Scientific articles

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SOLVING MINERALOGY PROBLEMS
WITH THE HELP OF THE "ORIGIN" PACKAGE

Abstract. Algorithms for solving typical mineralogical problems associated with quantitative x-ray spectral analysis and quantitative x-ray phase analysis using the program "Origin" are developed. The calculation of the areas and midpoint of spectral lines using the tabular processor of the program "Origin" is considered. Various approaches to determining the parameters of spectral lines using the least squares method using the standard functions of the program "Origin" were tested. The creation of a user function for approximation of diffraction maxima by the Cauchy function taking into account the doublet character of K_a series of x-rays is also considered. Various built-in algorithms for smoothing functions (based on averaging, polynomial approximation and Fourier analysis – synthesis) were tested to find weak diffraction maxima against strong noise; optimal schemes for the application of these algorithms were found. The considered algorithms can be applied in universities when processing the results of laboratory works on the topics "Analysis of spectra of emission of atoms", "Quantitative x-ray spectral analysis" and "Quantitative x-ray phase analysis".

Key words: x-ray spectral analysis; x-ray phase analysis; least squares method; signal processing; smoothing functions; noise suppression.

Introduction. In the study of minerals in Geology and Mineralogy, the most important stage of the analysis is to determine the chemical composition and phase composition of the studied mineral samples. X-ray spectral analysis is the most common method for determining the composition, it allows to determine both the qualitative and quantitative composition of the sample using the emission x-ray spectra of the sample [1,5]. X-ray phase analysis is widely used to solve the problem of crystal phases identification and determination of their relative fractions in minerals. It is based on the determination of interplanar distances by radiographs, and then a search is carried out on the databases of the corresponding phases [2,4].

The determination of wavelengths in x-ray spectral analysis and the determination of interplane distances in X-ray phase analysis is based on the application of the Bregg-Wolfe formula, in which the measured parameter is the position of the diffraction maximum angle on the diffraction graph [3,4]. Quantitative X-ray spectral analysis and quantitative X-ray phase analysis are based on determining the areas under diffraction maxima and calculating through these areas the ratio of the number of elements or the ratio of the number of phases. This task is greatly complicated in cases where the diffraction lines of the phases overlap and it is not possible to distinguish individual lines in simple ways. In this case,

algorithms based on the least squares method (LSM) or on the methods of solving integral equations by A.N. Tikhonov regularization methods are used [6,7].

Usually such problems are solved with the help of expensive specialized programs or algorithms and programs created by users in such environments as Matlab, Fortran, etc. [8-12]. In the latter case, it is necessary to create long texts of algorithmic programs in programming languages, which can be done by experienced programmers only. Some tasks of this problem, however, can be performed very efficiently with the "Origin" package [13,14]; it does not require complex programming, and most of the necessary computational operations can be performed at the OSD level.

The purpose of this work is to develop a methodology for the analysis of radiographs using the "Origin " package, in particular methods for the precise determination of the angular position of the integral intensities and the angular width of the lines using the least squares method.

Research methods. In the case of X-ray spectral analysis and X-ray phase analysis, the typical view of the intensity dependence on the diffraction angle is as in figure 1. The functional dependence can be represented as several maxima 1-7, located on a smoothly changing background.
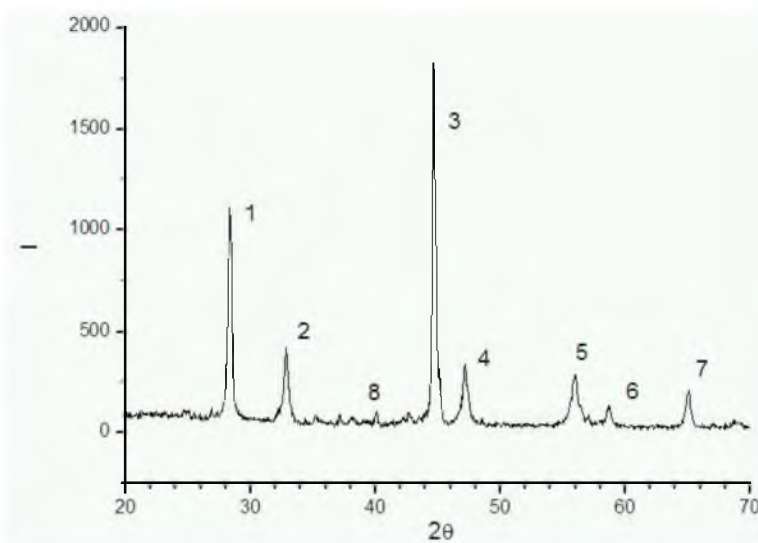

