Joint ICTP-IAEA School on Novel Experimental Methodologies for Synchrotron Radiation Applications in Nano-science and Environmental Monitoring

Tutorial on XRF Data Analysis

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AXES
Antwerp X-ray Analysis, Electrochemistry & Speciation
University of Antwerp

21 Nov 2014

X-ray fluorescence spectrum analysis

From Axil over WinAxil to bAxil

In the beginning: 1974 - 1978 Ph.D. at University of Antwerp, Belgium

The task: make a program to determine the net peak area in XRF spectra

The tools:

Computer: PDP-11/45

Memory:	64 kByte memory
Disk:	4 MByte
OS:	RT11
Input:	Punch cards, paper tape

Programming:

Fortran IV and assembler

UNIVERSITEIT ANTWERPEN

UNIVERSITAIRE INSTELLING ANTWERPEN

DEPARTEMENT SCHEIKUNDE

FOTONENGEÏNDUCEERDE RÖNTGENFLUORESCENTIE-ANALYSE VAN AËROSOLEN

PIERRE VAN ESPEN

Promotor:

Prof. Dr. F. ADAMS

Proefschrift ingediend voor het bekomen van de graad van Doctor in de Wetenschappen (groep: scheikundige wetenschappen)

Wilrijk, 1978

Men kan echter gebruik maken van het lineaire verband tussen de positie van de piek en de energie enerzijds en tussen het kwadraat van de breedte en de energie anderzijds:

$$P_j = C_1 + C_2 E_j \qquad (3.18)$$

$$W_j^2 = C_3 + C_4 E_j \qquad (3.19)$$

Aan deze relaties is voldaan voor de fluorescentielijnen van de elementen, mits inachtneming van de doubletopsplitsing. De piekbijdrage in het spectrum kan dan geschreven worden als:

$$Y_i = \sum_j \frac{O_j}{\sqrt{2\pi}(C_3 + C_4 E_j)^{1/2}} \exp\left[-\frac{1}{2}\frac{(C_1 + C_2 E_j - x_i)^2}{C_3 + C_4 E_j}\right] \qquad (3.20)$$

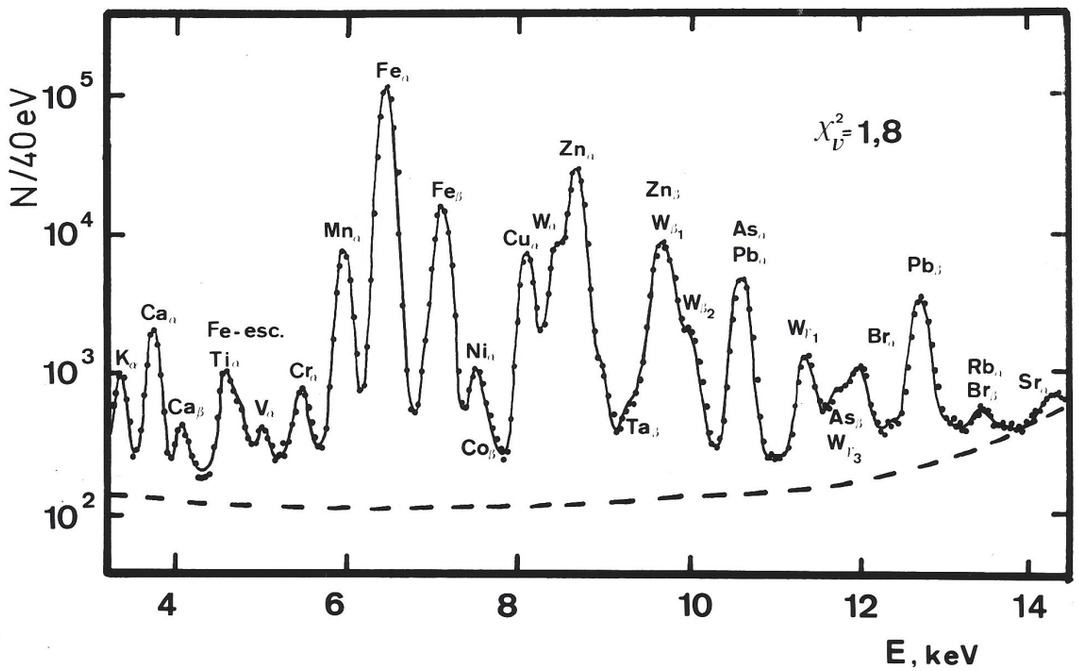
waarbij de sommatie gebeurt over het aantal pieken in het beschouwde deel van het spectrum. Wordt het spectrum aldus beschreven, dan is het niet langer nodig de positie en de breedte van elke piek afzonderlijk te bepalen, maar hoeven slechts de 4 calibratieparameters C_1 - C_4 geoptimaliseerd te worden. Er moet opgemerkt worden dat dit principe enkel toepasbaar is indien de energie van alle in het spectrum aanwezige pieken gekend is, wat in tegenstelling tot bijvoorbeeld gamma-spectra, het geval is bij Röntgenspectra.

Een verdere reductie van het aantal parameters kan bereikt worden door gebruik te maken van de constante intensiteitsverhouding die er bestaat tussen de pieken van een element. Wanneer deze verhouding niet beinvloed wordt door absorptie kan het fluorescentiespectrum beschreven worden door:

$$Y_i = \sum_j O_j \sum_k \frac{R_{jk}}{\sqrt{2\pi}(C_3 + C_4 E_{jk})^{1/2}} \exp\left[-\frac{1}{2}\frac{(C_1 + C_2 E_{jk} - x_i)^2}{C_3 + C_4 E_{jk}}\right] \qquad (3.21)$$

Hierbij heeft de eerste sommatie betrekking op het aantal elementen die een bijdrage in het spectrum geven en de tweede sommatie op het aantal lijnen van elk element j. R_{jk} is de opgegeven intensiteitsverhouding van piek k tot de hoofdpiek (k=1) in groep j.

De op deze manier bekomen beschrijving heeft grote invloed op de computeranalyse van het spectrum. In de eerste plaats treedt er een sterke vermindering op van het aantal te optimaliseren parameters en bijgevolg ook van de geheugenvereisten van de



Figuur 3.15 Fit van een complex spectrum van een industrieel aërosolmonster. In totaal zijn meer dan 100 fluorescentielijnen van 18 elementen aanwezig.

1977 First publication

NUCLEAR INSTRUMENTS AND METHODS 142 (1977) 243-250 ; © NORTH-HOLLAND PUBLISHING CO.

A COMPUTER ANALYSIS OF X-RAY FLUORESCENCE SPECTRA

P. VAN ESPEN, H. NULLENS and F. ADAMS

Department of Chemistry, University of Antwerp (U.I.A.), B-2610 Wilrijk, Belgium

A method is presented for the non-linear least-squares analysis of low-energy X-ray spectra obtained by tube-excited X-ray fluorescence analysis. The method is based on a description of the full energy peaks as Gaussian distributions and the background as a polynomial. System constraints are used to keep peak position and resolution consistent with predetermined calibration expressions. The least-squares routine is based on the Marquardt algorithm but parameters are confined within predetermined physically significant intervals. The method is implemented in the computer program AXIL written in Fortran IV for a PDP 11/45 system. Tests are described which prove that the program is able to provide reliable values for the parameters.

