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Intercomparison of PIXE spectrometry software packages

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FOREWORD

During the last decade the IAEA has organized several intercomparison exercises with the task of comparing the ability of computer programs for spectral analysis to extract peak areas and corresponding uncertainties. The first intercomparison, organized in 1995, was related to gamma ray analysis software packages, and the second one, organized in 1997, was devoted to alpha particle spectrometry software packages. For both intercomparisons, dedicated sets of test spectra were prepared. Full results were published in IAEA-TECDOC-1011 and 1104. The test spectra prepared and used for intercomparisons were included on diskettes attached to the TECDOCs.

During the year 2000, an exercise was organized to make a similar intercomparison of widely available software packages for analysis of particle induced X ray emission (PIXE) spectra.

This TECDOC describes the method used in this intercomparison exercise and presents the results obtained. It also gives a general overview of the participating software packages. This includes basic information on their user interface, graphical presentation capabilities, physical phenomena taken in account, way of presenting results, etc. No recommendation for a particular software package or method for spectrum analysis is given. It is intended that the readers reach their own conclusions and make their own choices, according to their specific needs.

This TECDOC will be useful to anyone involved in PIXE spectrum analysis. It will be useful to a wide range of persons: university students, technical staff doing PIXE spectrometry, software programmers, scientists interested in technical aspects of data analysis in PIXE spectrometry, software operators and even executives or project managers who might be involved in setting up a project in this field or involved in the process of purchasing equipment and software for such projects.

This TECDOC includes a companion CD with the complete set of test spectra used for intercomparison. The test spectra on this CD can be used to test any PIXE spectral analysis software package.

S. Fazinic of the Division of Physical and Chemical Sciences was the IAEA officer responsible for this publication.

EDITORIAL NOTE

CONTENTS

1. Introduction

An Advisory Group Meeting was organized 5–9 December 1994 in Vienna to discuss the requirements for nuclear analytical software. The meeting mainly addressed questions related to gamma ray analysis software. Based on the recommendations from this AGM, an intercomparison of *gamma ray* spectrum analysis software based on a newly prepared set of test spectra was performed in 1995. Full results, including the diskette with the test spectra, were published as an IAEA TECDOC [1]. In addition, two papers [2,3], giving brief explanations of the test spectra, intercomparison method used and most important results, were published.

The second intercomparison, held in 1997, was devoted to *alpha-particle* spectrometry software. Complete results, including the diskette with the test spectra, were published as an IAEA TECDOC [4]. In addition, two brief reports were published [5,6].

During 1999, the plan arose to make a similar intercomparison of widely available software for analysis of *PIXE* spectra, based on a set of newly prepared spectra. In an inter-laboratory comparison for PIXE laboratories, organized in 1996/97 by the IAEA, a number of PIXE laboratories were requested to perform the analysis of reference material BCR CRM 38 (fly ash) embedded in filters. Out of 43 laboratories invited to participate, 14 laboratories submitted results. Analysis of these results, as presented in the intercomparison report [7] shows that some laboratories submitted results that differed significantly from the certified and recommended values. Participation in proficiency testing schemes [8] of this type provides laboratories with an objective means of assessing and demonstrating the reliability of the data they are producing. Such tests may help laboratories to find the reasons for failures in providing correct analysis. However, it is not easy task to deduce the specific reasons based on intecomparison exercise like the one mentioned above. This is because the quality of reported results reflects all stages of the analysis, including quality of the specimen submitted, sample manipulation, instrumentation design, beam handling, and spectral data processing. One would have to analyze all these aspects to find a reasonable conclusion. Having this in mind, it was decided to limit the task of this intercomparison exercise to compare only ability of computer programs for spectral analysis to extract peak areas and corresponding uncertainties, with the intention to isolate only uncertainties of spectral analysis from all other aspects of a method.

A somewhat similar intercomparison of spectral data processing techniques in PIXE was organized in 1985 by Campbell *et al* [9]. However, in the meantime new programs have been developed, the old ones improved and some are no longer in use. As in the case of gamma, alpha and other spectroscopy methods, most PIXE laboratories today tend to use one of the several existing easily available data analysis computer codes. Several laboratories use their own developed programs. Altogether there are about ten computer codes used by PIXE laboratories to process the measured spectra. Under the present work a new set of test, reference and calibration spectra was prepared and an intercomparison of presently used data analysis programs was organized. This set of spectra may be also useful for future intercomparisons or for testing new programs in the development stage, and therefore it is available from the IAEA.

In this report we describe in detail how the test, reference and calibration spectra were acquired and reference values were established. The intercomparison method is described. Detailed properties of the participating programs are given based on answers to the questionnaire sent to possible participants. The results of the intercomparison are presented. Brief reports on preparation of test spectra and intercomparison results have been given in Refs [10, 11].

2. Intercomparison spectra

2.1. General remarks

Two possibilities for generation of test spectra were considered: by measurement or by simulation. Spectra may be simulated by the Monte Carlo method (see for example Refs [12,13]). They can also be created by direct calculation, for example by using the available VIBALab computer code [14]. Simulation offers the advantage of knowing exactly what the "true" contents of the spectra are. However, limitations are that some phenomena might not be simulated that are present in real spectra, e.g. secondary fluorescence, radiative Auger electron emission and distortion of background by the detector point spread function. In addition, in an intercomparison exercise, such spectra will give biased results that tend to favour analysis codes employing the same models used to generate test spectra. Therefore, it was decided to create real measured spectra. This approach was also followed in the previous IAEA intercomparison exercises [1,4]. In order to make the test spectra as useful as possible, it was decided to measure them by using 'typical' instrumentation and procedures adopted by most PIXE laboratories. This means that spectra were to be recorded with a 1024 conversion gain spanning an energy range of 0 to ~22 keV, using pileup rejection, using a typical detector of medium quality, and for a typical proton charge or acquisition time, as opposed to a detector of very high quality and a lengthy acquisition time that would not be economically feasible in practical analysis.

Measured, real test spectra raise the problem of establishing the "true" contents or reference values of the spectra. In the 1995 IAEA gamma ray spectrometry intercomparison, this problem was solved by acquiring a spectrum of a radionuclide source for a very long time to serve as the reference spectrum, and by acquiring spectra during shorter times to obtain test spectra [1,2]. The "high statistics" reference spectra were used to establish "true" reference ratios for intercomparison purposes. Two gamma ray analysis programs were used independently to determine "true" peak areas in the reference spectrum. The reference peak areas in the corresponding test spectra were then determined from the ratio of measuring times between the test and reference spectra.

As opposed to the situation in gamma ray spectrometry, where the expected numbers of disintegrations in a source are strictly a function of time, in PIXE the proton beam current determines the X ray emission rate and may fluctuate in time. However, the "true" ratio of peak areas in a spectrum acquired with a larger total charge (reference case) and those in a spectrum acquired with a smaller total charge (test case) may be estimated from the ratio of the total numbers of counts in the two spectra. The relative uncertainty in this ratio will be negligibly small as compared to the relative uncertainties in individual peak areas. It is therefore possible to employ spectra with excellent statistics (reference spectra) to provide information of superior quality on spectra with normal statistics (test spectra). Possible time-dependent changes in the sample (like evaporation of some elements due to sample irradiation by proton beam) during spectrum acquisition, leading to real differences between reference spectrum and test spectrum, may be excluded by recording in list mode and then using e.g. each tenth count for the test spectrum, and the other nine for the reference spectrum (collect for 10 units in total).

Peak shapes in PIXE spectra are generally modeled by a Gaussian function with a low-energy exponential tail and/or shelf, ending in a long horizontal feature extending to zero energy. The parameters characterizing these aspects are X ray energy dependent and vary among X ray detectors. Since different peak shape models may be used by different programs, it appears impractical to impose a specific definition of peak area. Even after normalization to e.g. the most intense peak in the spectrum, the peak area ratios obtained might vary from program to program.

Therefore, in addition to test spectra, it has been decided to measure a set of single element standard spectra with excellent statistics. A result that should be the same for all analysis programs is the ratio of the $K_{\alpha 12}$ or $L_{\alpha 12}$ peak area obtained from a test spectrum to the corresponding area obtained from a single element standard spectrum with excellent statistics (with each participant using his or her own peak area definition). It was therefore decided to employ these ratios for intercomparison purposes. This set of single element spectra is also useful to calibrate the system before analysis of test spectra.

In practice, PIXE analysis is performed on thick, thin and intermediate samples. It was decided to employ single element standard spectra obtained from thin samples, and test spectra obtained from thin and thick samples. Programs able to deal with the complexities of thick sample PIXE analysis would also be advanced enough to employ the line shapes provided by the thin standard spectra. It was decided to prepare a limited number of test spectra that will represent several typical samples usually analysed by PIXE laboratories, including:

(i) a thin sample of aerosol material on a thin polycarbonate backing;
(ii) a thick stainless steel alloy sample containing both Nb and Mo,
(iii) a thick sample of biological material prepared as a pellet, and
(iv) a thick glass sample.

