 5. Light elements lines in the spectrum recorded without vacuumization of the specimen.

contrast similar to that of the complex focusing crystal-diffraction scheme demanding high-power primary radiation sources. In Figs. 2, 3, the experimental calibration functions for chromium and lead aqueous solutions measured using the new scheme (Fig. 1) are shown. Using these calibration functions, it is possible to determine Cr and Pb in aqueous solutions beginning from 0.05 ppm, thus corresponding to the data of atomic absorption analysis using the optical spectral lines.

In Fig. 4, a fragment of the spectrum is shown containing Ti–K_{α}, V–Kα, Mn–K and Cr–Kα lines measured for standard sample of an aluminium alloy. The analytical line contrast is high enough to provide 0.1–0.2 ppm detectability threshold for those elements in aluminium alloys. These values are at least an order lower than in the standard X-ray fluorescent analysis. An important advantage of the scheme is a compact arrangement of the X-ray tube anode, the secondary emitter, the sample, and the solid-state detector, which gives a possibility to register the radiation from light elements up to magnesium without evacuation or helium filling of the working volume. Indeed, with 10 mm distance between the sample and the detector input slit, air attenuates the Si–Kα intensity by 2.6 times, Al–Kα by 4.7 times, Mg–Kα by 12.6 times. Due to high aperture of our X-ray optic scheme (Fig. 1), such attenuation does not impair the acceptable quality of the spectra in the analytical line range of the elements (Fig. 5). For Mg and Si in aluminium alloys, 0.02 % mass detectability threshold was attained which is quite enough for quantitative measurement of the elements.

4. Summary

The primary spectrum monochromatization using the secondary emitter provides the line contrast practically similar to that attained with monochromatization in the focusing crystal-diffraction scheme. Comparing to the standard XFA scheme, a 100-fold advantage in contrast is provided, hence, the detectability threshold is lowered by 50 to 100 times. The compact arrangement of the primary and the secondary emitters, the sample, and the detector provides reliable registration of light elements up to magnesium without any sample evacuation or helium atmosphere.

References

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Рентгенофлуоресцентне визначення "слідів" домішок із застосуванням вторинного випромінювача та твердотільного детектора

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Досліджено можливості визначення "слідів" домішок у легкому матеріалі методом РФА в рентгенооптичній схемі із вторинним випромінювачем. При потужності трубки 0,01 кВт забезпечується практично така ж контрастність ліній, як і у фокусуючій кристал-дифракційній схемі з потужним джерелом 1,2 кВт. Стократний виграш в контрастності у порівнянні зі стандартною схемою РФА забезпечує визначення хрому та свинцю у водних розчинах за експериментальними функціями градуювання, починаючи з 0,05 ppm, а межа виявлення домішок Ti, V, Cr та Mn в алюмінієвих сплавах знижена до 0,1÷0,2 ppm. Компактність схеми дозволяє реєструвати лінії легких елементів без вакуумування проби.