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THE LIMITS OF RESOLUTION AND DETECTABILITY IN X-RAY MICROPROBE ANALYSIS OF GLASS USING THE ENERGY DISPERSIVE SYSTEM

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Two important characteristics were investigated studying the possibility of use of the energy dispersive spectrometer: resolution limit of the two near concentrations and the limit of detectability. The resolution limit was studied experimentally on series of silicate glasses in which the content of SiO_2 *steeply changed of 1%. The limit of detectability was studied on series of identical glasses with various content of* ZnO.

RESOLUTION LIMIT

The following parameters of the X-ray spectrometer are significant studying the resolution limit: its accuracy, its reproducibility, short and long time stability. The same parameters must have also the classical wavelength spectrometer. While using an energy dispersive spectrometer the systematical errors caused by spectra processing are added further.

Resolution limit was studied for the near concentrations of the SiO_2 on three glasses with the following real contents of SiO_2 in each of them: 77.84 % SiO_2, 78.84 % SiO_2 and 79.84 % SiO_2. Because of the high content of SiO_2 and thus high ratio of the peak of SiK_α no special attention was payed to the background substraction. The Edax analyser modell 711 equipped with minicomputer and software Edit Nova was used for the measurement. By means of these programmes it is possible to substract the background with a simple digital filter and separate the peaks in the way described in [1], [2]. For the establishment of the intensity after fitting the Gaussian curve on the peak, the area under curve 1.2 FWHM in width is determined. The whole area is not used for the insufficient coincidence of the Gaussian curve with the tails of the peak. This way about 85 % of the whole area of the peak is taken into account. Systematic error caused by separation of the peaks quickly increases with the inproper calibration of the spectrometer. Gain of the DC amplifier is extraordinarily stable, but the position of the zero level changes with time and with temperature. Even with the stabilized instrument in a climatized laboratory the shift of about 1—2 eV . hour^{-1} takes place. Each glass of the above mentioned series was twice measured and the measurement of the first glass was then repeated.

Measurement was carried out at 15 kV accelerating voltage and at the beam current of $1 . 10^{-9}$ A. To avoid the alkali-migration the area about 60×70 μm was scanned instead of that of point analysis. The measuring interval (so called life time) was 40 s. The intensity of SiK_α line was determined in the three following ways:

1. After background substraction using Gaussian curve the separation was provided.

2. After background substraction the content of all channels under the peak curve was determined to calculate the area under the peak curve.

3. Without background substraction the area of the window in width of 220 eV was established (i.e. 11 channels). The center of this window was always identical with the maximal value of the peak. FWHM of the SiK_α peak is 140 eV.

The experimental results are shown in Fig. 1. Intensities are plotted in counts. It is apparent that the stability of the measurement and its reproducibility are satisfactory, differences are about 0.5 % rel., with the exception of middle glass (up to 2 %) probably due to its worse homogeneity.

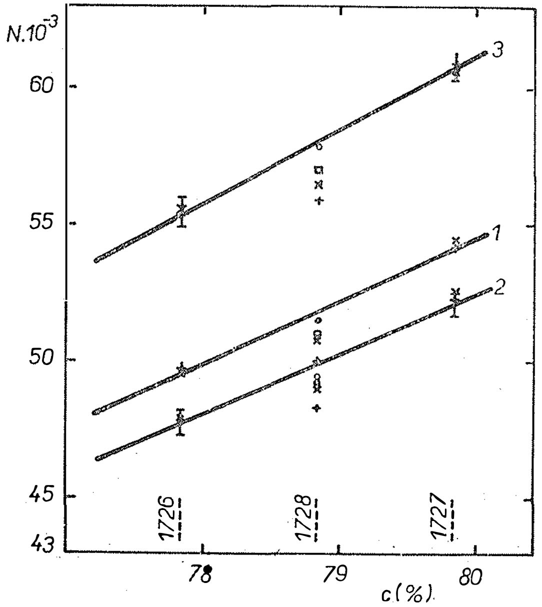

Fig. 1. Plot of number of counts N against concentration c of SiO_2*. Life time 40 s. Number labeled to lines determine method of peak stripping (see text).*

1 — peak stripping after background substraction (program EM-stripping).
2 — Integral of the peak after background substraction (program EM-intensity).
3 — Integral of the selected window (11 channels without background substraction.)