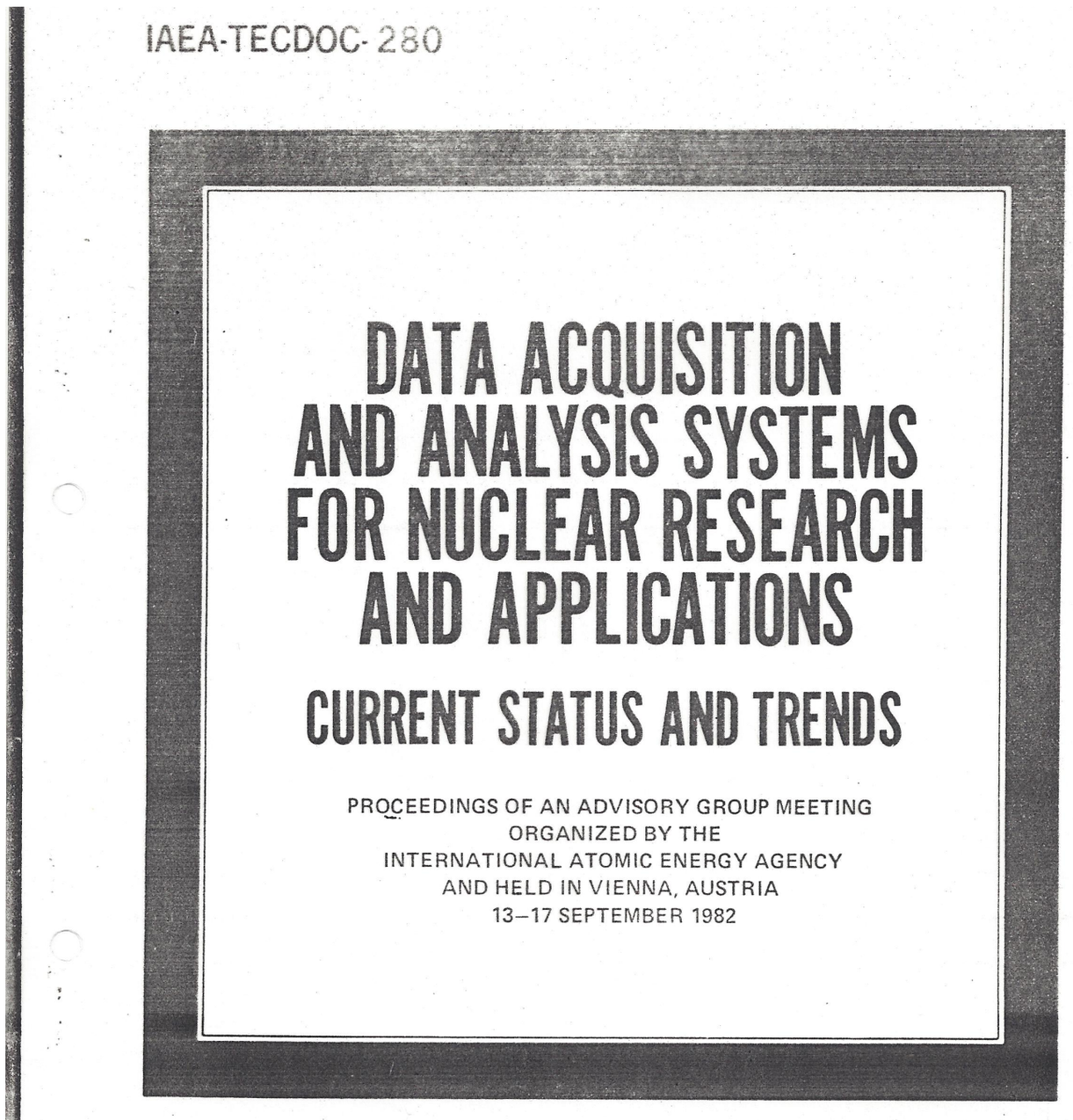
First time mentioning a computer program called AXIL

AXIL = **A**nalysis of **X**-ray spectra by **I**terative least Squares

1980 First (commercial) Axil version in FORTRAN
Running on PDP-11 computers
Distributed by Canberra-Positronika, Belgium

1981 Canberra USA: Canberra S228 RT/AXIL X-ray Analysis Software

1982 IAEA got interested in AXIL



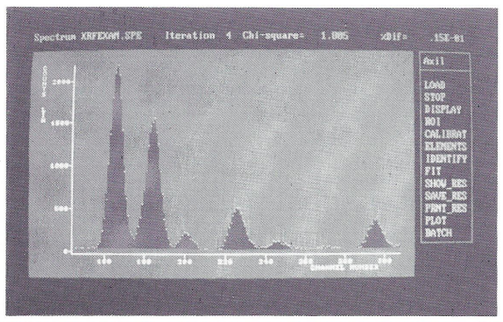
1984 IBM-PC version development started
with the help of Canberra-Positronika, Belgium

CANBERRA PACKARD

AXIL-PC

FEATURES:

- SPECTRUM TRANSFER from the different CANBERRA MCA'S and other sources to PC using standard RS-232 interfaces
- User-friendly package with help, overlapping menus, and graphical representations
- Powerful non-linear least squares spectrum deconvolution package for complex XRF, EPMA, PIXE or other kind of X-ray spectra (max. 2048 channels)
- No calibration needed
- Print of results and plot of spectrum fit on economical printer
- Interactive and batch operation possible
- Possibility to use different deconvolution setups
- Dump of results in ASCII files, readable by popular databases

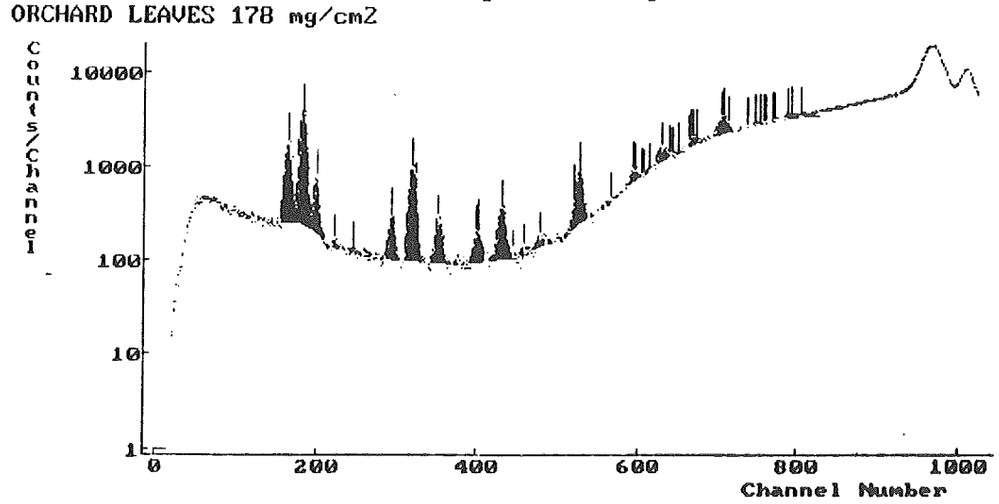


1987 IAEA contract for PC version
(J. Dolnicar)

1989 AXIL Version 3.0 release
OS: DOS
FORTRAN and C

Axil-QXAS package
IAEA

```
Axil X-ray Analysis Package
  Spectrum analysis
    * Perform spectrum fitting
    * Specify parameters for spectrum analysis
    * X-ray library management
```




```
Axil
LOAD
STOP
DISPLAY
ROI
CALIB
X-LINES
KLM-MARK
FIT
REPORT
SAVE_RES
PLOT
@BATCH
BACKGRND
```

