

INFLUENCE OF SUBSTRATE MATERIAL ON K_{α} -LINE FLUORESCENCE INTENSITY IN CHROMIUM THIN FILMS

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Amplification factors for chromium K_{α} -line fluorescence excited by emission from substrates fabricated from various metals were calculated using an auxiliary system comprising thin layers of chromium deposited on a polymer film. It was found that the chromium K_{α} -line fluorescence intensity amplification was greatest for the iron substrate.

Keywords: x-ray fluorescence analysis, thin-film thickness, amplification factor, influence of substrate, polymer-film substrate.

Introduction. X-ray fluorescence (XRF) analysis of complex multi-component samples is known [1] to have a serious problem because of the dependence of the analytical signal on the elemental and phase composition and the sample structure and morphology as a result of matrix effects. The influence of the matrix on the excitation efficiency of XRF of a determined element is considered to be one of the principal reasons for the variation of the measured signal with a constant analyte content in the sample. X-ray fluorescence of a substrate that is excited simultaneously with the film material is an important factor that affects the thin-film fluorescence intensity. The thin film can experience additional excitation due to substrate emission if the fluorescence emission is strong enough.

Seminal information on the mutual influence of elements on films deposited on various substrates was published by Hirokawa et al. [2]. In certain instances, the substrate excitation intensity can be so large that it is comparable with that of the film itself. Later, copper K_{α} -line fluorescence intensities were measured for Cu films 0.5–3.0 μm thick under conditions where glass, silver, and germanium were used as substrates [3]. It was shown that the intensities differed markedly as functions of film thickness, confirming the existence of additional excitation of the film by the substrate. An even greater effect was observed for silver films of these same thicknesses using tin as the substrate (a comparison was made with silver films on glass). The relative change of fluorescence intensity reached 25% for film 3- μm thick.

A theoretical treatment of selective fluorescence excitation of an element of an unsaturated layer of arbitrary thickness by emission from elements of the substrate bulk showed [4] that emission from substrate elements could in certain instances have a substantial influence on the fluorescence intensity of unsaturated layer elements that should be considered in performing XRF analysis.

The goal of the present work was to study systematically the influence of fluorescence emission from substrates of pure bulk metal plates ($\geq 99.9\%$ purity) on the fluorescence intensity of chromium thin films of various surface density that were deposited on them.

Experimental Part. An EDX-720 energy-dispersive analyzer (Shimadzu, Japan) was used to study the influence of substrate material on the fluorescence intensity of chromium thin films. Table 1 presents the optimum excitation conditions and the energies of the principal lines of K -series and K_{α} -edge absorption of elements in the substrate and chromium thin films. The area of the sample irradiated by the tube was 0.8 cm^2 .

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TABLE 1. EDX-720 Spectrometer* Optimum Operating Conditions

Element	Energy, keV [5]			Rh-tube operating regime**
	K_α	K_β	K_q	$I, \mu\text{A}$
Al	1.487	1.553	1.560	368
Si	1.740	1.829	1.840	351
Ti	4.509	4.932	4.965	228
V	4.950	5.428	5.464	44
Cr	5.412	5.947	5.989	38
Mn	5.895	6.491	6.538	34
Fe	6.400	7.058	7.111	31
Co	6.925	7.650	7.710	26
Ni	7.473	8.265	8.332	25
Cu	8.042	8.906	8.981	24
Zn	8.632	9.572	8.981	36
Ge	9.876	10.983	11.104	33
Mo	17.446	19.609	19.609	31

* Liquid N₂-cooled Si(Li) detector; 10-mm collimator.

** $P = 50 \text{ W}$; $U = 30 \text{ kV}$; 60-s exposure time.

Reference samples. Reference samples (RS) were prepared using vacuum thermal sputtering in a VU-1A apparatus. A weighed portion of metal was degassed beforehand at a temperature close to the melting point. The starting material was a bulk plate of metallic chromium that was used to calculate the relative intensity $I_{\text{cr}}^0/I_{\text{cr}}^\infty$ of chromium.