Figure 1 – Functional dependence of intensity on diffraction angle in case of phase analysis of polycrystalline sample

If the maxima are located without overlap, as in the case of 1, 2, 4-7 in figure 1, then in the "Origin" environment, it is advisable to calculate the determination of the positions of the lines as the position of the center of gravity of the figure formed by the graph and the background line, and the integral intensity as the area of this figure. To do this, first select a separate line, then find the background value at the edges of the lines, create a column describing the background as a linear function of the angle, and subtract the background function from the intensity values (2nd column), writing the result in the fourth column. Next, the 5th column is created equal to the slow multiplication of the elements of the 1st and 4th columns. Then through the menu "statistics\descriptive statistics\statistics in columns" calculate the sum of the elements of all columns. The area of a line is proportional to the sum of the elements of the 4th column, and the position of the center of gravity of the line is equal to the sum of the elements of the fifth column and the sum of elements of the fourth column. Thus, you can find the position of the center of gravity of the line and the area of the isolated line.

Results of the analysis of poorly resolved spectral lines. In the case of overlapping lines as in figure 1 (3rd line) or to improve the accuracy of determining the parameters of isolated lines, it is necessary to use the decomposition of a complex line into components using the least squares method (LSM). Then, using the parameters of the lines, you can find the positions of their center of gravity and the area of each line. In the package, the LSM is activated using the "analysis\fit multi peaks" menu; next, select the form of the "Gaussian" or "Lorentzian" peaks. In the case of Lorentzian, the decrease in intensity from the maximum to the edges of the line is slower than in the case of Gaussian.

In the case of Lorentzian, the shape of the line is given by the formula:

$$y = y_0 + \frac{2A}{\pi} \frac{w}{4(x - x_c)^2 + w^2}$$

In this formula: X_c - position of the center of gravity of the line; W - half-width of the line at half its height; A is the area of the figure below the line.

In the case of a Gaussian, the shape of the line is given by the formula

$$y = y_0 + \frac{A}{w\sqrt{\pi/2}} e^{-2\frac{(x-x_c)^2}{w^2}}$$

X_c - position of the center of gravity of the line; W - half-width of the line at half its height; A is the area of the figure below the line.

In both cases, each line is defined by 3 parameters. Another parameter describes a uniform background.

To determine the parameters of the lines in the program "Origin" after activating the menu "analysis\fit multi peaks\" you should specify the number of peaks and their approximate width. Next, double-click to mark the vertices of each peak. After that, the results of approximation of the experimental curve by Gaussians (Lorentzians) and a table containing the parameters of these peaks will appear on the graph.

Figure 2 shows an enlarged fragment of the X-ray (peaks 1 and 2 in figure 1) and the results of its decomposition into lorentzians.
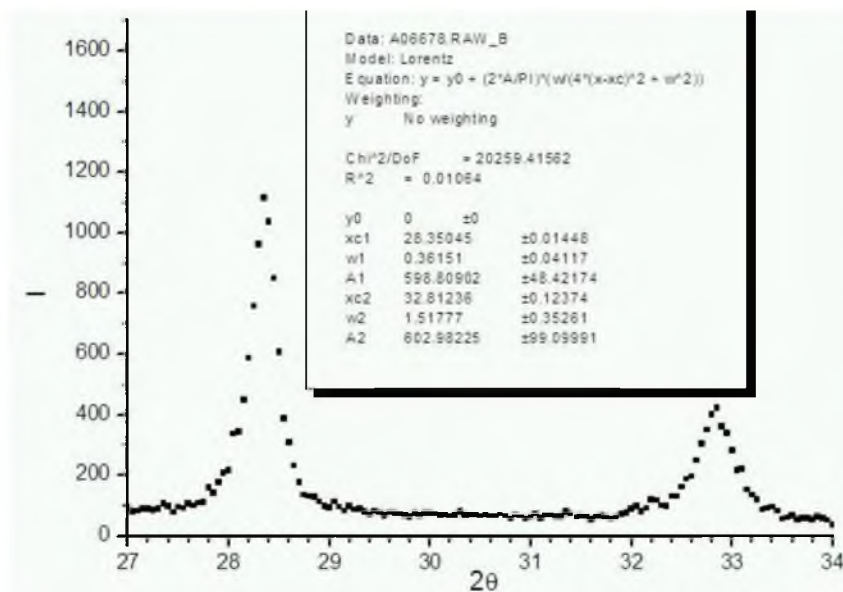