The reproducibility of results is satisfactory, although its deterioration due to imperfect homogeneity of measured glass cannot be excluded. Further follows from the picture that all three used ways of establishement of intensity are equal at the proper calibration of the spectrometer.

The zero shift of the energetic scale of the analyser is another problem. At the zero shift of 10 eV the intensity drop in the two first methods was about 3 %, in the third method intensity increased about 1 % (apparently in the frame of statistical fluctuations of counts).

At the shift of 20 eV the intensity drop in the first two cases was 10 %. The third method gave results of 1.4 % higher then previously.

The third method is less sensitive to proper calibration. Unfortunately it is possible to use it only when the analysed peak is not overlapped by the neighboring peak. At the high content of Al_2O_3 in glass, for example, the peaks for Al and Si would overlap and the third method would give negative results. It is apparent from Fig. 1 that with a properly adjusted spectrometer and at good stability (particularly constant temperature) the 1 % difference in concentration is possible for reliable resolution. Further we have investigated the possibility to shorten the time of measurement (life time) to 10 sec. The result is introduced on Fig. 2. It is apparent that the resolution of the 1 % difference in the content of SiO_2 is still possible in this case, but owing to much higher statistical fluctuations it is less reliable because the accuracy of the measurement is not sufficient due to a small number of pulses (cca 15,000).

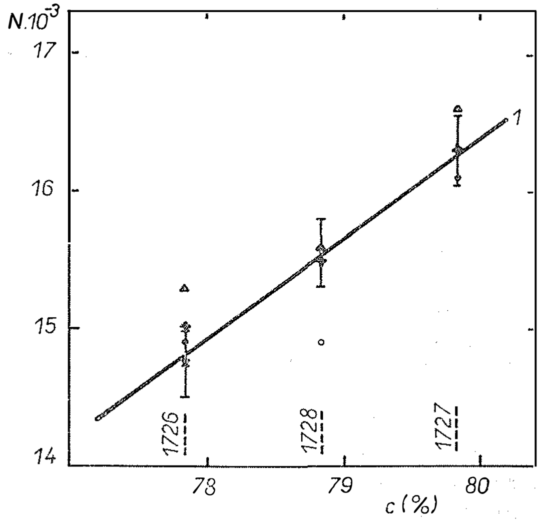

Fig. 2. Plot of number of counts N against concentration c of SiO_2. *Life time 10 s. (Program EP-peak stripping).*

LIMIT OF DETECTABILITY

When the limit of detectability is studied, both, the highest precision (the lowest statistical fluctuations) and the highest distance of characteristic X-ray signal from the background are required. Energy-dispersive spectrometer gives a very high background and has poor resolution, so that the peak-to-background ratio is very low, up to 2 orders compared with the wave-length spectrometer. Therefore the background substraction from X-ray spectrum becomes very important. EDAX spectrometer model 711, equipped by the minicomputer uses simple digital frequency filter, which identifies peaks as areas exceeding the backround by more than two standard deviations; these areas are then substracted from the spectrum see [1], [2], [3], [4]. When this filter is applied to the spectrum, only a background remains and after substraction of this background from the original spectrum net peaks are obtained for further processing. However, this filter cannot distinguish randomly cumulated pulses (statistical fluctuations) so that a number of "strange" peaks, which do not represent any element, remains in the spectrum. These "strange" peaks randomly change their position when digital filtering is applied to the new spectrum.

Peaks representing X-ray lines are distorted after filtering. This phenomenon causes suppression of the X-ray intensities measured and involves systematic error in following peak stripping.