The surface density m_s of chromium thin films was found by weighing polymer substrate before and after sputtering the film on a VRL-20g balance to an accuracy $\pm 5 \mu\text{g}$. A compensation method was used in order to avoid error associated with the mass difference of the substrate and sputtered film [6].

One method for increasing the accuracy of XRF analysis of very thin films is to use RS sets of the same thickness [7–9]. With this, the linear dependence of the relative fluorescence intensity on the thin-film surface density should be preserved [10]:

$$I_{\text{rel}} = I_A^0/I_A^\infty = \alpha_A m_A, \quad (1)$$

where I_A^0 and I_A^∞ are the fluorescence intensities of element A recorded from the thin film and the corresponding bulk sample (with subtraction of background intensity); α_A , a coefficient that is determined from films with a known surface density.

Two RS sets consisting of thin single-component chromium films sputtered onto polymer film ($\text{C}_{10}\text{H}_8\text{O}_4$)_n of thickness 5 μm and substrate of polymer film were used to construct a calibration curve (Fig. 1). Surface densities of six RS in one set were measured in the range 25.2–287.9 $\mu\text{g}/\text{cm}^2$. This RS set was used to check the linear dependence between the relative fluorescence intensity and the film surface densities. In the other set, all six RS had the same surface density 287.9 $\mu\text{g}/\text{cm}^2$. This set was used to calculate coefficient α_A and its uncertainty $\Delta\alpha_A$.

According to Eq. (1), coefficient α_A is a quantity equal to the slope of the calibration curve. A least-squares method that enabled both α_A and uncertainty $\Delta\alpha_A$ to be found was used for the calculation. It should be noted that thin films with a low surface density contributed significantly to the uncertainty in the measurement of the relative chromium intensity I_A^0/I_A^∞ and calculation of the surface density [11].

It was found that the uncertainty in the determination of coefficient α_{Cr} for the set in which the RS had different surface densities, $\alpha_{\text{Cr}}(1) = 350.5 \pm 1.5 \text{ cm}^2/\text{g}$, was greater than that, $\alpha_{\text{Cr}}(2) = 351.1 \pm 0.2 \text{ cm}^2/\text{g}$, for the set in which all six RS had the same maximum achievable surface density. This coefficient was used for further studies.

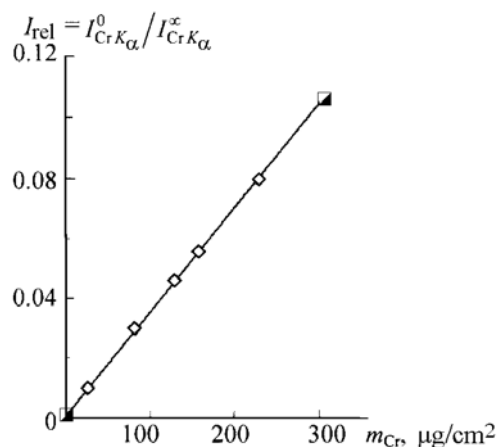


Fig. 1. Relative intensity of chromium K_{α} -line for two complexes of six reference samples with identical (♦) and different (◇) surface densities; results coincide at points (◆).

Preparation of the auxiliary system. The study of the influence of XRF of various substrate materials on the fluorescence intensity of three chromium thin films of different surface densities that were deposited on them was complicated by the fact that chromium thin films of the same surface density had to be deposited on substrates of various metals in order to establish the desired dependence.

We proposed using simply prepared uniform single-layered and single-component layers obtained by sputtering chromium onto a polymer-film substrate in order to solve this problem. Sequential placement of a certain combination of layers in a special holder enabled thin-film–substrate compositions to be formed that were analogous to films on the substrates intended for the analysis. The novelty of the approach consisted of the formation of the studied systems immediately before XRF analysis by sequential placement of substrates of various metals and several chromium thin layers deposited on polymer film. Because the thin film on the polymer was not destroyed during the analysis, it could be used repeatedly to study other thin-film systems. The auxiliary sample was a coating (Cr/polymer)/A, the upper layer of which was chromium sputtered onto polymer film; the lower layer, the substrate bulk (A). They were used in combination with a whole series of substrate samples that were already available to us in order to form the studied systems.