Figure 2 – The enlarged fragment of the radiograph (figure 1) and the results of its decomposition into lorentzians

The parameters of the lorentzians are given in the table inserted in figure 2, and the Protocol of the "Origin" program on the solution of this problem is given in figure 3.

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[23.11.2019 08:26 "/Graph2" (2458810)]
Lorentz(2) fit to A06678.RAW_B:

Chi^2/DoF     20259,41562
R^2           0,01064

Peak          Area          Center        Width         Height
------------------------------------------------------------------
1             598,81        28,350        0,36151       1054,5
2             602,98        32,812        1,5178        252,92
------------------------------------------------------------------
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Figure 3 – Protocol of the "Origin" program on the solution of the problem shown on figure 2

In the case of X-ray diffraction, the shape of the lines is approximated by the Cauchy function in the best way. This function is described by the Lorentzian squared. Also, the background near the X-ray line is often described not by a constant, but by a linear function of the angle. To improve the accuracy of analysis we must take into account the doublet nature of X-ray radiation, namely: instead of one line we must take into account two. The intensity and relative position of these lines is determined in accordance with the spectrum of K_a series of X-rays emitted by atom. There is no such function in the library of "Origin" ready-made functions. However, the program "Origin" provides the ability to create your own user function. To do this, go to the menu section "Analysis\Nonlinear Curve Fit\Advanced Fitting Tool\". In the window that appears, through the "Function\" menu, select the creation of a new function, set the number of its parameters (=7) and write in the window an expression characterizing the Cauchy function with 4 maxima:

P1 * P2 / (P2 ^ 2 + (x - P3) ^ 2) ^ 2 + P1 * P2/ (P2 ^ 2 + (x - P3 - 0,14) ^2) ^2 / 2 + P4 * P5 / (P5 ^ 2+ + (x -P6) ^ 2) ^ 2 + P4 * P5 / (P5 ^ 2 + (x - P6 - 0,14) ^ 2) ^ 2 / 2 + P7.

The number 0.14, calculated from the table data on the wavelengths of the doublet lines shows the shift of the K_{a2} component of the K_a doublet from the K_{a1} component by the diffraction angle in this formula; also, the formula takes into account that the K_{a2} component is weaker than K_{a1} by two times.

Next, through the "Action\Simulate\" menu, approximate values of the parameters P1 ... P7 of the user function should be set. After that, the menu item "Action\Fit" is activated ; in the new window that appears, press the "1 iter" button several times until the approximating curve of the red color approaches with satisfactory accuracy to the experimental points. The results of the parameter definition can be seen using the "Action\Parameters" menu.