Distortion of peaks was tested on calculated Gaussian peaks of 10,000 pulses and 60 pulses of height, respectively, with energy corresponding to ZnK$_\alpha$ line. Total area of the first peak was 104,132 pulses, spread in 36 channels. After application of digital filter, the height of this peak decreased to 9,900 pulses and its total area was 102,278 pulses (difference about minus 2 %). The total area of the second peak was 612 pulses, which was spread in 24 channels. After digital filtering its height was 48 pulses and consisted of only 16 channels. The shape of the peak was visibly changed. non-Gaussian and non-symmetric. The total area was only 417 pulses, i.e. for 32 % lower. It is evident, that to use a digital filter is more convenient for high peaks than for low peaks, the slope of which is not so sharp.

The second disadvantage of the background substraction program is, that the information about substracted background is not stored, so that any statistical treatment of the distance of peaks from background is impossible. It is not possible to use the program peak-to-background ratio for this purpose, because this gives the ratio of the net peak intensity to the total background (in all spectrum). It is clear, that both, peak and background areas should be measured in the identical band of the spectrum (so called window). If the width of the window increases (we suppose that the centroid of the window is identical with the centroid of the peak), the area of the background increases approximatelly linearly, but the area of the peak increases according to the integral of the Gaussian curve, reaching constant value in the limit (i.e. if the window width is from $-\infty$ to $+\infty$). It means that with the expansion of the window the precision of the measurement increases (as the standard deviation increases with square root of total number of pulses), but peak-to-background ratio decreases.

It seems that window width equal 1.2 FWHM, which is used in peak stripping programs, is too high when small peaks are stripped. Therefore the optimal window width should be found.

The limit of detectability of Zn in silicate glass was studied experimentally. Peak of ZnK$_\alpha$ line is far from other peaks in the spectrum, so that no special peak stripping was required. Two identical glasses, containing 0.10 % and 0.15 % ZnO were prepared. Accelerating voltage was 20 kV, specimen current $1 \cdot 10^{-9}$ A, life time 100 s. Fig. 3 shows part of X-ray spectrum of the glass No 1719. containing 0.10 % ZnO. Fig. 3b shows the expanded part of the same spectrum. Fig. 3c shows the spectrum after background substraction. Peak ZnK$_\alpha$ is marked by a vertical line. It can be seen, that occasional "strange" peaks can be even higher than proper peaks. Fig. 3d and 3e show spectrum of glass No 1721, containing 0.15 % ZnO. Fig. 3f shows the comparison of original spectrum with this spectrum after background substraction. It is evident that "strange" peaks are formed by the use of digital filter. In order to find the optimal width, the window was expanded step by step from 1 channel up to maximal number of channels. The background was established as a difference of the total number of pulses in selected window and the number of pulses in the same window after background substraction. The value $P - 2\sqrt{2B}$ (where P is the number of pulses of the peak and $2\sqrt{2B}$ is a doubled standard deviation σ, B is the number of pulses of background) was taken as the resolving criterion of the peak to the background. These values are presented in Tab. I. It can be seen, that if we take into the account only the height of the peak (1 channel) the peak needs not be statistically resolved from the background, even the P/B ratio is maximal. On the other hand, when maximal number of channels is chosen, the possibility to resolve the peak from the background is also very low. In our case the optimal window width was 9 channels, i.e. 180 eV.

Table I

Specimen No 1719 Number of channels	0.10 % ZnO					
	$P + B$	P	B	$2\sqrt{2B}$	$P - 2\sigma$	P/B
1	456	35	421	58	-23	0.083
3	1312	99	1213	98	1	0.081
5	2144	148	1996	126	22	0.074
7	2978	180	2798	150	30	0.064
9	3781	197	3584	169	28	0.055
11	4569	205	4384	187	18	0.047
13	5347	208	5139	203	5	0.040
Specimen No 1721 Number of channels	**0.15 % ZnO**					
	$P + B$	P	B	$2\sqrt{2B}$	$P - 2\sigma$	P/B
1	449	59	390	56	3	0.151
3	1412	168	1244	100	68	0.135
5	2287	254	2033	128	126	0.124
7	3170	315	2855	151	164	0.110
9	4029	348	3681	172	176	0.094
11	4846	361	4485	190	171	0.080
13	5635	365	5270	205	160	0,069