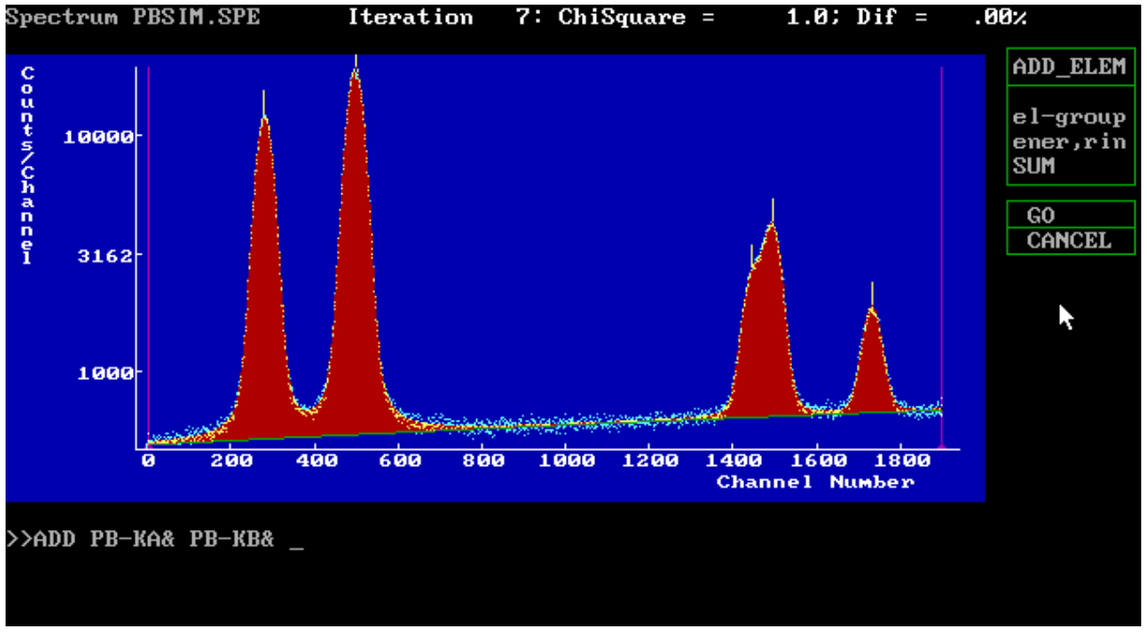
AXIL IBM-PC V3.00 02-06-1989 15:54:32
Spectrum: ORCHARD.SPE

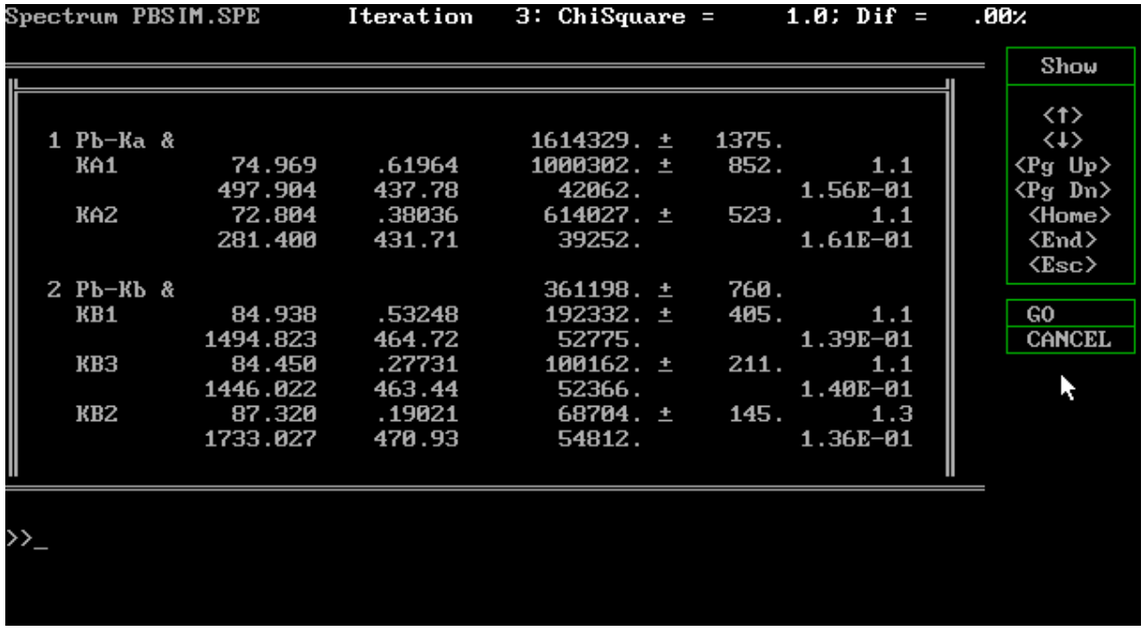
Region of interest: channels 145 - 828; ChiSqr = 2.9

Line	Ener. (KeV)	Peak area	st.dev.	Chi_sq
K -Ka	3.313	14546. ±	135.	3.49
Ca-Ka	3.691	31567. ±	183.	.99
Ti-Ka	4.509	243. ±	44.	.61
Mn-Ka	5.895	1864. ±	58.	.86
Fe-Ka	6.399	8486. ±	95.	3.04
Cu-Ka	8.041	1312. ±	53.	.78
Zn-Ka	8.631	3084. ±	69.	.73
Br-Ka	11.908	2837. ±	125.	1.37
Rb-Ka	13.375	4931. ±	194.	.93
Sr-Ka	14.142	16847. ±	257.	1.44
Pb-La	10.542	7425. ±	96.	3.36

With contributions from
Koen Janssens
Vicente Osorio, Gabriel Bernasconi... (IAEA)

```
Axil X-ray Analysis Package

* Spectrum format conversion
* Spectrum fitting
* Quantitative analysis
* Utilities
```





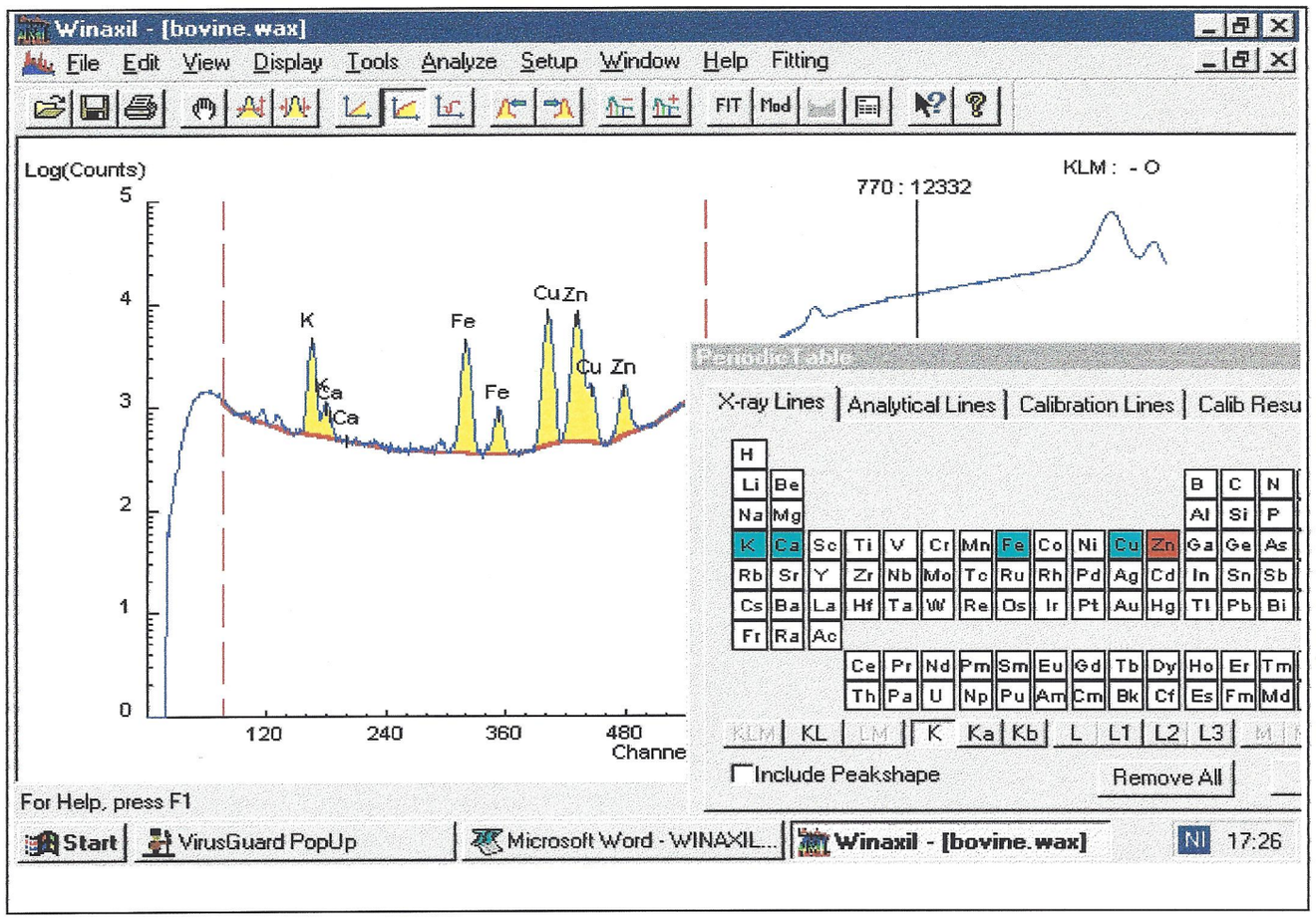
1996 WinAxil
OS: MS-Windows (Windows-95, Windows-XP, ...)
Fitting engine: C-Library (DLL)
User Interface: C++, Microsoft Foundation Classes