2.2. Measurement and preparation of intercomparison spectra

All spectra were measured by using 3 MeV proton beam. The angle between proton beam and specimen normal was 0° and angle between X ray detector and specimen normal was 45°. All spectra were collected with the same detector, electronic chain and geometry. The detector used was Canberra series 7300, model Sl30165; with active area 30mm^2; nominal resolution 165 eV; crystal thickness 3 mm; and Be window 25 μm. Amplifier used was Canberra model 2020 with shaping time 12 μs and PUR ON. ADC was Canberra model 8075, gain 1K. Dead time was max 5% with count rate about 1000 cps (max 1500).

By using multiparameter data acquisition system, a set of high statistics spectra corresponding to biological, aerosol, glass and alloy samples were collected in list mode by recording all events one after another in a sequential file. The already mentioned VIBALab computer code [14] was used in order to optimise experimental parameters.

The following four spectra were recorded:

(i) aero.asc → prepared by measuring a thin aerosol sample on a thin polycarbonate backing. The actual sample was a candidate for a certified reference material "Prague urban dust" supplied by the Analytical Quality Control Services (AQCS), the IAEA Seibersdorf Laboratory. The spectrum was measured by using a kapton filter of nominal thickness 50 μm between the detector and the sample.

(ii) alloy.asc → prepared by measuring thick sample of a standard reference alloy material NIST 1249 "Inconel 718". Main constituents specified in the certification document are: Ni-53.29w%, Cr-18.45w%, Fe-17.6w%, Nb-5.19w%, Mo-3.09w%, Ti-0.957w%, Al-0.563w%, Co-0.325w%, Cu-0.145w%, Mn-0.109w%, Si-0.106w%. The spectra were collected with an Al filter of nominal thickness 53 μm between the detector and the sample.

(iii) bio.asc → prepared by measuring thick sample of biological material. Two IAEA candidate reference materials, i.e. algae (IAEA-413) and lichen (IAEA-338), were mixed with graphite and pelletised. The spectra were measured by using a mylar filter of nominal thickness 170 μm between the detector and the sample. The sample matrix, estimated by analysing the corresponding RBS spectrum by the SIMNRA program [15], consists approximately of: H-5w%, C-61w%; N-5w%; O-26w%, K-2w%, Ca-1w%.

(iv) glass.asc → prepared by measuring thick sample of a medieval glass sample. The spectra were measured by using the kapton filter (the same one used to measure the aero.asc spectrum) of nominal thickness 50 μm between the detector and the sample. The sample matrix, estimated by analysing the corresponding RBS spectrum by the SIMNRA program, consists approximately of: O-47.5w%, Na-10w%; Al-2w%; Si-38w%, K-1.5w%, Ca-1w%.

These measured spectra were than used to extract "low statistics" test spectra and the corresponding "high statistics" reference spectra. The test spectra were prepared by taking every tenth count from the measured list files. The rest of the counts were put in the high statistics reference spectra. In such a way the expected peak area ratios between test spectra and reference spectra are 1:9 exactly. The test and reference spectra obtained in this way have been saved as ASCII files, 1024 channels in one column.

Generally, one can use the measured spectra to extract different test spectra having expected peak area ratios between test spectra and reference spectra 1:n, where n is any number. The reason why we have taken the choice of n=9 is that such obtained test spectra are typical in a sense of measurement time and beam current accumulated to acquire them. In addition, these test spectra have both high and low statistics peaks and are typical examples of real PIXE spectra. Figures 1 to 4 show aero, alloy, bio and glass test spectra extracted from the measured data by using n=9. On each figure few most prominent Kα peaks are indicated by the corresponding element symbol.

Figure 5 shows a section of 'aero' reference and test spectra as an example, where the high-statistics (reference) and low-statistics (test) channel contents are shown together, the latter after multiplication by 9. From the figure one can see that the latter are noisier but have the exact same shape as the former.

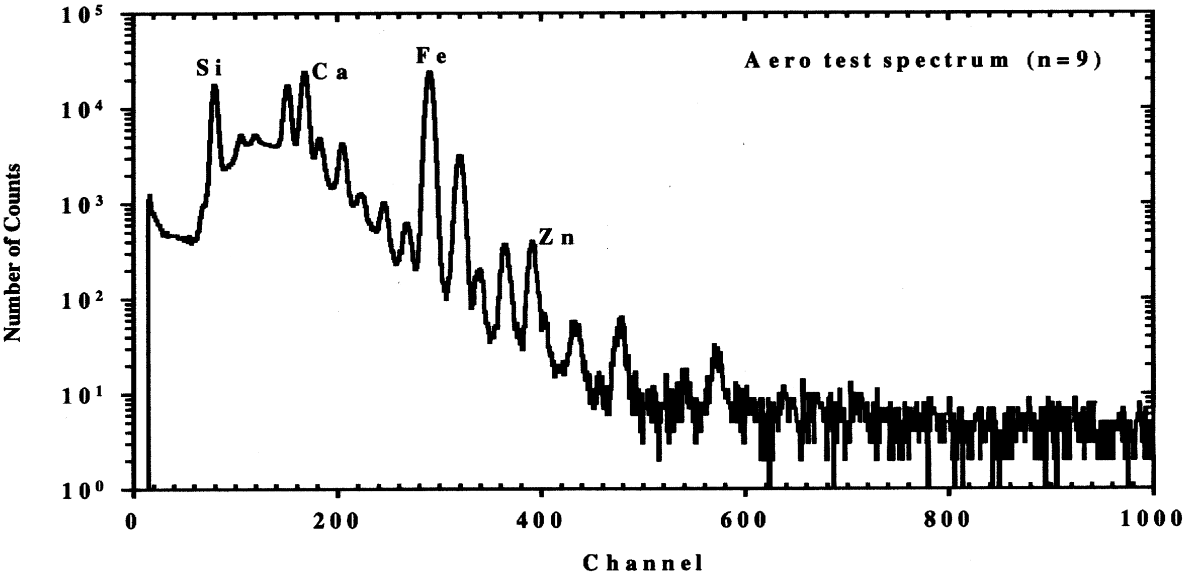

FIG. 1. Aero test spectrum.

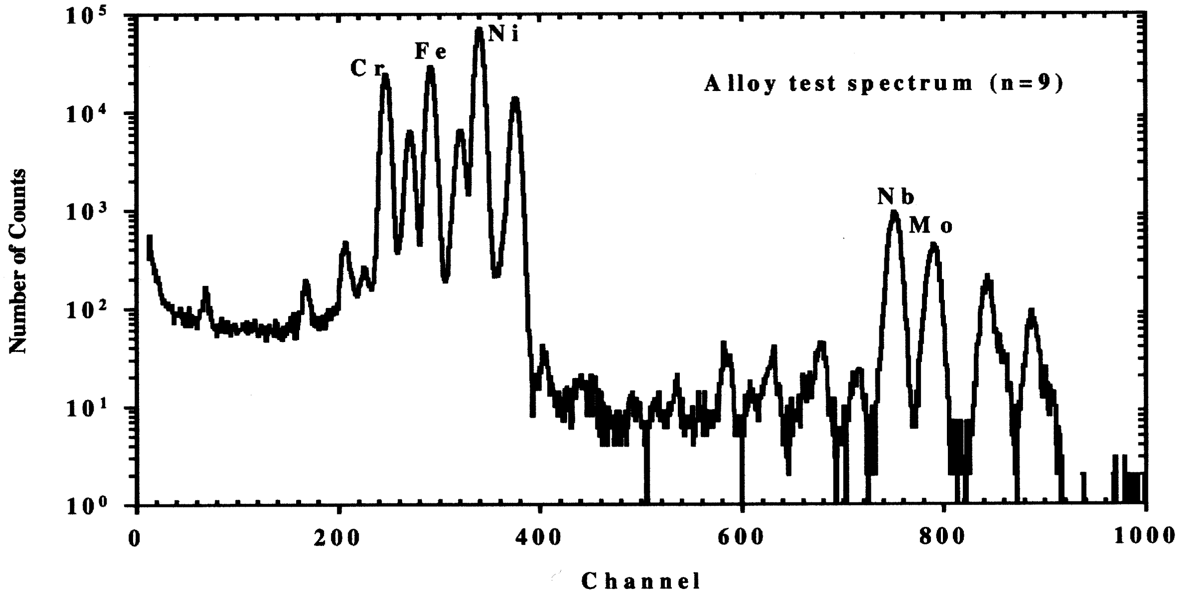

FIG. 2. Alloy test spectrum.

For intercomparison exercise peak areas (and not individual channel contents) are used. Figure 6 has been constructed to demonstrate that the peak areas between reference and test spectra exhibit 1:9 ratio with Poisson distribution. To create this figure, 1024 channels were grouped in 128 bins, each containing 8 channels. In that way, the bin width (~170 eV) corresponds approximately to 1 FWHM of recorded X ray peaks. The figure shows the differences between expected (9) and actual ratios between high-statistics (reference) and low-statistics (test) bin contents, normalised to corresponding uncertainties computed assuming Poisson distributed data.

