

PHYSICOCHEMICAL MEASUREMENTS

MEASUREMENT OF STRUCTURAL PARAMETERS BASED ON X-RAY EMISSION SPECTRA WITH ENERGY-DISPERSIVE DETECTION

V. P. Gavrilenko,^{1*} A. V. Zablotskii,^{1,2}
S. A. Korneichuk,³ A. Yu. Kuzin,¹
T. A. Kupriyanova,⁴ O. I. Lyamina,⁴
P. A. Todua,^{1,2} M. N. Filippov,^{1,4}
and V. Ya. Shklover³

UDC 543.427:543.44

The feasibility of using the diffraction peaks in x-ray emission spectra detected with energy dispersion for measuring the spacing between lattice planes in crystalline substances is demonstrated.

Keywords: x-ray fluorescence analysis, energy dispersion spectrometer, diffraction peaks.

x-Ray fluorescence microanalyzers with capillary optics for focusing the exciter beam and energy-dispersive spectrometers have come into widespread use over the last decade. And a new discipline, x-ray fluorescence microanalysis (XFMA) founded on the use of these microanalyzers, has come into existence. The technique of XFMA was originally based on an analogy with traditional, nonlocal x-ray fluorescence analysis (XFA) with crystal-diffraction spectrometers. In XFA, the analytical signal is excited by a broad beam of polychromatic radiation from an x-ray tube. It was not noted that the conditions for excitation and detection of the analytic in XFMA differ substantially from the conditions in XFA [1–3].

An instrument with capillary optics and an energy-dispersive spectrometer (EDS) can be regarded simultaneously as an emission spectrometer and a static diffractometer. Figure 1 illustrates the geometry of a spectrometer of this type with the exciting radiation normally incident on the sample surface. For positions of the tube and detector that have been fixed during the measurement process and polychromatic excitation, diffraction peaks with an energy of

$$E = 6.1992n/[d\sin((\varphi + \psi)/2)] \quad (1)$$

can appear, where E is the energy corresponding to the maximum of the diffraction peak, n is the diffraction order ($n = 1, 2, \dots$), d is the distance between the planes, φ is the angle between the directions of the focused x-ray beam and the sample surface, and ψ is the angle between the plane of the sample and the direction to the detector.

The spectral composition of the secondary x-ray radiation is more complicated when energy-dispersive spectrometers are used. Passage of the polychromatic radiation from the tube through the capillary leads to a sharp increase in the

¹ Research Center for the Study of the Properties of Surfaces and Vacuum (NITsPV), Moscow, Russia; e-mail: fgupnicpv@mail.ru.

² Moscow Institute of Physics and Technology (MFTI), Dolgoprudnyi, Moscow Region, Russia.

³ Systems for Microscopy and Analysis, Moscow, Russia.

⁴ Institute of General and Inorganic Chemistry, Russian Academy of Sciences (IONKh RAN), Moscow, Russia; e-mail: fil@igic.ras.ru.

* Deceased.

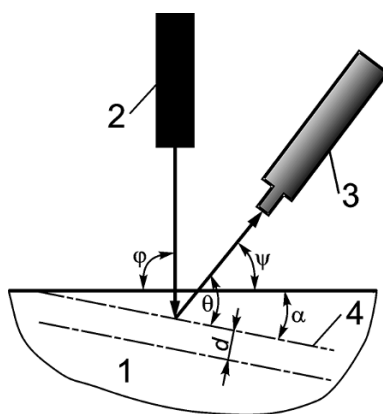


Fig. 1. Configuration of a spectrometer for x-ray fluorescence microanalysis with the primary radiation normally incident on the sample surface: 1) sample; 2) x-ray tube with capillary optics; 3) energy-dispersive spectrometer; 4) trace of the atomic plane; $\varphi = 90^\circ$ is the angle between the x-ray beam and the sample surface; θ and ψ are the angles between the direction to the spectrometer and the atomic plane and sample surface, respectively; α is the angle between the atomic plane and the sample surface; and d is the distance between lattice planes.