An example of using this algorithm for the case of the third maximum (see figure 1), which consists four closely spaced, almost merged maxima from the two phases (two maxima K_{a1} and K_{a2} from each phase) is shown in figure 4.
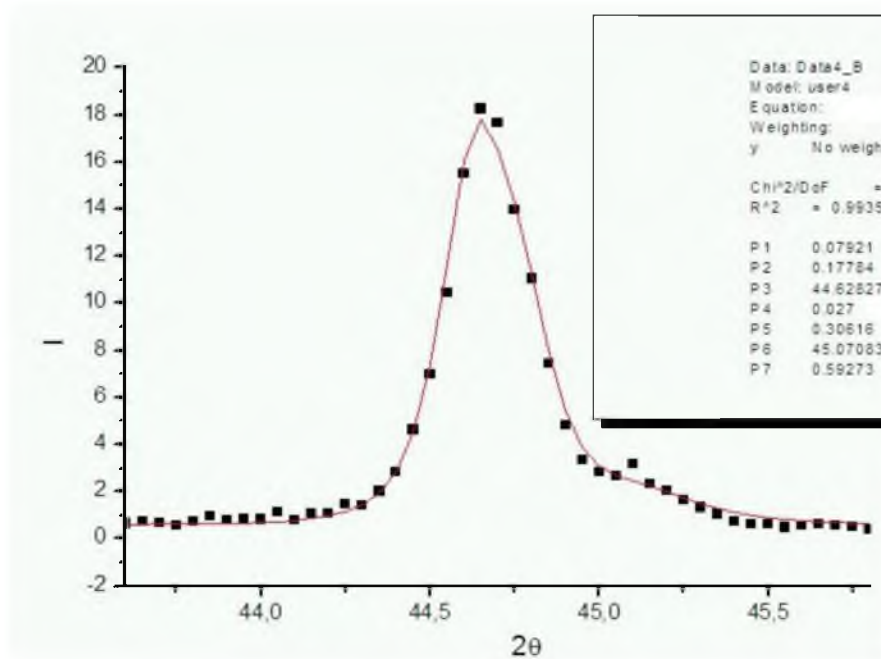

Figure 4 – The third maximum (shown in figure 1) and results of its decomposition into 2 components using Cauchy-function for aprocsimation of K_a –double spectra

The parameters of the Cauchy function for two maxima with doublet lines earch are inserted in figure 4.

The "Origin" program provides the possibility of smoothing functions in order to suppress noise in various ways to search for weak diffraction maxima. With these relatively simple algorithms, which are activated using the on-screen menu "Analisis\smoothing\", it is possible to smooth functions in three common ways.

The first group of smoothing algorithms (S-G - in figure 5) is based on smoothing through averaging the neighboring values of the function. You must correctly select the required number of points to the right and left of the calculated function value. This number should be increased in case of higher noise. However, excessive smoothing leads to smoothing and sharp maxima of the function and its sharp step differences.

The second group of algorithms (AA-in figure 5) draws a polynomial curve through the selected point and several adjacent points and selects the value of the polynomial at that point as the smoothed value. It is also necessary to choose the optimal number of points to the right and left of the calculated value of the function.

Smoothing functions based on using the third group of algorithms (FFT-in figure 5) are calculated via calculation of the Fourier image, correcting it in the high frequency domain and constructing a new corrected function as Fourier synthesis.

These three groups of anti-noise algorithms are activated using the on-screen menu In the Origin environment. The results of these algorithms work are presented in figure 5.
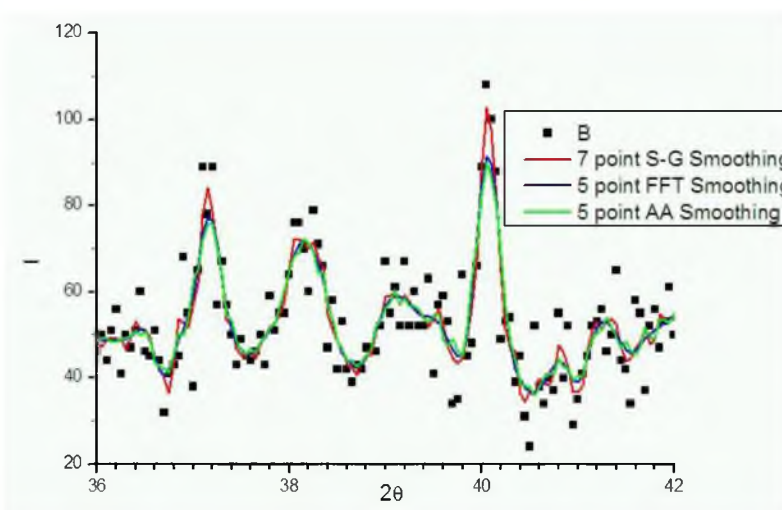

Figure 5 – The results of the application of smoothing algorithms:
S-G - through polynomial approximation; AA - by averaging the neighboring values of the function;
FFT - through the calculation and adjustment of the Fourier image

The best results of smoothing in our case of sharp maxima search against strong hindrances were reached at use of algorithms of smoothing through approximation (S-G) by a polynomial of the second order on 5-9 points. They should be applied to the processing of data with the aim of searching for weak diffraction peaks.