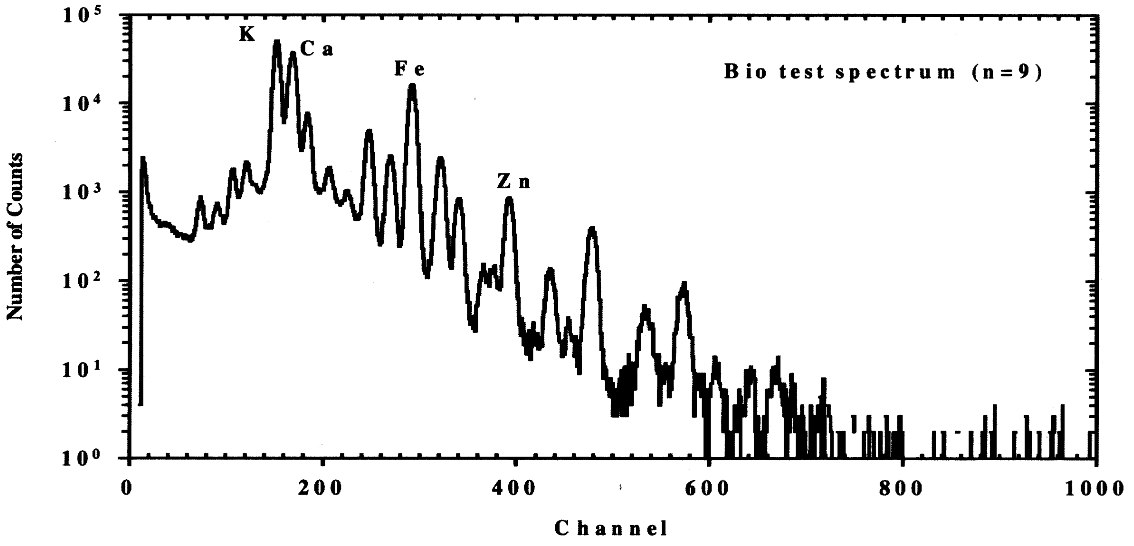

FIG. 3. Bio test spectrum.

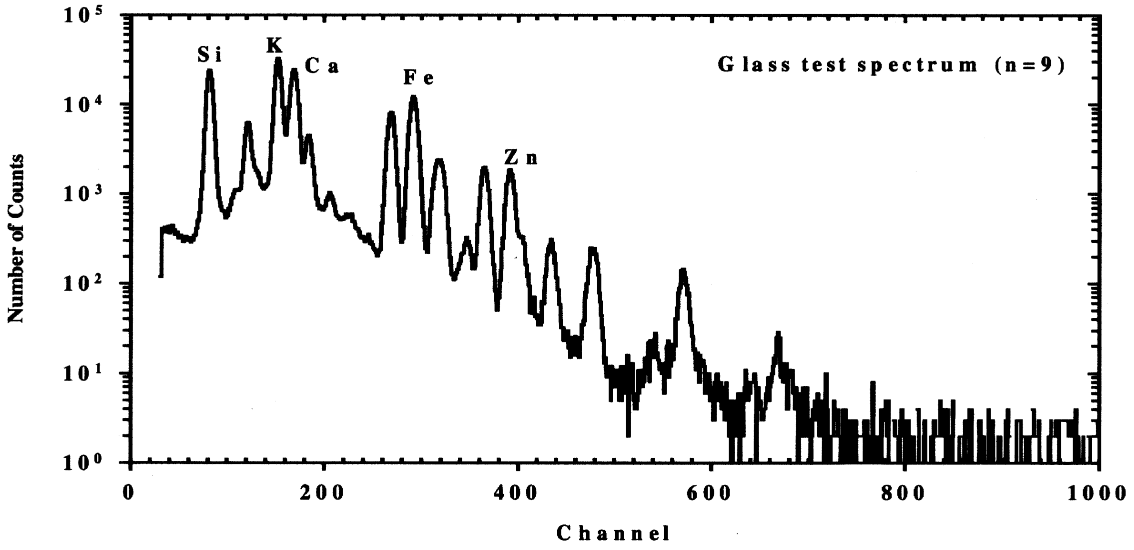

FIG. 4. Glass test spectrum

In addition, a set of single element thin films was used to measure 26 spectra, to be used for calibration and establishment of peak area ratios. The spectra of SiO_2, S, KCl, CaF_3, TiH_2 and V thin samples were measured by using the kapton filter of nominal thickness 50 µm — the same one used to measure the spectra of aerosol and glass samples. The spectra of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, GaP, As, CsBr, Rb, SrF_2, Y, Zr, Nb_2O_5, Mo, W, Pb and Hg were measured by using the mylar filter of nominal thickness 170 µm — the same one used to measure the spectrum of the biological sample. Most of the samples used were in the form of evaporated thin films deposited on thin polycarbonate backing. The thickness of these films, supplied by the Micrometer company, was for most of them about 50 μgcm^{-2}, while for some heavier elements it was in the order of about 200 μgcm^{-2}. Sulphur and TiH_2 samples were prepared by spreading a very thin layer of fine dust particles over a thin carbon tape and Mo sample was a thin metal foil. Some spectra have a few peaks of other elements present in the corresponding samples as contamination but these peaks do not influence their usefulness. All files are saved in ASCII format, 1024 channels in one column. Figure 7 shows three typical spectra (V, Cu, As).

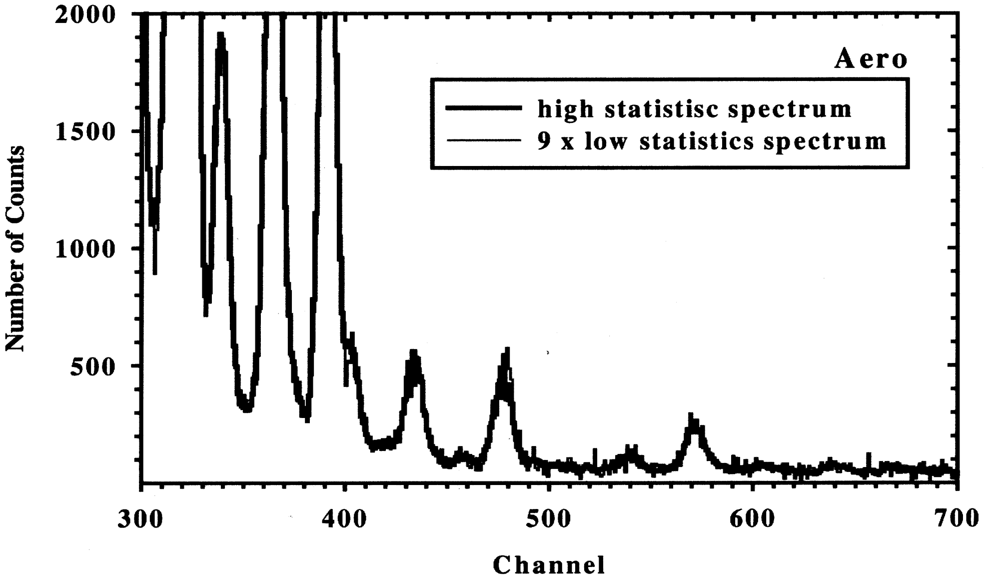

FIG. 5. A section of 'aero' reference and test spectra. The high-statistics and low-statistics channel contents are shown together, the latter after multiplication by 9.

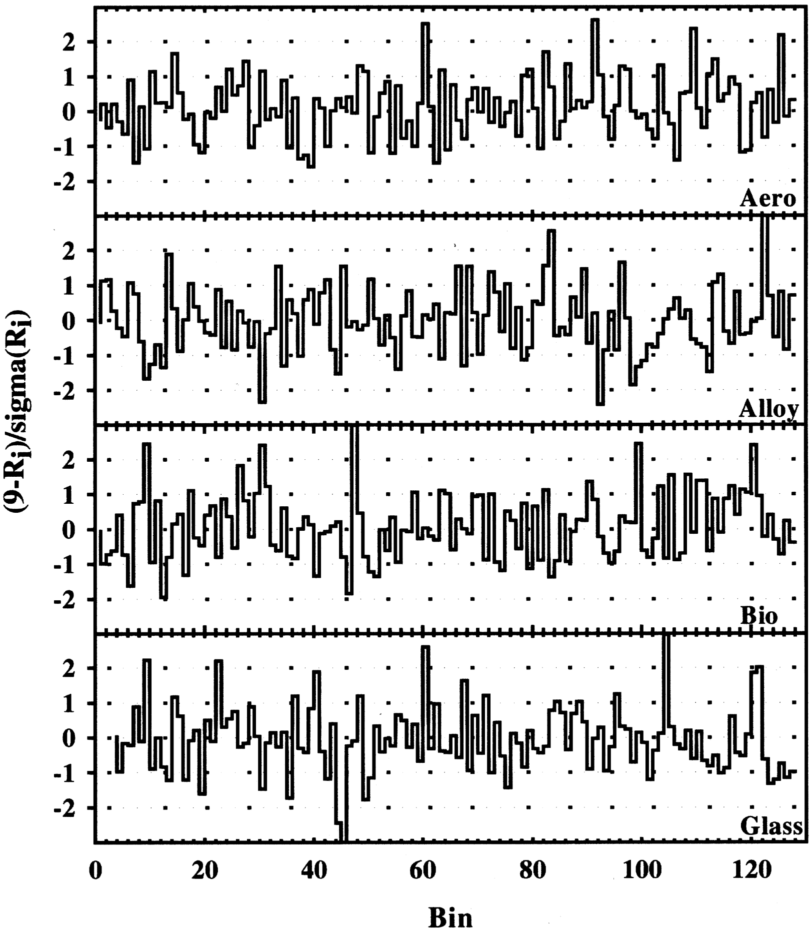

FIG. 6. The differences between expected (9) and actual ratios between high-statistics and low-statistics bin contents, normalised to related uncertainties computed assuming Poisson distributed data. Channels in the spectra were grouped in 128 bins (each containing 8 channels). The bin width corresponds in average to 1 FWHM of recorded X ray peaks.