With contributions from:
Boris Treiger
Igor Bondarenko
Vicente Osorio

Distributed by Canberra
Responsible: Vicente Osorio

CANBERRA EUROPE

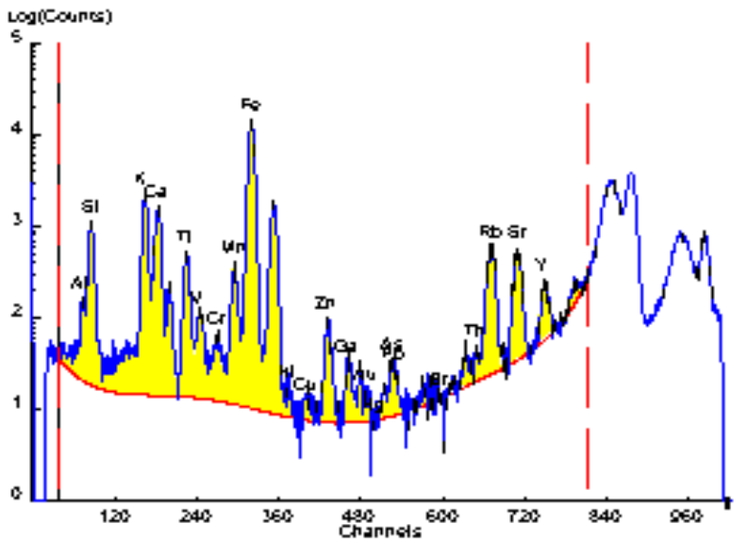
Model S-5005
WinAxil-PC X-Ray Analysis Software



Winaxil - jg1

File Edit View Format Window Help

Jg1.wax



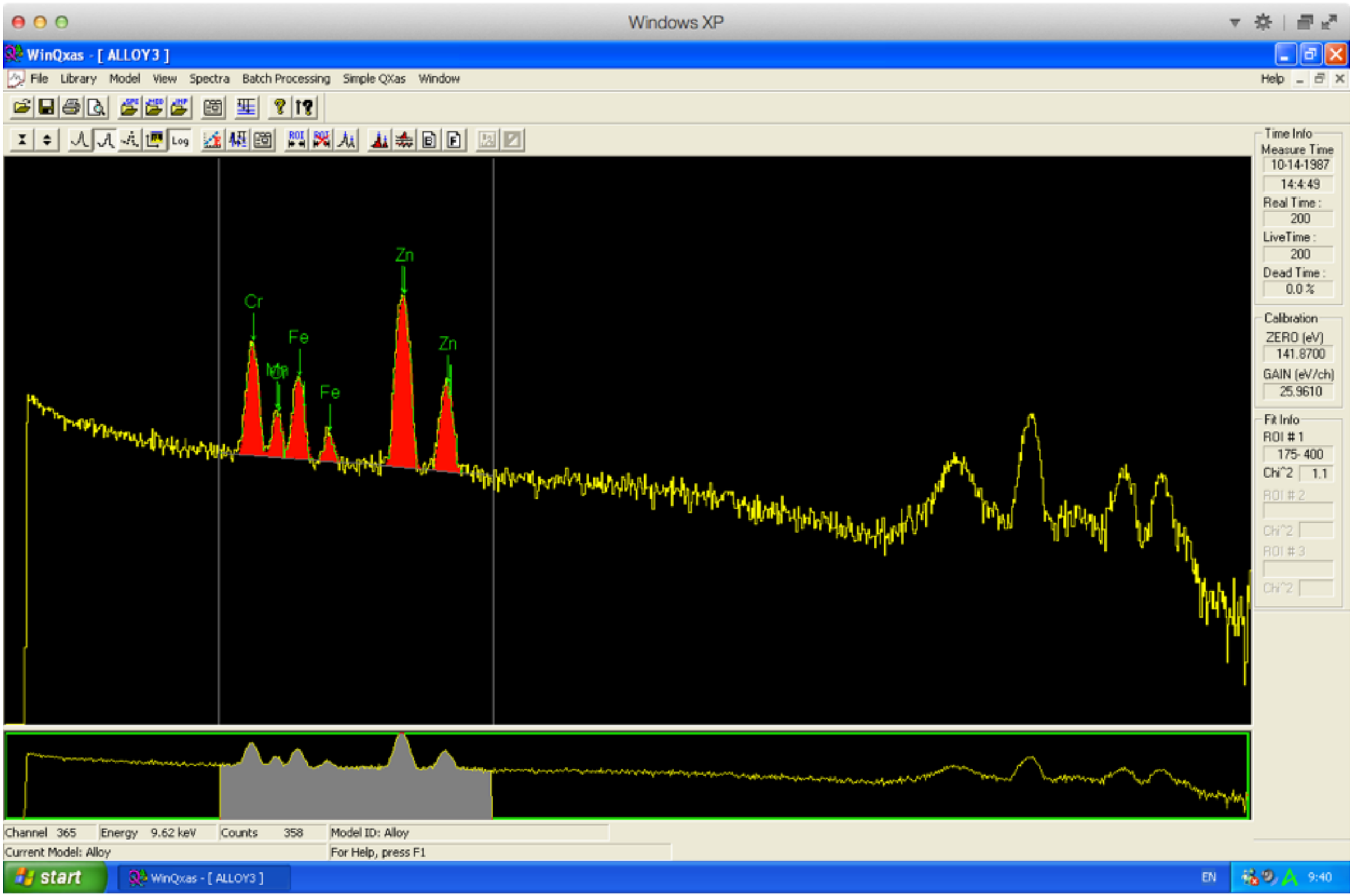
jg1

```
Spectrum: C:\WinAxil\Specdata\Test\Jg1.wax
Sample: GEOL
Fitting region: 38 - 811(ch)  0.78 - 16.19(keV)
Continuum: Exponential with 8 parameters
Chi-square: 1.411  5 iterations  Last change:
0.054

El Line      E(keV)      Area ± StdDev    Chi-Square

Al Ka         1.487       751 ± 37         1.0
Si Ka         1.740      7275 ± 90         2.7
K  Ka         3.313     16618 ± 128        1.1
Ca Ka         3.691     11615 ± 111        1.8
Ti Ka         4.509      4118 ± 70         1.4
V  Ka         4.950       303 ± 36         5.1
Cr Ka         5.412       212 ± 27         1.1
Mn Ka         5.895      2973 ± 61         1.5
Fe Ka         6.399    118722 ± 342        1.5
Ni Ka         7.472        62 ± 16         2.1
Cu Ka         8.041        72 ± 15         1.3
Zn Ka         8.631       852 ± 32         1.4
Ga Ka         9.243       278 ± 21         1.8
As Ka        10.532       -25 ± 36         1.8
Br Ka        11.908       -27 ± 17         4.8
Rb Ka        13.375      6653 ± 87         2.1
```