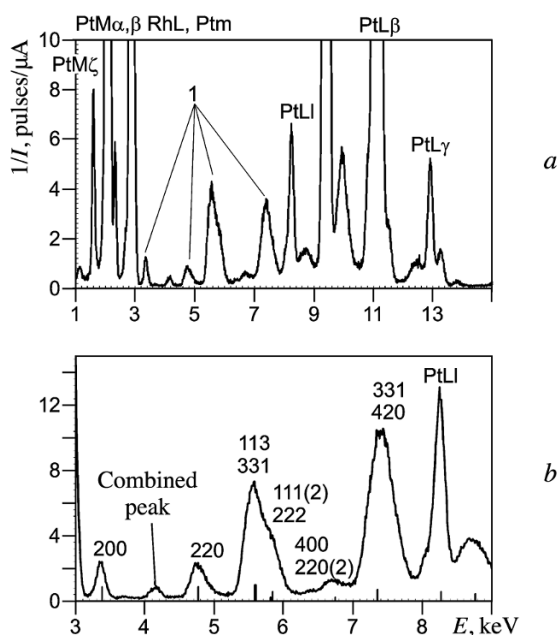


Fig. 2. Secondary x-ray spectrum of platinum for 1–15 keV (a) and diffraction peaks identified in it (b): 1) diffraction peaks.

intensity of the continuum emission at energies of roughly 5–10 keV, and this facilitates the appearance of highly intense diffraction peaks.

It has been shown [1] that for most pure elements, the diffraction peaks lie within a range of 3–11 keV and their intensity may amount to 10% or more of the intensity of the characteristic x-radiation. If several diffraction peaks can be detected in the spectrum, then once they have been identified, in some cases it is possible to calculate the distance between the lattice planes in the observed material and this technique can be used for structural analysis. Here we demonstrate the feasibility of phase

TABLE 1. Characteristic Diffraction Peaks of Platinum Obtained with an ORBIS x-Ray Fluorescence Microanalyzer

Position of peak E , keV	ΔE , eV	Intensity I , pulses/($\mu\text{A}\cdot\text{sec}$)	Interplanar distance d , Å
3.36 ± 0.02	0.37	1.20 ± 0.03	1.96 ± 0.01
4.76 ± 0.01	0.54	1.1 ± 0.5	1.387 ± 0.002
5.57 ± 0.01	1.05	4.0 ± 1.2	1.184 ± 0.001
6.69 ± 0.01	0.50	0.70 ± 0.05	0.985 ± 0.001
7.39 ± 0.07	0.99	5 ± 2	0.892 ± 0.008
8.73 ± 0.06	0.61	1.9 ± 0.5	0.756 ± 0.005

TABLE 2. Characteristic Diffraction Peaks of Platinum

Average interplanar distance, Å	Miller indices of corresponding reflex (hk1)	Relative intensity of peak, %
2.262	111	100
1.956	200	86
1.385	220	86
1.179	311	100
1.130	222	57
0.978	400	28
0.897	331	71
0.875	420	71

TABLE 3. Comparison of Interplanar Distances of Platinum

Data [4–7]			Data obtained by XFMA		Difference between the experiment and the data [4–7], Å
Miller indices of corresponding reflex (hk1)	Relative intensity of diffraction peak, %	Average interplanar distance, Å	Energy position of diffraction peak, keV	Interplanar distance, per Eq. (1), Å	
200	86	1.956	3.36	1.964 ± 0.012	-0.008
220	86	1.385	4.755	1.387 ± 0.002	-0.003
311	100	1.179	5.57	1.184	-0.006
400	28	0.978	6.695	0.985 ± 0.001	-0.007
331	71	0.897	7.395	0.892 ± 0.008	0.005

analysis of x-ray emission spectra for the example of metallic platinum (polycrystalline) with the primary beam normally incident on the sample.

x-Ray spectra of platinum were recorded on an ORBIS microanalyzer. A 1-mm-diam aperture and a polycapillary lens were used to shape the beam of exciting radiation. The voltage on the tube, with a rhodium anode, was 40 kV and the current was 200 μA . The Apollo SDD XRF energy-dispersive spectrometer had an 80-mm-diam window and a resolution of 132 eV. The time constant was $\tau = 50 \mu\text{sec}$, and the time to take a spectrum was 50 sec. The platinum spectra obtained with different currents on the tube were scaled to unit current.