Fig. 4 shows the plot of net peak area against the concentration. Horizontal lines represent corresponding 2σ levels. Full lines represent the case with 9 channels, dashed lines represent the case with 13 channels (260 eV). FWHM on ZnK$_\alpha$ peak was 200 eV. The crosses of the corresponding lines give the limit of the detectability. When optimal window width is chosen the limit is 0.08 % ZnO, when conventional (1.2 FWHM) width is chosen, the limit of detectability is lower, 0.09 % ZnO.

CONCLUSION

From measurements presented here follows that using energy dispersive X-ray spectrometer it is possible to distinguish 1 % difference at 80 % weight content of silica in the glass. This value is nearly identical with that established by wavelength dispersive spectrometer [4].

Neither limit of detectability under optimal conditions (short wavelength

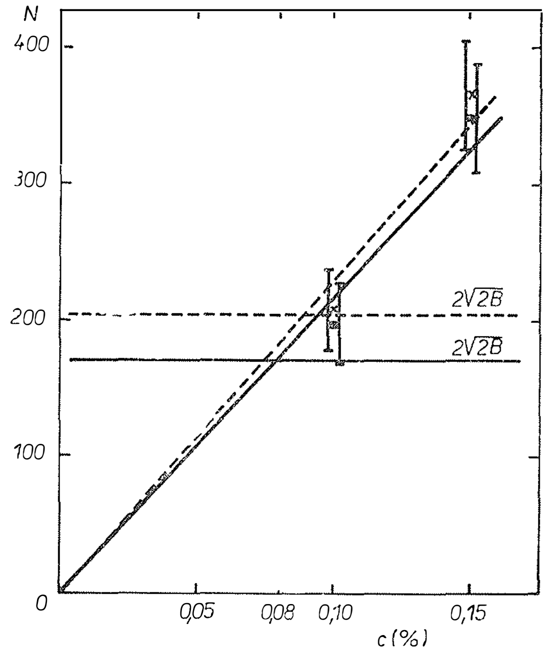

Fig. 4. Plot of net peak area (in counts N) against the concentration c of ZnO. *Full lines (squares) represent window width 9 channels, dashed lines (crosses) 13 channels.*

characteristic radiation in light elements matrix) is not much worse compared with the value obtained by wavelength dispersive spectrometer [4]. Both values are of the same order. However, measurement was not interfered by peak convolution and complicated shape of background.

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MEZE ROZLIŠENÍ A CITLIVOSTI V RENTGENOVÉ MIKROANALÝZE SKEL PŘI POUŽITÍ ENERGIOVĚ DISPERZNÍHO SPEKTROMETRU

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Mez rozlišení byla studována experimentálně na sérii tří vzorků silikátových skel obsahujících 77,84 %, 78,84 % a 79,84 % SiO_2. Měření bylo provedeno na elektronovém mikroanalyzátoru JXA-50 fy JEOL při použití spektrometru EDAX, model 711. Byly ověřovány tři rozličné způ-

soby odečítání intenzity rtg. čáry SiK_α z naměřeného spektra, aby bylo možné zjistit vliv správné kalibrace a stability spektrometru na mez rozlišení:

1. Po odečtení pozadí byla provedena separace píku SiK_α přizpůsobením Gaussovy křivky (program EM-peak stripping).
2. Po odečtení pozadí byla zjišťována plocha píku sečtením obsahu všech jeho kanálů (program EM-intensity).
3. Byl zjišťován obsah okénka o šířce 11 kanálů bez odečtení pozadí, přičemž střed okénka byl umístěn do maxima píku.

Závislost zjištěných intenzit na koncentraci je uvedena na obr. 1 a 2. Je vidět, že rozlišení jednoprocentního rozdílu při uvedených koncentracích je možné všemi metodami. Metoda 1 je nejcitlivější na správnou kalibraci, metoda 3 je nejméně citlivá. Jsou-li však píky malé a překrývají se se sousedními píky, je nutné použít metody 1.