For Help, press F1 | ChiSqr = 1.4 | Chan 38, 39 Counts | 05/22/98 | 11:05:16

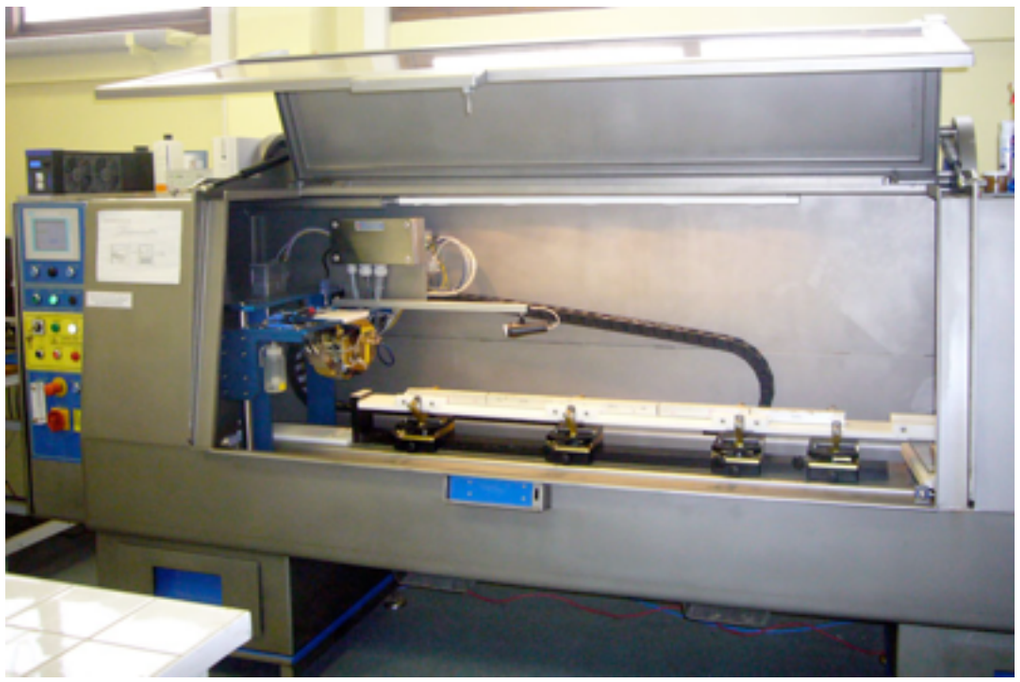
IAEA WinQXAS

Written mainly in Fortran
for MS Windows OS


Windows XP
WinQxas - [ALLOY3]
File Library Model View Spectra Batch Processing Simple QXas Window
Help
Log
Cr
Fe
Mn
Fe
Zn
Zn
Time Info
Measure Time
10-14-1987
14:4:49
Real Time :
200
LiveTime :
200
Dead Time :
0.0 %
Calibration
ZERO (eV)
141.8700
GAIN (eV/ch)
25.9610
Fit Info
ROI # 1
175- 400
Chi^2 1.1
ROI # 2
Chi^2
ROI # 3
Chi^2
Channel 365
Energy 9.62 keV
Counts 358
Model ID: Alloy
Current Model: Alloy
For Help, press F1
start
WinQxas - [ALLOY3]
EN
9:40

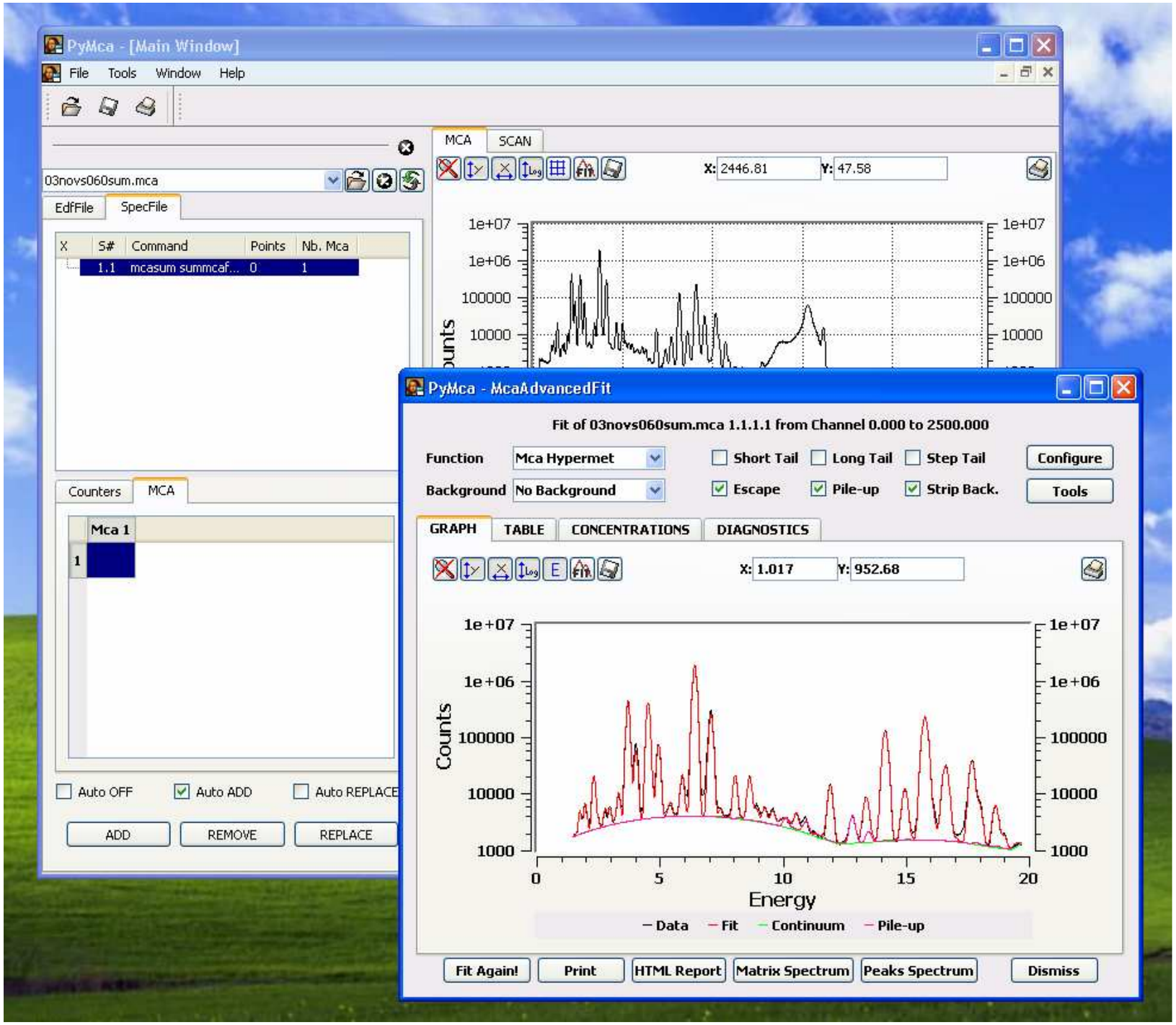
Fitting engine also used in:
Panalytical MiniPal
Panalytical Epsilon 5