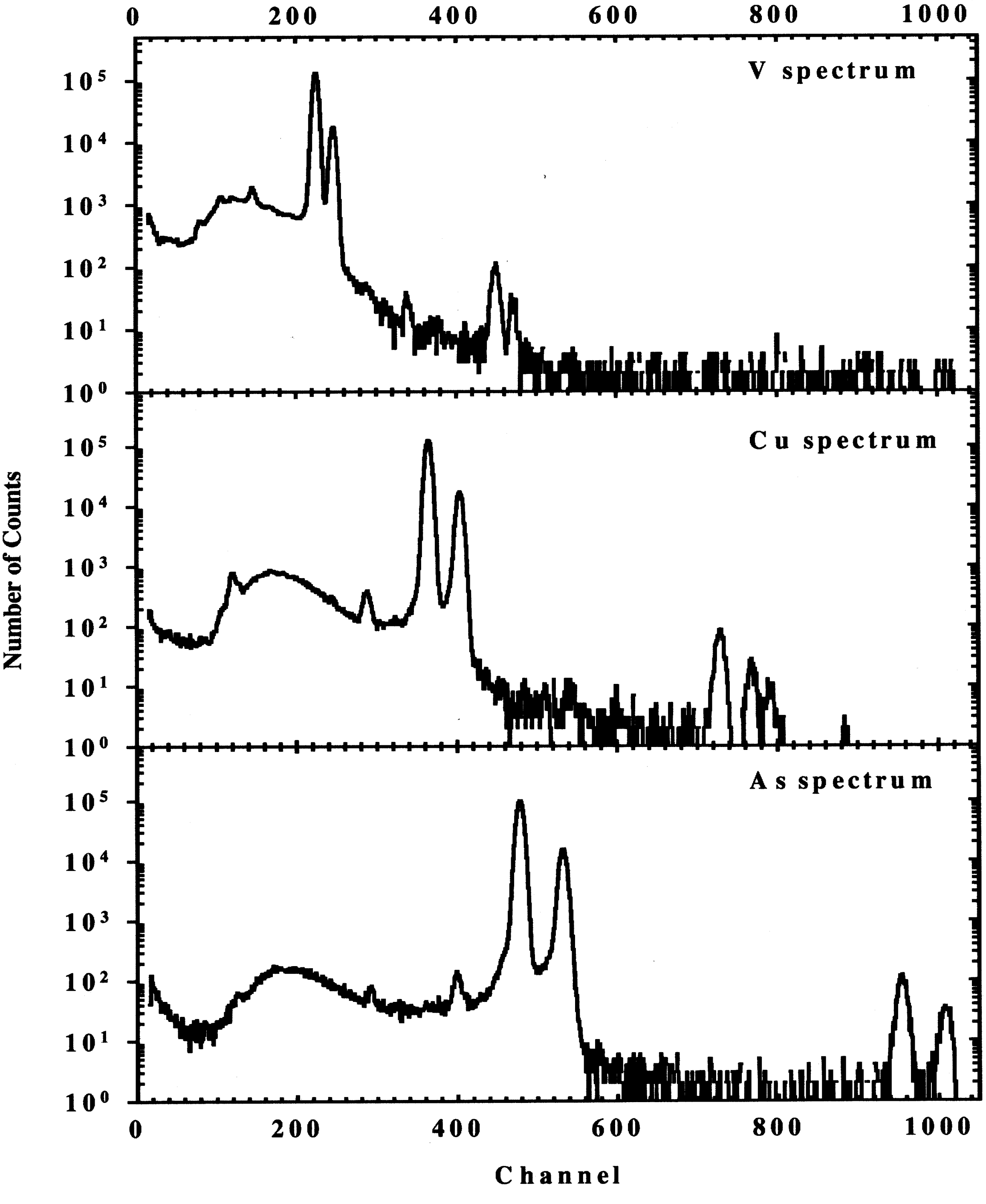

FIG. 7. Measured spectra of V, Cu and As thin targets. 26 such spectra from thin targets, spanning the element range from Si to Hg, were measured for calibration and calculation of peak area ratios.

2.3. Determination of reference data

GUPIX [16] and WinAxil [17] programs were used for analysis of the four "high-statistics" reference spectra that comprised 90% of the list mode data. This selection was based solely upon the widespread use of these two programs and due to the fact that two members of the staff involved in the exercise (J.L.C. and P. V.-E.) are their developers and experienced users, and it did not reflect any assumptions regarding their quality or performance. These two programs use different approaches in modelling spectra. They treat background in different way and use different methods to model low energy peak tailing. They have been used independently to analyse the reference spectra.

When the peak areas given by GUPIX and WinAxil agreed within or close to the quoted standard deviations, the two areas were averaged and the uncertainty was taken as the average of the two standard deviations. This tended to be the situation for peaks having high precision, e.g. potassium, calcium, iron. For those cases where there was not agreement within the statistical error quoted by either program, the average peak area was again recommended, but having an uncertainty equal to half the spread between the two fit results. This situation was encountered frequently, although not always, with the low precision peaks. For low-precision peaks there were instances when very close agreement between the programs was observed, with the difference in the two peak areas being much less than either of the statistical error estimates; in such cases the lower of the two statistical errors was adopted as the uncertainty. Some results are flagged as dubious, e.g. cases where only one of the two programs reported a finite area for a particular line.

The ratios R_{ref} to be used for intercomparison exercises are defined as

$$R_{ref} = \frac{A_{ref}}{A_{standard\text{-}ref}} \frac{1}{n} \times 10^6 \tag{1}$$

where A_{ref} is the principal peak area for a specific element in the “high statistics” reference samples spectrum (aero, alloy, bio or glass), $A_{standard\text{-}ref}$ is the corresponding peak area for the same element as above in the single element standard spectrum, and n is a factor defined as a ratio of total number of counts in a reference spectrum and its corresponding test spectrum (we have used n=9 to prepare the test spectra).

The uncertainties in these ratios were taken to be the relative uncertainties of the A_{ref}, i.e., the thin standard peak area uncertainties were considered to be negligible.

Table 1 shows recommended reference values R_{ref} with associated uncertainties for all four spectra, obtained by taking n=9 and using the procedure described above.

3. Intercomparison method

All the spectra (four test spectra and 26 single element standard spectra) were supplied to possible intercomparison participants in June 2000, with instructions and a questionnaire. Results on peak areas and associated uncertainties from seven laboratories arrived within the specified time frame. After that, the high statistics reference spectra were processed to establish reference ratios in a way described in previous sections, and intercomparison results were analyzed.

The reference ratios R_{ref} , given in the Table 1, were compared with the reported ratios R_{rep} defined as

$$R_{rep} = \frac{A_{rep}}{A_{standard\text{-}rep}} \times 10^6 \tag{2}$$

where A_{rep} is the principal peak area for a specific element in a test spectrum (aero, alloy, bio or glass) as reported by intercomparison participants, and $A_{standard\text{-}rep}$ is the corresponding peak area for the same element as above in the single element standard spectrum, also as reported by intercomparison participants.

The uncertainties in the R_{rep} ratios were taken to be the relative uncertainties of the A_{rep} as reported by the intercomparison participants, i.e., the thin standard peak area uncertainties were considered to be negligible.

A statistical comparison of reported and reference peak area ratios was performed, based on standardized residuals or z-scores, i.e. the differences between reported values and reference values divided by their own uncertainties.

TABLE 1. REFERENCE VALUES FOR PEAK AREA RATIOS FOR ALL FOUR TEST SPECTRA, PROCESSED BY WINAXIL AND GUPIX, AND CALCULATED BY USING EQUATION 2 (WITH n=9).