Mez citlivosti byla studována na dvou identických sklech o obsahu 0,10 % a 0,15 % ZnO. Naměřená spektra jsou uvedena na obr. 3. Byl zjišťován vliv digitálního filtru na spektrum při odečítání pozadí. Zejména malé píky jsou filtrací značně deformovány a snížení intenzity dosahuje až několika desítek procent. Dále byl studován vliv šířky zvoleného okénka na odstup píku od pozadí tak, že okénko bylo rozšiřováno z 1 kanálu až na celou šířku píku (13 kanálů). Výsledky jsou v tab. I. Optimální šířka okénka byla 9 kanálů pro čáru ZnK_α, tj. 180 eV. Závislost intenzity čáry ZnK_α na koncentraci ZnO je uvedena na obr. 4. Z tohoto grafu plyne, že mez citlivosti je 0,08 % ZnO při intervalu spolehlivosti 2σ. Mez citlivosti při použití energiově disperzního spektrometru, tedy za optimálních podmínek, není o mnoho horší než hodnota získaná vlnově disperzním (krystalovým) spektrometrem, neboť obě rtg. hodnoty jsou stejného řádu.

Obr. 1. Závislost počtu pulsů N na koncentraci c SiO_2. *(Life time 40 s.) Číslo označující příslušnou linii určuje metodu stripování píků (viz text).*
1 — stripování po odečtení pozadí (program EM-stripping).
2 — Integrál píků po odečtení pozadí (program EM-intensity).
3 — Integrál „okénka" o vybrané šířce (11 kanálů) bez odečtení pozadí.

Obr. 2. Závislost počtu pulsů N na koncentraci SiO_2. *(Life time 10 s) (program EP-peak stripping).*

Obr. 3. Spektrum charakteristického rtg. záření ze skla obsahující pík ZnK_α*, spektrum zaznamenáno při 20 kV urychlovacího napětí, proud vzorkem* $1 \cdot 10^{-9}$ *A. (Life time 100 s.)*
a) Vzorek č. 1719 obsahující 0,10 % ZnO.
b) Totéž spektrum roztažené.
c) Spektrum po odečtení pozadí. Pík ZnK_α *je označen svislou čarou.*
d) Vzorek č. 1721 obsahující 0,15 % ZnO.
e) Spektrum po odečtení pozadí. Pík ZnK_α *je označen svislou čarou.*
f Porovnání původního spektra se spektrem po odečtení pozadí.

Obr. 4. Závislost velikosti plochy pod píkem (v počtu pulsů N) na koncentraci c ZnO. *Plná čára (čtverečky) znázorňuje šířku okénka 9 kanálů, přerušovaná čára (křížky) reprezentuje šířku okénka 13 kanálů.*

ПРЕДЕЛЫ ИДЕНТИФИКАЦИИ И ЧУВСТВИТЕЛЬНОСТИ В РЕНТГЕНОВСКОМ МИКРОАНАЛИЗЕ СТЕКОЛ ПРИ ПРИМЕНЕНИИ ЭНЕРГИЕГО-ДИСПЕРСИОННОГО СПЕКТРОМЕТРА

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Исследовали экспериментальным путем пределы идентификации на серии трех образцов силикатных стекол, содержащих 77,84 %, 78,84 % и 79,84 % SiO_2. Измерения проводили с помощью электронного микроанализатора JXA-50 фирмы JEOL с применением спектрометра EDAX, модель 711. Оценивались три различные способы отсчета интенсивности рентгеновских линий SiK_α из измеренных спектров с целью установить влияние правильной калибрации и стабильности спектрометра на пределы идентификации:

1. после отсчета фона проводили сепарацию пика SiK_α приспособлением кривой Гаусса (программа EM — peak stripping);
2. после отсчета фона установливали поверхность пика суммированием всех его каналов (программа EM — интенсивности);

3. устанавливали содержание окошка шириной 11 каналов без отсчета фона, причем центр окошка помещали в максимум пика.