AVAATECH XRF core scanner



PyMCA (ESRF) uses a very similar fitting engine
based on the AXIL code

V.A. Solé - European Synchrotron Radiation Facility



Started off as
spectrum fitting

Now very large system

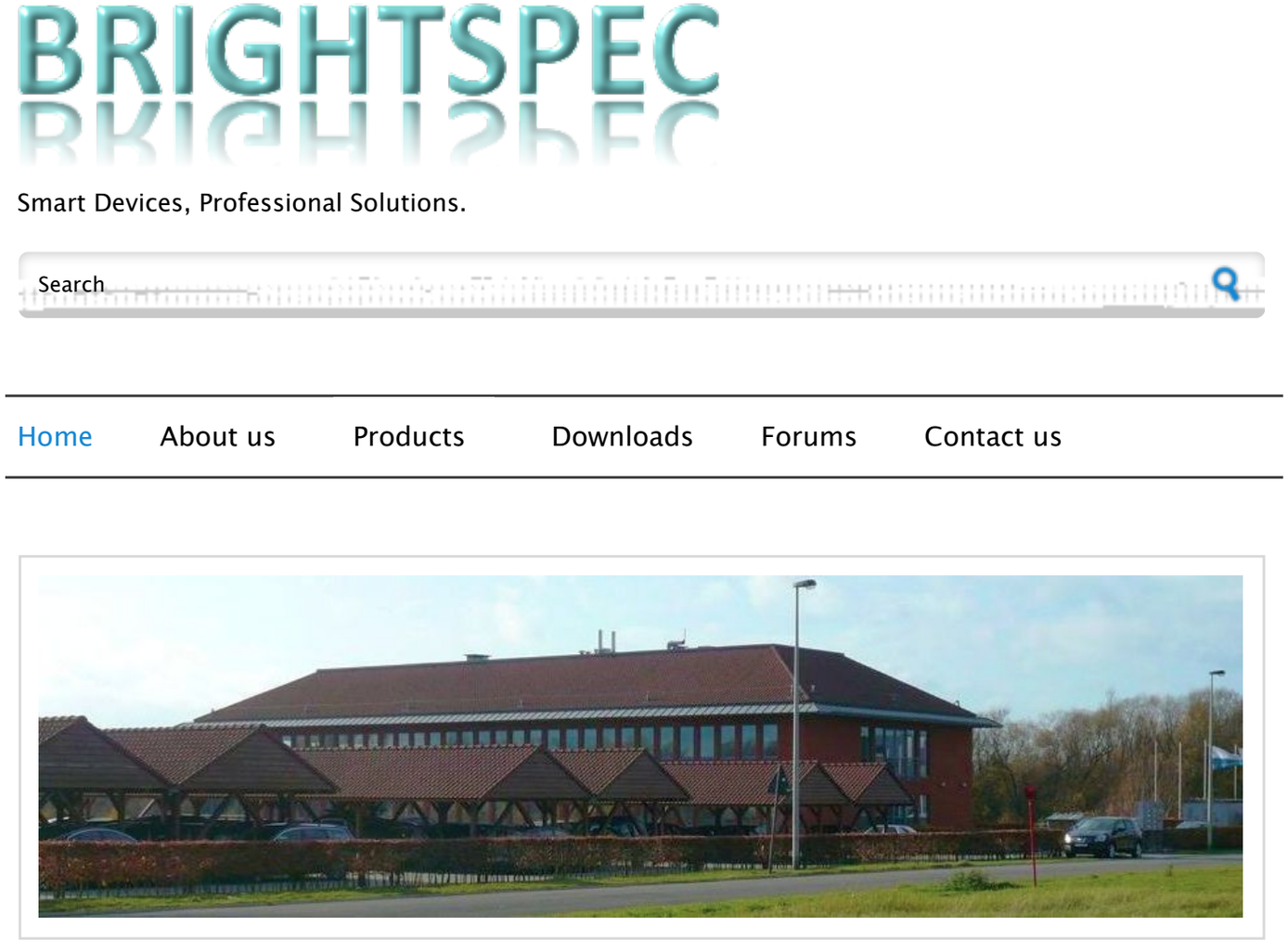
Quantitative analysis
Batch processing
Data visualisation

multi-platform
Windows, Linux, Mac

Using python

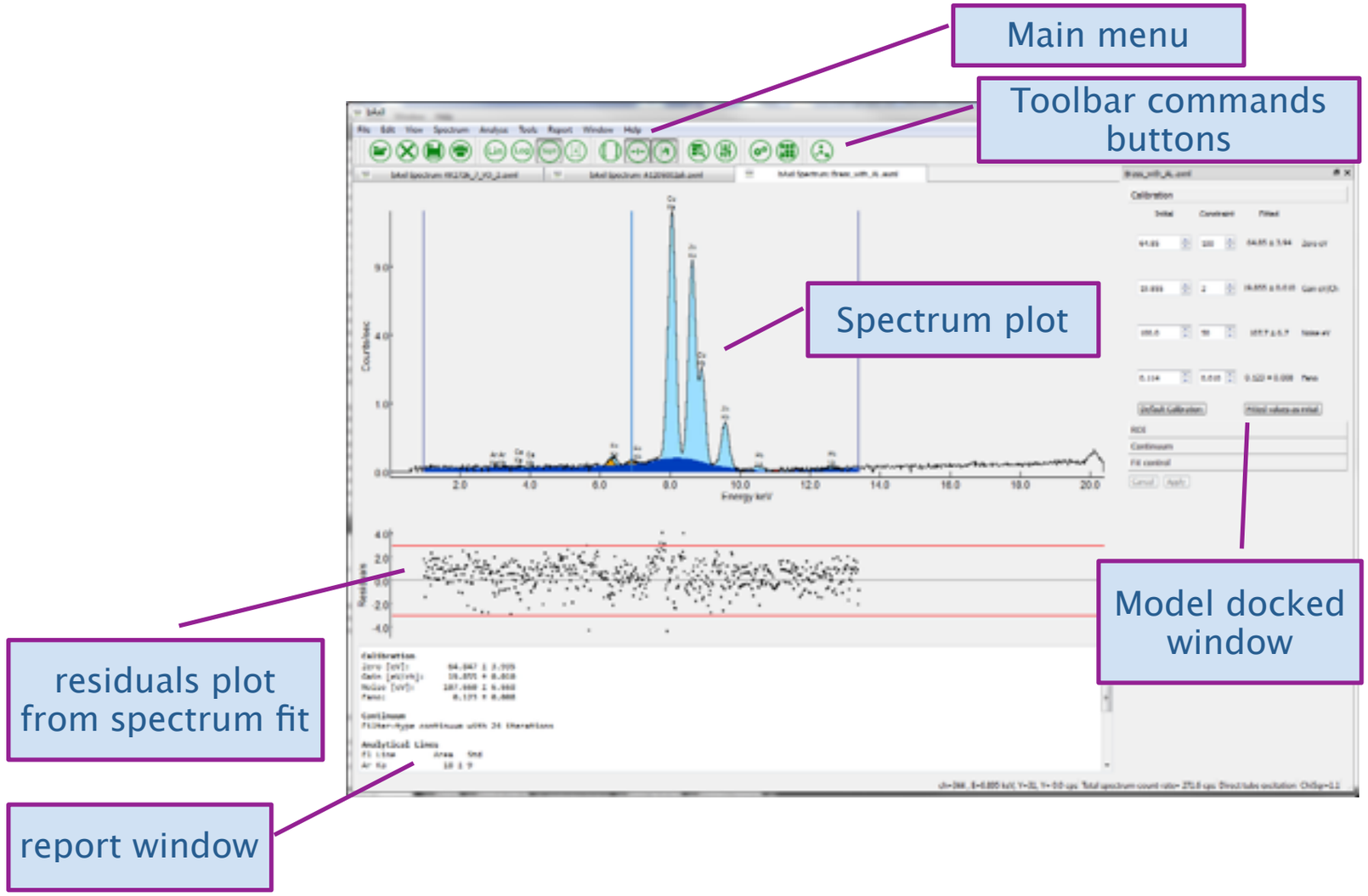
Now bAxil
OS: Windows, Linux, Mac
User Interface: C++ using Qt development environment
Engines: ANSI C++