Conclusion. Algorithms for solving typical mineralogical problems associated with quantitative X-ray spectral analysis and quantitative X-ray phase analysis using the program "Origin" are developed.

These algorithms can be also used in universities when processing the results of laboratory work on the topics "Analysis of the emission spectra of atoms", "Quantitative x-ray spectral analysis" and "Quantitative x-ray phase analysis".

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«ORIGIN» ПАКЕТІ АРҚЫЛЫ МИНЕРАЛОГИЯ ЕСЕПТЕРІН ШЕШУ

Аннотация. «Origin» бағдарламасы арқылы сапалы және сандық рентгенді спектралдық талдау және сапалы, сандық рентгенді фазалық талдау негізінде минералогия мен материалтануға қатысты типтік міндеттерді шешу алгоритмдері әзірленді. Дифрактограммада максимумдарды жартылай автоматты іздеу проңедуралары, «Origin» бағдарламасының кестелік проңессоры, соның ішінде күрделі немесе симметриялы емес формадағы сызық көмегімен спектральді сызықтардың ауырлық аудандары мен орталықтары есептелді.

«Origin» бағдарламасына енгізілген стандартты аппроксимациялайтын функцияларды (Лоренц, Гаусс және басқа) пайдалана отырып, ең аз квадраттар әдісінің көмегімен спектрлік сызық параметрлерін анықтаудың түрлі тәсілдері бақылаудан өтті. Сонымен қатар, дифракциялық максимумды аппроксимациялау үшін пайдаланушы функциясын құру әдісі қарастырылды, аталған әдіс спектрлік және дифракциялық сызықтардың дәл аппроксимациясын қамтамасыз етеді, рентген сәулесінің k – сериясының дублеттік сипатын ескере отырып, аппроксимациялық функцияларды құру жолдары көрсетілді. Функция мәндерін бірнеше жақын орналасқан нүктелерде орташалауға; түрлі дәрежедегі полиномдармен аппроксимациялауға және функция мәні ретінде осы полином мәнін таңдауға; Фурье-бейненің жоғары жиілікті бөлігін түрлі тәсілдермен басу арқылы Фурье – анализ-синтезге негізделген функцияларды тегістеудің түрлі кіріктірілген алгоритмдері сынақтан өтті. Осы алгоритмдерді күшті кедергілер аясында әлсіз дифракционды максимумдарды іздеу үшін қолдану жолдары көрсетілді; аталған алгоритмдерді қолданудың оңтайлы схемалары анықталды. Мысал ретінде «Origin» пакетінің көмегімен төрт фазалы материалдың ұнтақ үлгісінің дифракционды спектрін талдау жұмыстары қарастырылды. Аталған спектр спектрді рентгенді флюоресценттік талдау мен зертханаларда рентгенді фазалық талдау үшін қолданылатын екі типтік жүктелген дифрактометр арқылы алынды. Аз квадраттар әдісі бойынша іріктелетін параметрлері бар функциямен аппроксимация негізінде қарапайым құрауыштарға әлсіз спектральді желілерді ыдырату жолымен рентгенограммаларды талдаудың аталған әдістерін қолдану ерекшеліктері қарастырылды. Қарастырылған алгоритмдерді заттардың, минералдар мен материалдардың фазалық құрамы мен құрылымын зерттеуге мамандаған ғылыми және өндірістік зертханаларда қолдануға болады. Шағын өзгерістермен әзірленген әдістемелерді хроматография, радиофизика мен электротехникадагы өтпелі және шектік үдерістерді цифрлық осциллографиялау әдісімен алынган экспериментальды деректерді талдау барысында қолдануға болады. Сонымен қатар, бұл әдістемелерді университеттерде бакалавр мен магистрлер орындайтын зертханалық жұмыстар нәтижесін өңдеу кезінде «атомдарды шыгару спектрлерін талдау», «сандық рентгенді спектралдық талдау» және «сандық рентгенді фазалық талдау», «Рентгенді спектроскопия», «Мессбауэрдік спектроскопия», «Эксперимент нәтижелерін өңдеу», «есептеу практикумы» тақырыптары бойынша қолданылады. Сипатталған әдістемелерді пайдалану барысында деректерді өңдеуде еңбекті көп қажет ететін – қолмен атқарылатын жұмыстар барынша азайтылып, жұмыс кезінде кездейсоқ жасалатын қателіктер азаяды әрі деректерді өңдеу үдерісі жеделдетіледі.