El.	Aero		Alloy		Bio		Glass	
	R_{ref} [x10^6]	Rel. error [%]	R_{ref} [x10^6]	Rel. error [%]	R_{ref} [x10^6]	Rel. error [%]	R_{ref} [x10^6]	Rel. error [%]
Si	0.2076	2	--	--	--	--	0.3311	1.3
S	0.01122	7	--	--	0.007989	7.5	0.001667	16
Cl	0.00913	9	--	--	0.01028	6	0.03822	2
K	0.06789	0.6	--	--	0.2389	1	0.1631	0.4
Ca	0.1529	0.32	--	--	0.2344	0.6	0.1689	0.3
Ti	0.02333	4	0.002778	4	0.00751	7	0.002944	7
V	0.002156	11	--	--	0.001822	14	0.000597	6
Cr	0.004622	1	0.1773	0.4	0.03239	0.26	0.000178	30
Mn	0.002622	4	0.00333	50	0.01384	0.6	0.06309	0.6
Fe	0.19	0.18	0.2313	0.25	0.1276	0.21	0.09222	0.2
Co	0.000633	13	0.00622	10	0.000567	10*	0.01309	0.25
Ni	0.001544	1.5	0.6211	1	0.007222	0.7	0.000604	4.6
Cu	0.002844	1.8	0.00211	25	0.000848	2.5	0.01667	1
Zn	0.002933	1	--	--	0.007278	0.6	0.01576	0.5
As	--	--	--	--	0.002356	1.4	--	--
Br	0.0001056	8	--	--	0.000171	8	0.000192	10
Rb	--	--	--	--	0.0000608	10	0.0000356	23
Sr	0.000402	9	--	--	0.000671	9	0.000547	12
Zr	0.00025	18.5	--	--	--	--	--	--
Nb	--	--	0.01106	1.5	--	--	--	--
Mo	--	--	0.01106	1.5	--	--	--	--
W	--	--	0.000989	12	--	--	--	--
Pb	0.0004167	4	--	--	0.0016	3.5	0.002467	3.5
Hg	--	--	--	--	0.000119	10	--	--

* Dubious, e.g. only one of the two programs reported a finite area.

In the case of a “hit” (ratio reported both in the reference results and in the test results), two z-scores could be computed: A z-score related to the quality of ratio determination based on the uncertainties in the reference files

$$z_{ref} = \frac{R_{rep} - R_{ref}}{\sqrt{n\sigma_{ref}^{2} + \sigma_{ref}^{2}}} = \frac{R_{rep} - R_{ref}}{\sqrt{10\sigma_{ref}^{2}}} \tag{3}$$

and a z-score related to the statistical control of the analysis program based on both the reference uncertainty and the uncertainty reported by the analysis program

$$z_{rep} = \frac{R_{rep} - R_{ref}}{\sqrt{\sigma_{rep}^{2} + \sigma_{ref}^{2}}} \tag{4}$$

where R_{ref} and R_{rep} are the reference and reported peak area ratios, σ_{ref} and σ_{rep} their uncertainties, and n is defined by Eq.(1). The uncertainties are the overall uncertainties at the 68% confidence level (i.e. 1σ errors). While z_{ref} may be used to identify potential biases in results, z_{rep} indicates if R_{ref} and R_{rep} are statistically different. The generally accepted criteria used to interpret the z_{rep} values are given in Table 2 [7,18].

TABLE 2. INTERPRETATION OF z_{rep} VALUES [7, 17].

z_{rep} score value	Are R_{ref} and R_{rep} statistically different?
$\lvert z_{rep} \rvert < 1.64$	No
$1.64 < \lvert z_{rep} \rvert < 1.95$	Probably not, but more data is needed
$1.95 < \lvert z_{rep} \rvert < 2.58$	Not clear
$2.58 < \lvert z_{rep} \rvert < 3.29$	Probably yes, but more data needed
$3.29 < \lvert z_{rep} \rvert$	Yes

From the z-scores, reduced sums of squares χ_r^2 can be computed for any category of results with

$$\chi_r^2 = \frac{1}{N}\sum_{i=1}^{N} z_i^2 \tag{5}$$

where N is the number of results in the category.

If the reference ratio was missing, the reported ratio was considered to be a “false hit” and only the second z-score could be computed, using zero both as the reference ratio and as its uncertainty. If the reported ratio was missing, it was considered a “miss” and only the first z-score was computed. Missing a noisy peak or reporting a false hit with a high uncertainty in the ratio do not result in high z-scores and are therefore “allowed” in this test.

From the z-scores, reduced sums of squares χ_r^2 were computed for different categories of peaks:

- High-precision ratios: Hits for which the ratio of reference peak ratio and reference ratio uncertainty is larger than $10\sqrt{n}$ (n = 9). The factor $\sqrt{n}$ takes account for the σ_{ref} values being $\sqrt{n}$ smaller than the corresponding σ_{rep}.
- Low-precision ratios: Hits for which the ratio of peak area ratio and uncertainty was less than $10\sqrt{n}$
- All matches: All peaks belonging to the previous two categories
- Misses
- False hits
- Total: All previous categories

For the three “hit” categories, two χ_r^2-values were computed: one based on z_{rep} values denoted $\chi_{r,rep}^2$, and one based on z_{ref} values denoted $\chi_{r,ref}^2$.

4. Participating programs

The participating programs are: Geopixe [13], Gupix [16], Pixan [19], Pixeklm [20], Sapix [21], Winaxil [16], and Witshex [22]. The peak area results reported by Geopixe show the areas of the major line Kα (i.e. the sum of $K\alpha_1$ and $K\alpha_2$) up to Fe. It uses split $K\alpha_1$, $K\alpha_2$ for higher Z. There is a similar strategy for L lines. Peak area ratios reported by Gupix were calculated by using as a principal line Kα for all elements up to Z=16, $K\alpha_1$ for all elements above Z=17 and $L\alpha_1$ for heavy elements. The peak area results reported by Pixan were given for Kα (i.e. the sum of $K\alpha_1$ and $K\alpha_2$) or in few cases for the Lα X ray lines. The peak area results reported by Pixeklm show the areas of the major line Kα, (i.e. the sum of $K\alpha_1$ and $K\alpha_2$). The peak area results reported by Sapix for all spectra are given as a list of Kα and Kβ areas for all elements except Si where a K peak area is given. For elements where L lines were used, results were given as areas of up to 10 different lines of L series. In this case $L\alpha_{1,2}$ areas were used for ratio computations. Only areas of principal lines (K, Kα and Lα) were used to obtain ratios. Since no separation in overlapping peaks of Pb Lα and As Kα was given in the case of the "bio" sample, Pb Lβ and As Kβ were used to obtain area ratios in both test and single element spectrum. In case of Winaxil, for Al, Si and P, the area of the K line (i.e. Kα+Kβ) was reported. For the element S to Zr the area of the Kα (i.e. $K\alpha_1 + K\alpha_2$) was reported. Areas of L lines are reported as Lα (i.e. $L\alpha_1 + L\alpha_2$). The program was used and separate results reported in two modes: without (Winaxil1) and with (Winaxil2) peak tails accounted for. In case of Witshex, the results for all spectra were given as a list of areas for the principal lines of elements. In all cases, Kα or Lα were used. Witshex was operated and separate results reported in two modes: by using the "parametric background" and by using the "rolling ball background", to be referenced as Witshex1 and Witshex2 in the remainder of this report. More details about the participating programs are given below, based on received answers to the questionnaire sent to potential participants. Therefore, the status of the software given here is as of November 2000.

4.1. GEOPIXE — QUANTITATIVE PIXE ANALYSIS AND IMAGING PROGRAM

Required Operating system: VAX/VMS New version for PC NT/PC Windows available mid 2001.

Graphical representations available:

PIXE calibration: Efficiency.

Spectra: Spectra, Fits, Background, Pile-up, Residuals.

Note the resulting fit includes background and can be directly compared and overlaid on the original spectrum data to properly assess the fit quality. While residuals are available, it is always best to be able to directly view the quality of a fit against the data.

Images:

- Quantitative PIXE images using Dynamic Analysis (DA)
- Projection of concentration onto end-member mineral fractions
- Grey and false-colour
- Zoomed images
- PIGE imaging

Line profiles:

- Concentration profiles extracted directly from PIXE DA images.

Graphics options: The new version uses a graphical user interface for spectrum display, integrated with PIXE imaging using the Dynamic Analysis method. The interface facilitates:

- Energy calibration of spectra
- Identification of X ray lines, marking of all X ray lines for elements
- Fitting of PIXE spectra
- Calculation of model PIXE yields for thick, thin, or layered targets (including fluid inclusions), including secondary fluorescence
- Building the DA transform matrix for imaging (including on-line imaging)
- Sorting of E,X,Y list mode event data using the DA method or using energy windows
- Generation of quantitative concentration images in units of ppm.μC
- Generation of statistical concentration variance images to complement concentration
- Correction of images for changing sample composition on a pixel-by-pixel basis
- Display of resulting quantitative PIXE DA images
- Image processing (smoothing, noise reduction, edge enhancement)
- Image display operation (zoom, pan, contrast, minimum conc, maximum conc, colour tables, etc., export and printing)
- Interrogation of images directly for compositions over arbitrary areas
- Extraction of concentration line profiles of selected areas and projected along interactively specified directions
- Measurement of feature sizes in images
- Extraction of PIXE spectra from selected arbitrary regions of an image
- Export of images as HTML pages linked to GIF images.

Are K_α, K_β treated as singlets or multiplets?

K_α treated as singlet up to Fe and multiplet ($K_{\alpha1}$, $K_{\alpha2}$) for Z>26.
K_β treated as singlet up to Ar and multiplet for Z>18.
L_α treated as singlet up to Sb and multiplet ($L_{\alpha1}$, $L_{\alpha2}$) for Z>51.

Energy calibration (linear, quadratic, other):

Linear: yes quadratic: yes other (higher polynomial terms): yes

Expression used for FWHM calibration: $W^2 = a_1^2 (E - E_w) + a_0^2$ where W is the FWHM, and a_0, a_1, E_w are constants. a_0, a_1 are fitting variables, while E_w is set to E_L, the lowest energy in the fitting range. This offset improves the "orthogonality" of these non-linear fitting parameters, and improves fit reliability and stability. A similar approach is used for energy calibration [23].