Results and Discussion. Chromium thin films of the same thickness on substrates of polymer, polycore, and iron were prepared in order to establish the influence of substrate material on the chromium K_{α} -line fluorescence intensity. The surface densities of these films were found gravimetrically as $143.6 \pm 0.9 \mu\text{g}/\text{cm}^2$. Furthermore, the surface densities of these films that were determined by XRF analysis using the function given in Fig. 1 showed that they were significantly different because the thin film could receive additional excitation due to substrate emission if the substrate fluorescence emission was strong enough.

It was observed that the surface density of the film on the polymer agreed with the value determined gravimetrically but differed from that for the film on polycore substrate, which was slightly lower. It was found that the background intensity measured next to the K_{α} -line from the chromium layer sputtered onto polymer was almost five times less than the analogous film deposited on polycore. This was also evident from the reduced surface density of the thin film on polycore. Fluorescence emission of the elements in the polycore aluminum-oxide ceramic (99.8% Al_2O_3 , 0.1% B_2O_3 , and 0.1% MgO) that was used as substrate was not taken into account because it did not affect the fluorescence of the upper layers. However, the sharp rise of the background had to be considered. The polymer film $(\text{C}_{10}\text{H}_8\text{O}_4)_n$ that was used as substrate for chromium also did not destroy the proportionality between the thickness of the chromium layer and the fluorescence intensity of its analytical line although it weakened the emission intensity of the elements contained in the substrate bulk. The surface density of chromium film on iron substrate was 1.36 times greater than that determined gravimetrically and was $195.6 \mu\text{g}/\text{cm}^2$. Thus, the exciting action of the bulk iron

TABLE 2. Amplification Factors of K_{α} -line Intensity of Chromium Thin Films in (Cr/polymer)/A System by Emission of Bulk Substrate

Parameter	System type (Cr/polymer)/A								
	Polymer	Mn	Fe	Co	Ni	Cu	Zn	Ge	Mo
$m_{Cr1} = 26.5 \pm 0.9 \mu\text{g}/\text{cm}^2$									
$I_{CrK_{\alpha}}^{Cr/A} \pm 0.003, \text{ counts}/\mu\text{A}$	4.583	5.967	8.451	7.342	5.843	5.665	5.518	5.169	4.267
$K = I_{CrK_{\alpha}}^{Cr/A}/I_{CrK_{\alpha}}^{Cr/pol}$	1.000	1.302	1.844	1.602	1.275	1.236	1.204	1.128	0.931
$m_{Cr2} = 137.6 \pm 0.9 \mu\text{g}/\text{cm}^2$									
$I_{CrK_{\alpha}}^{Cr/A} \pm 0.027, \text{ counts}/\mu\text{A}$	23.659	25.504	32.224	30.165	28.793	28.320	27.539	25.788	22.098
$K = I_{CrK_{\alpha}}^{Cr/A}/I_{CrK_{\alpha}}^{Cr/pol}$	1.000	1.078	1.362	1.275	1.217	1.197	1.164	1.090	0.934
$m_{Cr3} = 305.3 \pm 0.9 \mu\text{g}/\text{cm}^2$									
$I_{CrK_{\alpha}}^{Cr/A} \pm 0.025, \text{ counts}/\mu\text{A}$	52.494	55.696	66.930	64.095	62.205	61.208	59.843	56.694	49.134
$K = I_{CrK_{\alpha}}^{Cr/A}/I_{CrK_{\alpha}}^{Cr/pol}$	1.000	1.061	1.275	1.221	1.185	1.166	1.140	1.080	0.936