Түйін сөздер: рентгенді спектралдық талдау, рентгенді фазалық талдау, ең кіші квадраттар әдісі, сигналдарды өңдеу, функцияларды тегістеу, шуды бәсеңдету.

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РЕШЕНИЕ ЗАДАЧ МИНЕРАЛОГИИ С ПОМОЩЬЮ ПАКЕТА "ORIGIN"

Аннотация. Разработаны алгоритмы решения типичных для минералогии и материаловедения задач, связанных с проведением качественного и количественного рентгеновского спектрального анализа и качественного и количественного рентгеновского фазового анализа с помощью программы "Origin". Рассмотрены процедуры полуавтоматического поиска максимумов на дифрактограммах, вычисление площадей и центров тяжести спектральных линий с помощью табличного процессора программы "Origin", в том числе линий сложной или несимметричной формы. Опробованы различные подходы определения параметров спектральных линий с помощью метода наименьших квадратов с использованием стандартных аппроксимирующих функций (Лоренца, Гаусса и других), встроенных в программу "Origin". Также рассмотрено создание функции пользователя для аппроксимации дифракционных максимумов на примере функции Коши, которая обеспечивает наиболее точную аппроксимацию спектральных и дифракционных линий, продемонстрировано построение аппроксимирующих функций с учетом дублетного характера k – серии рентгеновского излучения. Опробованы различные встроенные алгоритмы сглаживания функций, которые основаны: на усреднении значений функции в нескольких соседних точках; на аппроксимации полиномами различной степени и выборе значения этого полинома в качестве значения функции; на Фурье-анализе – синтезе с подавлением высокочастотной части Фурье-образа различными способами. Продемонстрировано применение этих алгоритмов для поиска слабых дифракционных максимумов на фоне сильных помех; найдены оптимальные схемы применения этих алгоритмов. В качестве примера рассмотрен анализ дифракционного спектра порошкового образца четырехфазного материала с помощью пакета "Origin". Этот спектр был получен на типичном двукружном дифрактометре, применяемом для спектрального рентгеновского флюоресцентного анализа и рентгеновского фазового анализа в лабораториях. Рассмотрены особенности применения перечисленных методов анализа рентгенограмм путем разложения плохо разрешенных (по

критерию Релея) спектральных линий на простые составляющие с помощью аппроксимации функцией с подбираемыми параметрами по методу наименьших квадратов. Рассмотренные алгоритмы можно использовать в научных и заводских лабораториях, специализирующихся на изучении фазового состава и структуры веществ, минералов и материалов. С небольшими изменениями разработанные методики можно использовать при анализе экспериментальных данных, полученных методами хроматографии, цифрового осциллографирования переходных и пороговых процессов в радиофизике и электротехнике. Также эти методики можно применять в университетах при обработке результатов выполнения лабораторных работ выполняемых бакалаврами и магистрами по темам «Анализ спектров испускания атомов», «Количественный рентгеновский спектральный анализ» и «Количественный рентгеновский фазовый анализ», «Рентгеновская спектроскопия», «Мессбауэровская спектроскопия», «Обработка результатов эксперимента», «Вычислительный практикум». При использовании описанных методик сводится к минимуму трудоемкая ручная работа при обработке данных, благодаря чему уменьшается риск случайных ошибок при работе, ускоряется процесс обработки данных.

Ключевые слова: рентгеновский спектральный анализ; рентгеновский фазовый анализ; метод наименьших квадратов; обработка сигналов; сглаживание функций; подавление шумов.

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