Expression used for efficiency: The detector efficiency function of Cohen [24] is used, together with contributions due to dead-layer, front contact, detector window and external filters (including pin-holes), losses due to Si (or Ge) escape (front and rear), and pile-up losses up to third order.

Expression used for peak-shape function: Gaussian peaks are used plus an exponential tail for incomplete charge collection plus a Stefan-Boltzmann shaped term. This peak shape function is used for K, L and M X rays lines, plus KLL and KLM radiative Auger lines, escape lines (Si K, Ge K_α, Ge K_β), and pile-up lines (double and triple pile-ups). A test is applied and only significant peaks use the tail terms. Up to 55 elements can be fitted, with K, L and M line groups for each. Each group includes lines and escape peaks (either Si or multiple Ge), up to 20 per group. Pile-up is treated as a separate "sum element" with up to 50 lines.

Phenomena taken into account:

Escape peaks (both Si(Li) Si K_α and Ge Ge K_α, Ge K_β)	yes
Radiative Auger	yes
Exponential tails	yes
Short steps (as a Stefan Boltzmann shaped function)	yes
Shelf	no
Pile-up treatment (both double and triple pile-ups, only one free parameter)	yes
Other satellites	no

NOTE: X ray relative intensities reflect integration over the complete thick target or arbitrary layered target structure (see below).

Are user-defined peak shapes allowed? No

What fitting algorithm is used:

Non-linear least squares with Poisson statistics weighting [23, 25].

A number of measures are used to improve fit stability and convergence. It uses up to 5 phases in the fit to stage the freeing of non-linear parameters for energy calibration, peak widths and tail functions. For each spectra, the program decides, based on peak intensities and spacings, whether to free certain parameters. Energy calibration frees only 1 parameter (offset) if there is only one peak present, both if more peaks exist and none of there are no significant peaks; similarly for widths. Tail parameters for tail strength and length of exponentials are set to database values for a given detector initially, but are freed in the fit if intense peaks are available and with suitable spacing. These decisions are controlled by the software, with no user parameters or intervention required.

What background functions are used? The SNIP statistics sensitive non-linear iterative peak-clipping algorithm is used [12], with or without correction for filter absorption and detector efficiency. User defined backgrounds are an option.

Matrix correction methods: PIXE X ray yields are integrated for all individual X ray lines over the target structure, which can be thin, thick or multi-layered. Secondary fluorescence is integrated out over this target structure. Target rotation and tilt are treated, as well as arbitrary detector angle [23].

By calculating separate X ray lines, the relative intensities used for fitting reflect the integrated target structure. This is essential for accurate fitting of spectra from layered targets such as solid and fluid inclusions in minerals, for example [26].

PIXE line yields are calculated in "generic" form, assuming no external filters and an ideal detector of unit solid angle. These yields are stored on disk for later use, often thousands of times. The experimental terms are added later for fitting and conversion of peak areas to concentration.

In the case of complex samples such as fluid inclusions, generic yields are calculated for the specific mineral matrix and for selected inclusion depth and thickness (ie. for selected thickness of 3 layers). And sets of files for combinations of depth and thickness are generated for one matrix (and for specific detector geometry and beam energy).

Concentrations are calculated from peak areas, PIXE yields, and experimental parameters. No standards or ratios to standards are used. This is a standardless approach. However, analyses of numerous standards are used to check performance as quality control.

What database of X ray line intensities is used? The database is based on Atomic and Nuclear Data tables, such as Cohen and Harrigan [27] for L lines and Krause and Salem et al. [28,29] for K lines, and then adjusted by fitting spectra from pure element and binary compound targets for 52 elements from Ca to U [23]. The user can edit this database via an interactive interface.

Line available for analysis, over the following atomic number ranges:

K lines C to U, Z = 6 to 92
L lines Ca to U, Z = 20 to 92
M lines Ta to U, Z = 73 to 92

Database used for detection system efficiency calculations: The method uses physical models for detection efficiency [24], corrected as per [23], escape losses through both detector front and rear [23] dead-layer, gold layer, and detector window absorption losses, geometrical effects and pile-up losses [23]. The database stores each detector parameter set for retrieval using an identification number. The user can edit the physical parameters.

Can a set of elements be specified? Yes, the user interactively identifies elements using the graphics spectrum interface and marks all lines for selected elements. The program also has a search function to identify all elements present based on peaks, proximity to line energies and a plausibility weighting scheme.

Reporting:

Summary report — Contains concentrations, 1-sigma uncertainties and detection limits (MDL; 99% confidence limit based on Poisson statistics). There are two forms of report, one for printing and one to load into a spreadsheet program. Each row contains results for a single analysis; up to 400 analyses (PIXE spectra) can be handled in a group.

Results are either concentration for thick samples, fluid inclusions, etc. or as areal density.

Output can also be ratioed to other analyses, standard values, as ppm or atomic fraction or projected onto end-member components.

Detailed reports — For each analysis (1 page per analysis), contains detailed sample information, experimental details (e.g. filters, detector parameter set used, integrated live-charge, beam energy), generic PIXE X ray yields file used, chi-squared and RMS error for fit. Then a table gives, for each element, details of peak areas, 1-sigma uncertainties (counts), yield factor, concentration, 1-sigma uncertainty (ppm), MDL (99% confidence limit), one row per element. The yield factor is the ppm/count value folding together generic yields with experimental parameters.

Fit Reports — The fit report gives details of detector parameters, fit options file and relative intensities file (from yield calculation), filter details, and the progress of the various phases of the fit showing reduced chi-squared and RMS errors. It also shows fitting results (with uncertainties) for energy calibration, peak width function and tail variables (see note above on fitting algorithm). Then it shows peak areas for each element fitted, the principal line used, chi-squared for each line, MDL (in counts) and comments on whether tails have been used for an element or whether some of its lines were not included in the fitting range or cut from the spectrum. It also lists any significant parameter correlations encountered in the fit, such as BaL — TiK, PbL — AsK and more subtle ones involving non-linear parameters.

Is the quantification in terms of concentration integrated with the fitting of the peaks or not? Spectrum fitting is integrated with concentration calculation and the reporting and graphical display of results in a module in GeoPIXE that combines fitting results, experimental details and generic yields to deduce concentrations. This module also does geometric modeling for fluid inclusion analysis. This module processes sets of analyses (up to 400 at present) en masse for efficient processing of large volumes of data. GeoPIXE has processed 114,000 PIXE spectra to date at the CSIRO alone. The batch fitting of series of spectra and the reduction of data to concentration and the display of concentration data as various plots (e.g. element and ratio scatter plots) generally proceeds in parallel.

What ions and energy ranges can be used? 2–5 MeV protons and alphas. Heavy ions are also catered for, but only approximately using binary encounter model cross-sections and ignoring multiple ionization and additional satellite peaks.

Output possibilities, report formats?

Outputs from GeoPIXE

Concentration results — summary and detailed report tables for printing and import into spreadsheets (see above). Element scatter, histograms and summary plots, as concentration, ratios, atomic fraction and end-member projected fractions.

Spectra results — Plots of spectra with overlaid fit, background and pileup. Output to printer, or PostScript files, and as GIF files or in computer graphics metafile format (CGM) for import into presentation software.

Image results — Concentration images can be output as GIF, linked via a HTML summary page showing thumb-nail versions of images and detailing experimental and sample parameters and image concentration scales and legends.

Line Profiles — Concentration profiles across selected arbitrary regions of images can be output like spectra, but displayed with points and error bars (1-sigma uncertainties) for each step, plotted against microns distance.

Other output formats are generally adapted with out collaborators to suite their software.

What spectrum file formats are accepted? Native GeoPIXE format, MARC Mpsys IMG format and various simple ASCII formats (to simplify input) are catered for now. Generally, additional formats, or conversion programs are developed with our collaborators to interface to their data acquisition and imaging software.

Can the spectra be manipulated and then saved to file? Yes. GeoPIXE has numerous functions for spectrum manipulation and processing (add, subtract, scale, divide, multiply, square-root, smooth, filter (various digital filters), calibrate, map onto new calibration, compress, subtract background, strip tails and escapes, simulate pileup, remove detector efficiency and filter absorption, auto-identify peaks, sum channels, perform peak area extraction, match spectra for yield in range, etc.) for interactive manipulation of single and multiple spectra. A macro programming features enables operations to be combined for routine use or special applications.

What QA/QC measures does the software take? The code generates 1-sigma errors and 99% confidence limit detection limits (MDLs). Values are reported as <MDL if below this MDL. Each fit shows a reduced chi-squared value and a RMS error (beyond the reduced chi-squared of 1), plus fitting results for energy calibration, widths and tails. The RMS error is a useful guide to spotting problems in a long batch run of numerous spectra processed together. Fitting correlations are also reported. These show any strongly correlated parameters, which may lead to fit instability. Reference material concentrations can be loaded and ratioed against analysis results.

Is there on-line help? A manual? A web page? There is copious on-line help (over 4 Mbytes), and a manual (300 pages approx.), in the current version. Conversion to the new PC version is underway. There is no web-page at present, although the new on-line help will probably use a web-page approach.