Зависимость установленных интенсивностей от концентрации приводится на рис. 1 и 2. Видно, что идентификацию однопроцентного различия при приводимых концентрациях можно проводить с помощью всех методов. Метод 1. оказывается наиболее чувствительным относительно правильной калибрации, метод 3. наименее чувствителен. Однако если пики небольшие и перекрываются с соседними пиками, то приходится применять метод 1).

Пределы чувствительности исследовали на двух идентических стеклах, содержащих 0,10 % и 0,15 % ZnO. Измеренные спектры приводятся на рис. 3. Устанавливали влияние дигитального фильтра на спектр при отсчете фона. Именно небольшие пики фильтрацией значительно деформируются и понижение интенсивности достигает нескольких десяток процентов. Далее рассматривали влияние ширины подобранного окошка на расстояние пика от фона так, что окошко расширяли с 1 канала до всей ширины пика (13 каналов). Результаты приводятся в табл. 1. В виде оптимальной ширины окошка оказывалось 9 каналов для линии ZnK_α т. е. 180 эВ. Зависимость интенсивности линии ZnK_α от концентрации ZnO приводится на рис. 4. Из графика следует, что пределы чувствительности составляют 0,08 % ZnO при интервале надежности 2σ. Пределы чувствительности при применении энергиево-дисперсного спектрометра при оптимальных условиях не гораздо хуже, чем величина, полученная с помощью волново-дисперсионного (кристаллического) спектрометра, так как обе рентгеновские величины того же порядка.

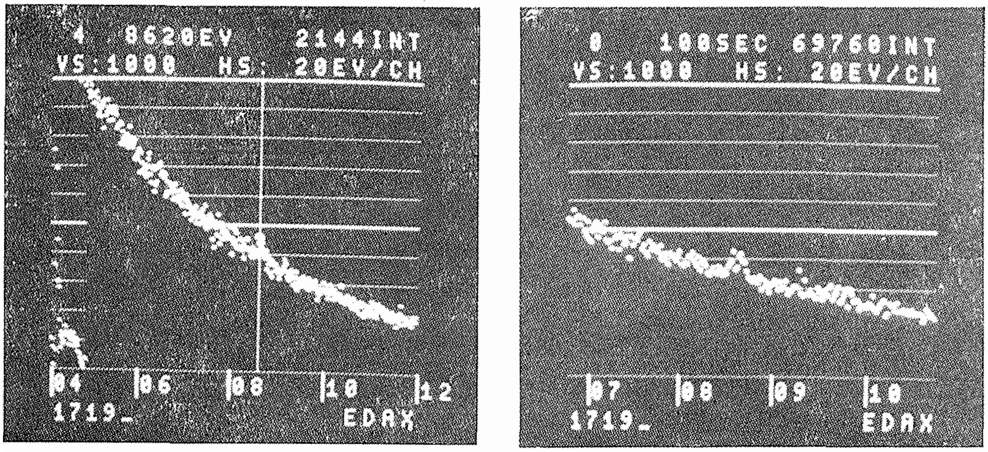
Рис. 1. Зависимость количества пульсов N от концентрации с SiO_2. (Life time 40 с). Номер, обозначающий соответствующую линию, определяет метод стрипования пиков (см. текст): 1 — стрипование после отсчета фона (программа EM — stripping), 2 — интеграл пиков после отсчета фона (программа EM — интенсивности), 3 — интеграл „окошка“ подобранной ширины (11 каналов) без отсчета фона.

Рис. 2. Зависимость количества пульсов N от концентрации SiO_2. (Life time 10 с).программа EP — peak stripping.

Рис. 3. Спектр характеристического рентгеновского излучения из стекла, содержащего пик ZnK_α, спектр заметили при 20 кВ ускорительного напряжения, ток образцом 1.10^{-9} A. (Life time 100 с.): а) образец = 1719, содержащий 0,10 % ZnO, б) тот же спектр расширенный, в) спектр после отсчета фона. Пик ZnK_α обозначен через вертикальную линию, г) образец = 1711, содержащий 0,15 % ZnO, д) спектр после отсчета фона. Пик обозначен через вертикальную линию. е) сравнение первоначального пика со спектром после отсчета фона.