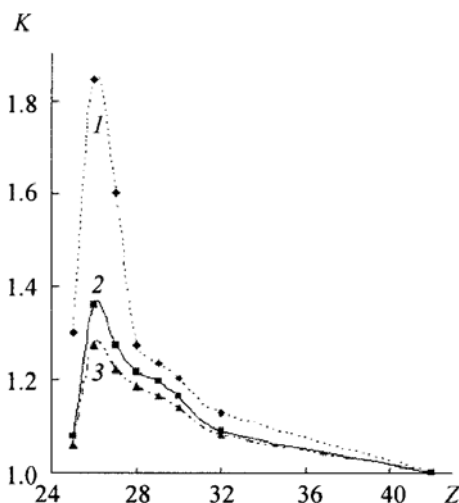


Fig. 2. Amplification factor ($K = I_{CrK_{\alpha}}^{Cr/A}/I_{CrK_{\alpha}}^{Cr/pol}$) of K_{α} -line fluorescence intensity for three chromium thin films as functions of substrate element atomic number (Z): $m_{Cr1} = 26.5$ (1), $m_{Cr2} = 137.6$ (2), $m_{Cr3} = 305.3 \mu\text{g}/\text{cm}^2$ (3).

substrate caused a sharp increase in the fluorescence intensity of the chromium thin film (Table 2). This led eventually to a significant increase of its surface density.

Amplification of chromium K_{α} -line fluorescence intensity by emission of substrate atoms in the (Cr/polymer)/A system. The surface density of the chromium films on polymer was $m_{Cr1} = 26.5 \pm 0.9$, $m_{Cr2} = 137.6 \pm 0.9$, and $m_{Cr3} = 305.3 \pm 0.9 \mu\text{g}/\text{cm}^2$. Substrates of polycore and quartz and the elements Al, Si, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ge, and Mo, bulk samples of which were used by us earlier as RS to calculate the relative fluorescence intensities of thin films of these elements, were placed sequentially below them immediately before the study. Then, K_{α} -line fluorescence intensities for the studied chromium films in the presence of bulk substrates $I_{CrK_{\alpha}}^{Cr/A}$ and the intensities of

these same films on polymer substrate $I_{CrK_{\alpha}}^{Cr/pol}$ were measured. The amplification factors $K = I_{CrK_{\alpha}}^{Cr/A}/I_{CrK_{\alpha}}^{Cr/A}$ were calculated (Table 2).

The influence of substrate material on the increase of fluorescence intensity of chromium films was explained by a selective excitation effect. Emission of substrate atoms in Al, Si, Ti, V, quartz, and polycore did not have an exciting influence on chromium fluorescence intensity because the energies of their K_{α} -lines were less than the energy of the Cr K_{α} -edge absorption.

This effect did occur for $Z \geq 25$ in the (Cr/polymer)/A systems. For all substrate elements starting with Mn, the energies of the K -series were slightly greater than the energy of the Cr K_{α} -edge absorption (Table 1). Because the fluorescence intensity of the K_{β} -line was several times weaker than that of the K_{α} -line, the latter would make the main contribution to excitation of the Cr K -spectrum. The exception was the Mn substrate. In this instance, only its K_{β} -line had excitation because its energy ($E_{K_{\beta}}^{Mn} = 6.491$ keV) was greater whereas the energy of the Mn K_{α} -line ($E_{K_{\alpha}}^{Mn} = 5.895$ keV) was less than the Cr K_{α} -edge absorption ($E_{K_{\alpha}}^{Cr} = 5.989$ keV).

Figure 2 shows the amplification factors of K_{α} -line fluorescence for three chromium thin films as functions of substrate element atomic number. It can be seen that the fluorescence intensity amplification factor decreased as the thickness of the chromium thin layer on a substrate of the same element increased. It was found that the amplification factor of the chromium K_{α} -line in the studied system (Cr/A) was greatest for iron substrate. Increasing the substrate element atomic number further led to its decrease. The further from each other the elements of the substrate and thin layer were located in the periodic table, the less was the effect of their mutual influence.

Conclusion. The influence of intensity amplification of chromium thin layer K_{α} -line fluorescence by substrate emission was studied using a uniform simply constructed auxiliary system (Cr/polymer)/A. Important advantages of using uniform chromium layers on polymer compared with traditional approaches where chromium thin layer is deposited directly on the substrate bulk are the more economical technical equipment and the ability to use them further for XRF analysis of other chromium-containing multi-layered and multi-component structures.

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