All data provided by: C. Ryan, CSIRO Exploration and Mining, North Ryde, Australia.

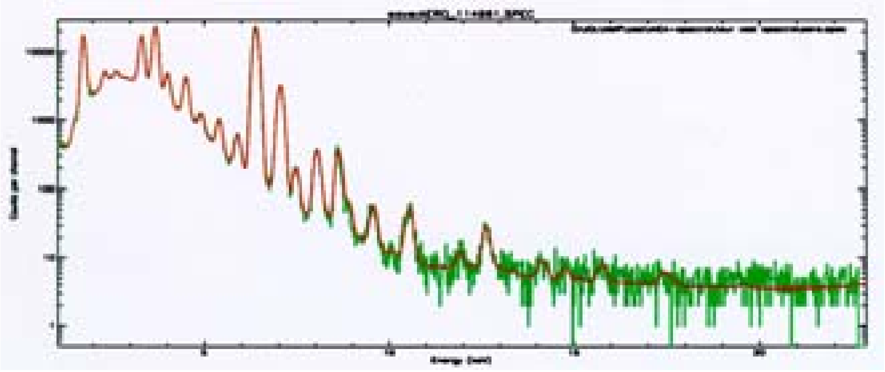

FIG. 8. GEOPIXE fit of the aero test spectrum.

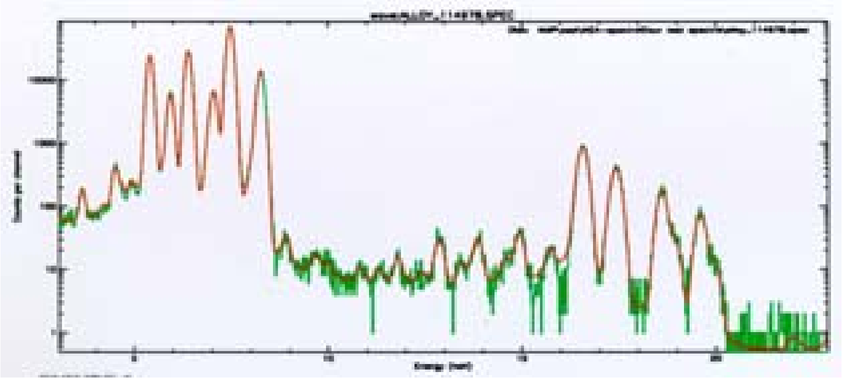

FIG. 9. GEOPIXE fit of the alloy test spectrum.

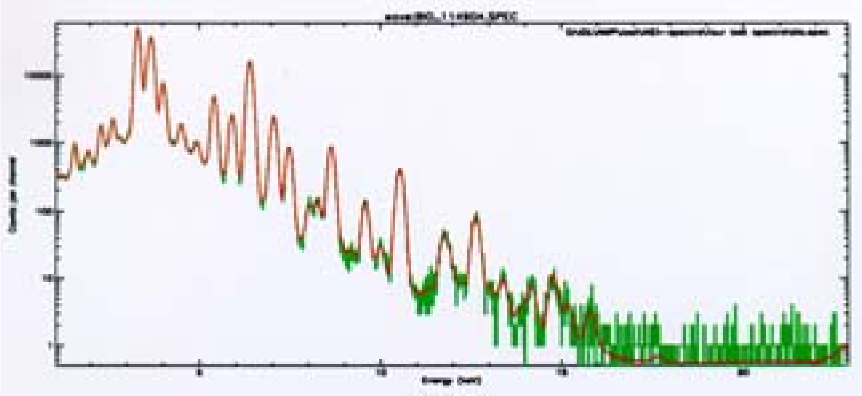

FIG. 10. GEOPIXE fit of the bio test spectrum.

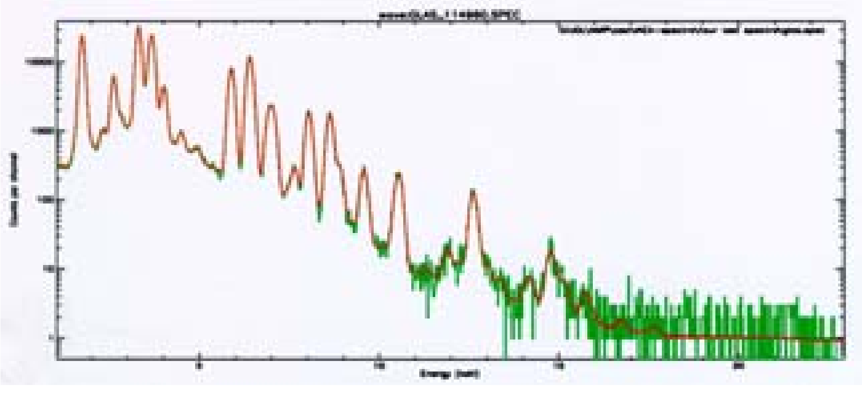

FIG. 11. GEOPIXE fit of the glass test spectrum.

4.2. GUPIX

What operating system/computer type does the software require? DOS/PC

Are graphical representations of spectra, fits, residuals, and calibrations available?

energy calibration	Yes ☐	No ☑	spectra	Yes ☑	No ☐
FWHM calibration	Yes ☐	No ☑	fits	Yes ☑	No ☐
efficiency calibration	Yes ☐	No ☑	residuals	Yes ☑	No ☐

What Graphics/Zoom/Color setting options are offered? Various.

Are K_α, K_β etc. treated as singlets or as multiplets?
singlets ☐ multiplets ☑

Energy calibration: linear, quadratic, other…
linear ☐ quadratic ☑ other ________________________________

What expression is used for FWHM calibration? $\sigma^2 = (a + bE)$

What expression is used for efficiency calibration? See Johansson & Campbell PIXE book.

What expression is used for peak shape function? Voigt with exp. Tails and flat steps.

What phenomena are taken into account?

escape peaks	Yes ☑	No ☐	pile up treatment	Yes ☑	No ☐
radiative Auger	Yes ☑	No ☐	other satellites	Yes ☑	No ☐
exponential tails	Yes ☑	No ☐ If Yes, how many? 2			
short steps	Yes ☑	No ☐ If Yes, how many? 1			
shelf	Yes ☑	No ☐			

Are user-defined peak shapes allowed? Yes ☐ No ☑

What fitting algorithm is used?
non-linear least squares ☐
Marquardt ☑
other ____

What background functions are used. Users define functions possible? TOP-HAT filter method.

What matrix correction methods (thick target corrections for X ray intensities) are used? Full matrix treatment including secondary fluorescence.

What database of X ray line intensities is used? Dirac-Fock theory with modifications.

- Can the user edit that database? Yes ☐ No ☑

But the user can define a "temporary element" (corresponding to any Z) having the line intensities that they prefer.

What lines are available for analysis (K,L,M,...) for what atomic number ranges?
K lines → atomic number range: 6–92
L lines → atomic number range: 22–92
M lines → atomic number range: 72–83; 90–92

What database is used for detection system efficiency computations? XCOM for μ/ρ

- Can the user edit that database? Yes ☐ No ☑

Can a set of elements to be determined be specified (or does the program look for all elements in the region)? Yes ☑ No ☐

What information is given in the report (peak areas and what kinds of associated uncertainties, concentrations and what kinds of associated uncertainties, what kind of detection limit)?
$K\alpha_{1,2}$, $L\alpha_1$, $M\alpha_1$, peak area; fit error; approx. statistical error; concentration; 3σ LOD.

Is the quantification in terms of concentrations integrated with the fitting of the peaks or not? Yes.

What ions can be used for excitation? In what energy ranges?
^{1}H up to 3 MeV
^{2}H up to 6 MeV
^{3}He up to 12 MeV
^{4}He up to 12 MeV
^{1}H up to 80 MeV

Output possibilities/report formats? Extensive text

What spectrum file formats are accepted? Two ASCII types; Oxford Instruments ASCII file; Nucleus PCA-II file; Guelph "Pseudo-ND66" file; ND/Canberra 6700; Ortec CHN.

Can spectra be manipulated (added, subtracted, filtered, ...) and then saved to file again? No.

What QA/QC measures does the software take? For example, does the program offer special options for handling reference material results, monitoring stability of time, etc.? Does it report χ_r^2 of fits, resolution parameters etc. that help in assessing the quality of the results? χ_r^2; residue plot; flags if resolution exceeds defined norm.

Is there on-line help? A manual? A web page? Extensive documentation. Help provided within the program. Some information at website.

All data provided by: J.L. Campbell and J.A. Maxwell, University of Guelph, Guelph, Canada.

4.3. PIXAN

What operating system/computer type does the software require? UNIX

Are graphical representations of spectra, fits, residuals, and calibrations available?

energy calibration	Yes ☑	No ☐	spectra	Yes ☑	No ☐
FWHM calibration	Yes ☑	No ☐	fits	Yes ☑	No ☐
efficiency calibration	Yes ☑	No ☐	residuals	Yes ☐	No ☑

What Graphics/Zoom/Color setting options are offered? Zoom and colours are available.