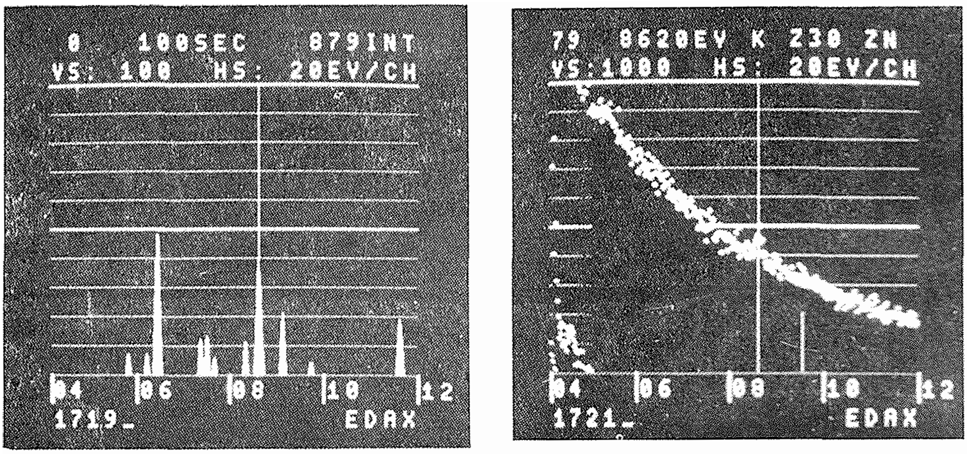
Рис. 4. Зависимость размера поверхности под пиком (в количестве пульсов N) от концентрации с ZnO. Сплошаян линия (квадратики) представляет ширину окошка 9 каналов, штриховая линия (крестики) ширину окошка 13 каналов.

Fig. 3. X-ray spectrum of glass showing peak ZnK_{α}*, taken at 20 kV, specimen current* $1 \,.\, 10^{-9}$ *A, (life time 100 s).*



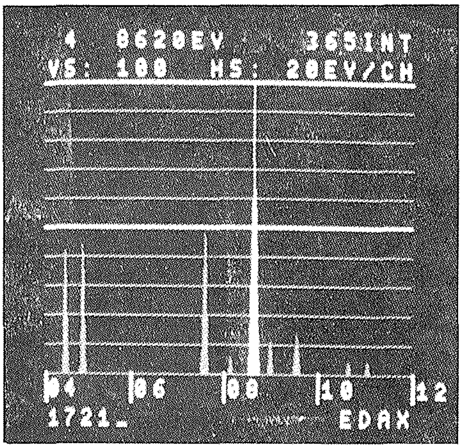
a) Specimen No 1719 containing 0,10 % ZnO.

b) The same spectrum, expanded.

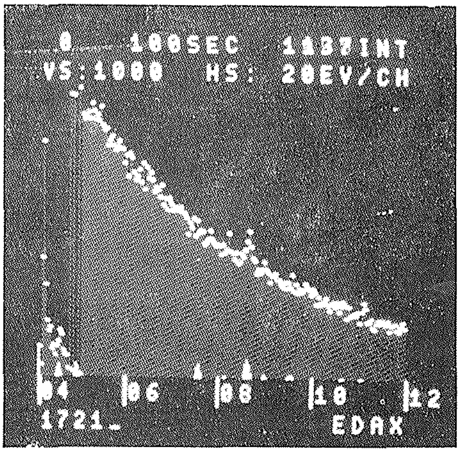


c) Spectrum after background substraction. ZnK_{α} *line is marked by a vertical line.*

d) Specimen No 1721, containing 0,15 % ZnO.



e) Spectrum after background substraction, ZnK_{α} *line is marked by a vertical line.*



f) Comparison of the original spectrum with the spectrum after background substraction.