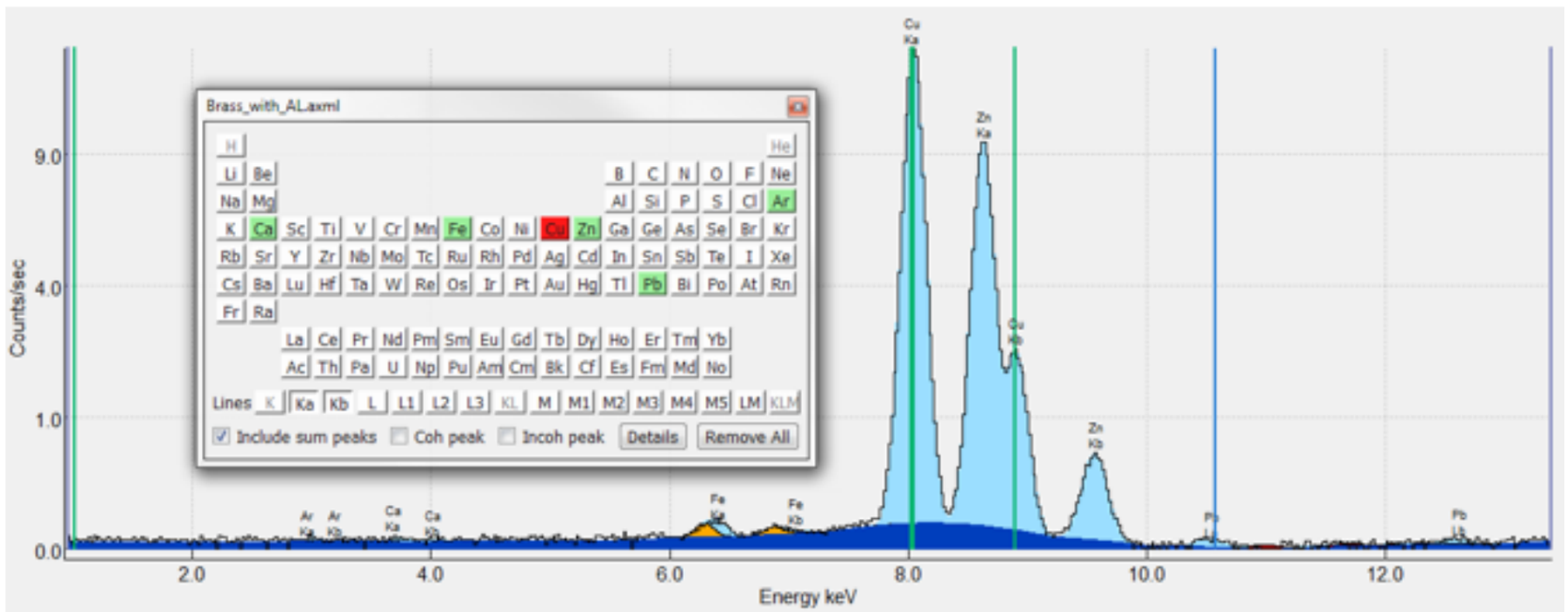
With contributions from:
Yamiel Abreu
Ibrahin Piñera
Vicente Osorio



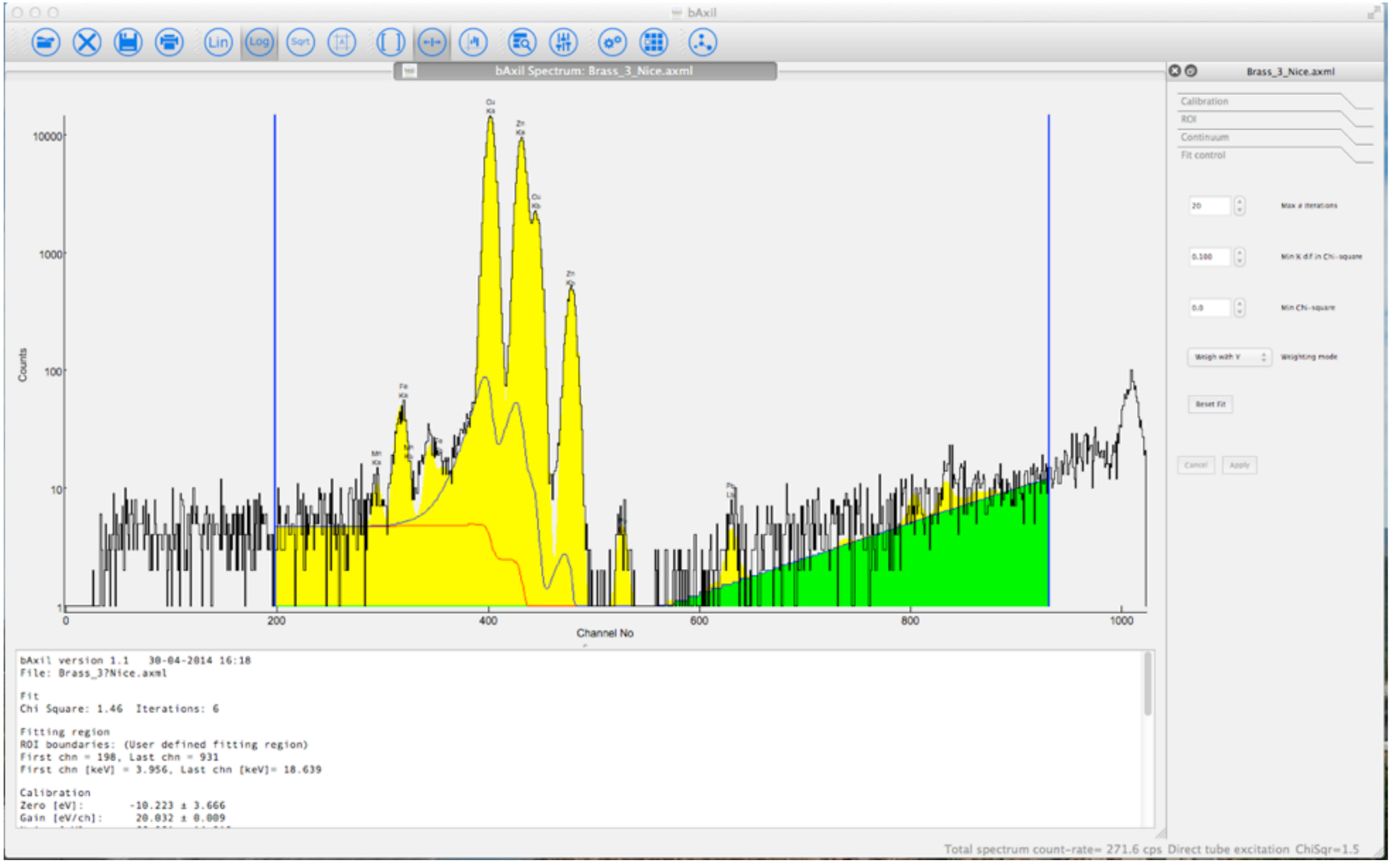
Distributed by BRIGHTSPEC
A spin-off of the University of Antwerp
See: http://www.brightspec.be/