Figure 2a shows experimental spectra of the secondary x-ray emission of the platinum for energies of 1–15 keV. Besides the peaks corresponding to the characteristic x-ray emission of the L - and M -series of the sample, this spectrum

includes loss peaks, multiples and sums, coherent and incoherent peaks of scattered characteristic radiation of the anode material, and peaks owing to diffraction of the exciting (primary) x-rays. When a polycapillary lens was used to shape the primary x-ray beam, the intensity of the diffraction peaks was 5 or more times greater than when an aperture was used. The peak at 4.17 keV corresponds to the combined peak of the characteristic platinum $PtM_{\alpha,\beta}$ radiation. This spectrum shows that most of the diffraction peaks and characteristic emission lines of platinum can be resolved. The energy position E and intensity I , as well as the energy intervals ΔE in which diffraction peaks can be observed with given Miller indices, are listed in Table 1. Also shown there are the separations between the planes of the platinum calculated using Eq. (1).

In order to identify the diffraction peaks in the experimental data for a given substance, it is necessary to compare the data with XFA databases. Interplanar distances of platinum from Refs. 4–7 and their averages are listed in Table 2. A comparison of the experimental values with the averaged diffraction peaks shows that the discrepancies for five of the peaks do not exceed 0.008 Å (see Table 3). In the case of traditional XFA, various sources recommend identification of 5–11 peaks for a phase determination. Using the XFMA, we have been able to identify 5 diffraction peaks. The diffraction peak of platinum 111 (first order reflection) corresponds to an energy of 2.88 keV. Here we also found peaks of coherent and incoherent scattering of the rhodium-anode tube, as well as a characteristic M-series emission line of platinum which does not have a standard designation and corresponds to an electronic $O_{IV,V}-M_{III}$ transition.

An interpreted segment of the secondary emission spectrum of platinum containing the diffraction peaks is shown in Fig. 2b. The shape of the peaks at energies of 5.6 and 7.4 keV and the values of ΔE for them indicate that these peaks are superpositions of several lines.

Conclusions. A qualitative phase analysis can be made using the 3–9 keV segment of an x-ray emission spectrum of polycrystalline platinum. The interplanar distances determined on the basis of the observed diffraction peaks differ from published data by less than 0.008 Å.

This work was supported by the Ministry of Education and Science of Russia using equipment at the MFTI Collective User Center for Unique Scientific Equipment in the Area of Nanotechnology (Project Identifier RFMEFI59414X0009).

REFERENCES

1. A. V. Zablotskii, A. A. Viryus, A. Yu. Kuzin, et al., “Components of the secondary x-ray spectrum with polychromatic excitation and energy-dispersive detection,” *Metrologiya*, No. 4, 9–17 (2013).
2. R. Woldset, *Applied x-Ray Spectrometry* [Russian translation], Energoatomizdat, Moscow (1977).
3. J. A. Nicolosi, B. Scraggse, and M. Hascke, “Analysis of sub-mm structure in large bulky samples using micro-x-ray fluorescent spectroscopy,” *Adv. x-Ray Anal.*, **41**, 227–233 (1997).
4. L. I. Mirkin, *Handbook of x-Ray Structural Analysis of Polycrystals*, Fizmatgiz, Moscow (1961).
5. S. S. Gorelik, Yu. A. Skakov, and L. N. Rastorguev, *x-Ray Diffraction and Electron-Optical Analysis*, Izd. MISiS, Moscow (1994).
6. A. V. Chichagov, A. B. Belonozhko, A. L. Lopatin, et al., “Computer-data system for crystal structure data on minerals (MINKRIST),” *Kristallografiya*, **35**, No. 3, 610–616 (1990).
7. A. S. Khrarov and I. V. Luk’yanov, *x-Ray Structural Analysis of Polycrystals: Handbook*, Kazan (Volga) Federal University, Kazan (2010), Pt. IV.