GUI

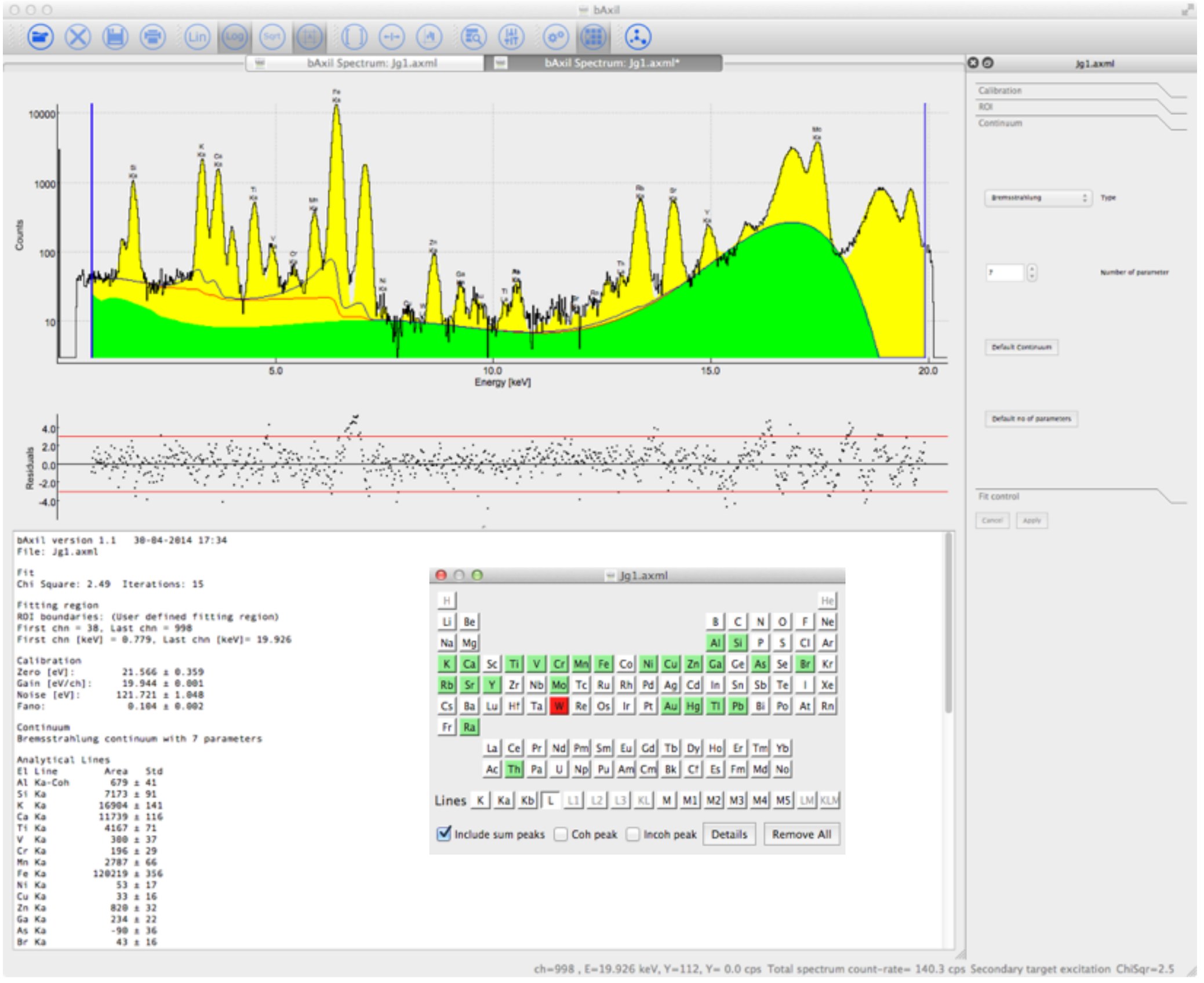

Main menu
Toolbar commands buttons
Spectrum plot
Model docked window
residuals plot from spectrum fit
report window


Brass_with_ALaxml
Counts/sec
Energy keV
Cu Ka
Zn Ka
Cu Kb
Zn Kb
Fe Ka
Fe Kb
Pb
Pb Lb
Ar Ka
Ar Kb
Ca Ka
Ca Kb
Include sum peaks
Coh peak
Incoh peak
Details
Remove All

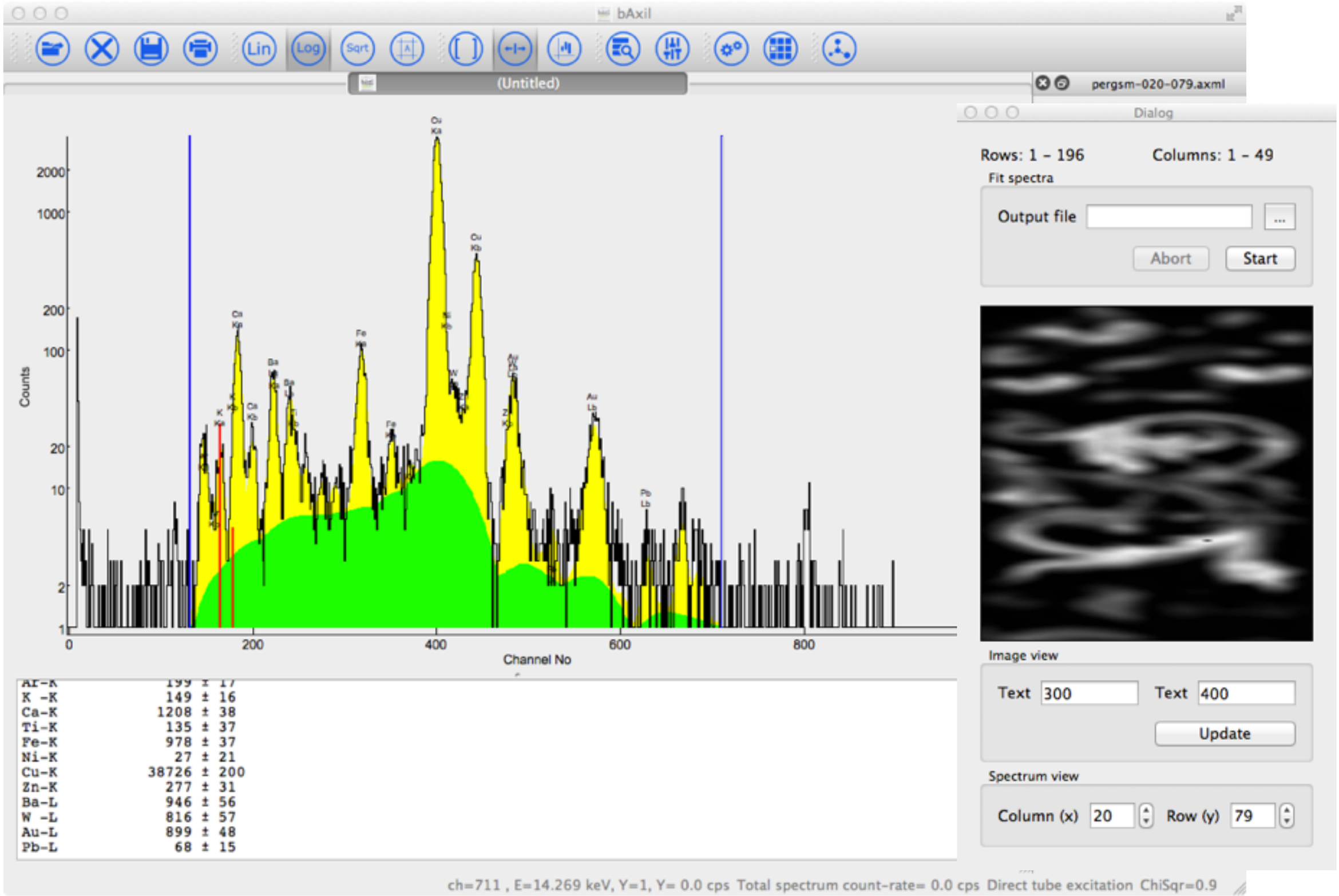
using steps and tails



fitting of coherent and incoherent scatter peaks



Fitting of image and line scan data



Common aspects

Spectrum evaluation

You have to build a “model”

- Determine which part of the spectrum to fit (ROI)
- Which elements, which “peak-groups”
  i.e. decide to fit Ka-Kb separately of not
- Find a background model
  filter background: easy, physically not realistic
  not compatible with peak shape

Quantitative analysis

Fundamental parameter:
specify excitation and detection conditions accurately

Empirical methodes:
extensive calibration with standards

Allow for batch processing
Read and write various spectrum file formats