Are K_α, K_β etc. treated as singlets or as multiplets?
singlets ☑ multiplets ☐

Energy calibration: linear, quadratic, other …?
linear☑ quadratic ☐ other ______________________________

What expression is used for FWHM calibration? $\sigma^2 = (p1+p2*E)^2$

What expression is used for efficiency calibration? $\varepsilon = T\ \varepsilon_i\ f_g\ f_{Be}\ f_{Au}\ f_d\ f_R$

What expression is used for peak shape function? Gaussian + Expon. Tail + step btw Kα and Kβ.

What phenomena are taken into account?

escape peaks	Yes ☑	No ☐	pile up treatment	Yes ☑	No ☐
radiative Auger	Yes ☐	No ☑	other satellites	Yes ☐	No ☑
exponential tails	Yes ☑	No ☐	If Yes, how many? ______________		
short steps	Yes ☑	No ☐	If Yes, how many? ______________		
shelf	Yes ☐	No ☑			

Are user-defined peak shapes allowed?
Yes ☐ No ☑

What fitting algorithm is used?
non-linear least squares ☑
Marquardt ☐
other ____

What background functions are used. User define functions possible? Polynomial background corrected for sample absorption and detector efficiency or iterative background.

What matrix correction methods (thick target corrections for X ray intensities) are used? Proton energy loss and X ray absorption are corrected for.

What database of X ray line intensities is used? For K lines Salem, for L Cohen and Harrigan.
- Can the user edit the database?
Yes ☐ No ☑

What lines are available for analysis (K,L,M,...) for what atomic number ranges?
K lines → atomic number range: B to Sm
L lines → atomic number range: Zr to U
M lines → atomic number range: NA

What database is used for detection system efficiency computations? Absorption calculated according to Theisen and Vollath algorithm (Victoreen rule).

- **Can the user edit the database?**
  Yes ☐ No ☑

Can a set of elements to be determined be specified (or does the program look for all elements in the region)? Yes ☑ No ☐

What information is given in the report (peak areas and what kinds of associated uncertainties, concentrations and what kinds of associated uncertainties, what kind of detection limit)? Peak areas, the sum of experimental, calibration and fitting error, and detection limits. Detection limits are calculated as MDL>3.3sqrt(N_b).

Is the quantification in terms if concentrations integrated with the fitting of the peaks or not? No

What ions can be used for excitation? In what energy ranges? Protons.

Output possibilities/report formats? Peak areas, Concentrations, with and/or without detection limits. Complete output contains also fitting parameters, Chi-sq, number of iterations, etc.

What spectrum file formats are accepted? Text file with 9 columns.
Can spectra be manipulated (added, subtracted, filtered, ...) and then saved to file again? No.

What QA/QC measures does the software take? For example, does the program offer special options for handling reference material results, monitoring stability of time, etc.? Does it report χ_r^2 of fits, resolution parameters etc. that help in assessing the quality of the results? Reference materials can be analysed first so that system parameters are optimised and then used to process unknown samples. Chi-sq is reported and spectra, fit and bacground are plotted for visual inspection. Warning (asterix) is placed next to the reported concentration if the reported value is smaller than MDL.

Is there on-line help? A manual? A web page? There is comprehensive manual available.

All data provided by: D. Cohen, I. Orlic, ANSTO, Menai, Australia.

4.4. PIXEKLM

What operating system/computer type does the software require? PC Pentium processor; minimum 1MB memory; SVGA monitor. Operation system: DOS 6.22, or WIN95.

Are graphical representations of spectra, fits, residuals, and calibrations available?

energy calibration	Yes ☐	No ☒	spectra	Yes ☒	No ☐
FWHM calibration	Yes ☐	No ☒	fits	Yes ☒	No ☐
efficiency calibration	Yes ☐	No ☒	residuals	Yes ☒	No ☐

What Graphics/Zoom/Color setting options are offered? The result of the fit is shown on the screen as a figure. It includes the original (measured) and fitted spectra, the sum of the fitted background and pile up contribution. The residual is also shown. The size and color of the figure may not be changed. Data of the above mentioned figure might be saved in an ASCII file, too. Using this file a proper figure can be made about the fit by the help of a plotter program.

Are K_α, K_β etc. treated as singlets or as multiplets?

singlets ☐ multiplets ☒

Energy calibration: linear, quadratic, other…?

Linear ☒ quadratic ☒ other ________________________

What expression is used for FWHM calibration? $\sqrt{a^2 + b^2 E}$

What expression is used for efficiency calibration?

$$\varepsilon(E) = \exp(-\mu_{Be}\, x_{Be} - \mu_{Au}\, x_{Au} - \mu_{Si1}\, x_{Si1})\,[\,1 - \exp(-\tau_{Si2}\, x_{Si2})]\,\eta$$

where x_{Be}, x_{Au}, x_{Si1} and x_{Si2} are the thickness of the Be window, the Au layer, the dead layer and the sensitive volume of Si, μ_{Be}, μ_{Au} and μ_{Si} are total mass attenuation coefficients of Be, Au and Si, τ_{Si} is the photoabsorption coefficients of Si. η is describing the escape contribution and is unity below the absorption edge of Si, and above the edge it is given with the following formula:

$$\eta = 1 - \frac{\omega_K}{2}\left(1 - \frac{1}{r}\right)\left(1 - \frac{\mu_K}{\mu_I}\ln\left(1 - \frac{\mu_I}{\mu_K}\right)\right)$$

where ω_K is the fluorescence yield of Si, r is the absorption jump of SiK, μ_I μ_K are mass attenuation coefficients of Si for energy of incoming SiK-line.

What expression is used for peak shape function?

$$\exp\left(-\frac{(E_i - E_o)^2}{2\sigma^2}\right) + p_{t1}^2 \exp\left[(E_i - E_o)\, p_{t2}^2\right] \operatorname{erfc}\left(\frac{E_i - E_o}{\sigma\sqrt{2}} + \frac{\sigma\, p_{t2}^2}{\sqrt{2}}\right)$$

The Gauss function can be replaced by the Voight-profile.

What phenomena are taken into account?

escape peaks	Yes ☒	No ☐		pile up treatment	Yes ☒	No ☐
radiative Auger	Yes ☐	No ☒		other satellites	Yes ☐	No ☒
exponential tails	Yes ☒	No ☐	If Yes, how many? 1			
short steps	Yes ☐	No ☒	If Yes, how many? _______________			
shelf	Yes ☐	No ☒				

Are user-defined peak shapes allowed?

Yes ☐ No ☒

What fitting algorithm is used?
non-linear least squares ☐
Marquardt ☒
other ____

What background functions are used. User defined functions possible?
The following possibilities are available:
1. *B(E)* background obtained by the peak-filing algorithm [30] or SNIP algorithm [12] is used in the form of *a+bB(E)*, here *a* and *b* are parameters to be fitted.
The following functions can be chosen for describing the background:

$$B(E_i) = T(E_i)\ \Sigma_{i=0,N} T(E_i — E_s)^i$$

$$B(E_i) = T(E_i) \exp \Sigma_{i=0,N} T(E_i — E_s)^i$$

$$B(E_i) = T(E_i) \exp \Sigma_{i=0,N} P_i\ C_i(E_i)$$

$$B(E_i) = T(E_i)\ \Sigma_{i=0,N} P_i\ C_i(E_i)$$

where N+1 is the number of P_i parameters of the background to be fitted, E_s is a constant introduced for numeric reason, $C_i(E_i)$ denotes Tchebycheff's polynomials. The response probability of the detector, the transmission of absorbers and the self-absorption of the sample are taken into account by the T(E) function. These effects can be neglected during the fitting of the background if this function is chosen as unit.
Initial values of P parameters can be determined by linear fitting of the background obtained by the above (at 1.) mentioned algorithms or found by numerical mode from the minimal values of the spectrum.
We mention here that at the forepart of the spectrum (in the range of the noise, where no peaks are present) and at the end part of the spectrum (slowly changing background), a polynomial background with few parameters can be applied, which continuously adjoins to the above described exponential background functions.

What matrix correction methods (thick target corrections for X ray intensities) are used? Stopping of projectiles, X ray absorption in target, secondary excitation.

What database of X ray line intensities is used? The program calculates the ionization cross sections by the ECPSSR theory (except partly M-subshells, see below), and using these and other necessary atomic physical quantities (fluorescence yields, Coster-Kronig yields, transition probabilities e.t.c.) determines the X ray production cross sections of individual lines, and modifies them with the response probability of the Si(Li) detector and the transmission of the applied absorber(s). Concentrations are calculated on the basis of the line of highest effective cross section value, obtained by the above described way, and the effective relative intensities of other lines are related to this line. Files, including atomic physical quantities are the compilation of partly experimental, but basically theoretical data. We do not give references here, they are usually used in the PIXE literature.

- **Can the user edit that database?**
  Yes ☒ No ☐

What lines are available for analysis (K,L,M,...) for what atomic number ranges?

K lines → atomic number range: 5–56
L lines → atomic number range: 17–92
M lines → atomic number range: 31–92

What database is used for detection system efficiency computations? ______________________

- **Can the user edit that database?**
  Yes ☒ No ☐

Can a set of elements to be determined be specified (or does the program look for all elements in the region)? Yes ☒ No ☐

What information is given in the report (peak areas and what kinds of associated uncertainties, concentrations and what kinds of associated uncertainties, what kind of detection limit)?
The program gives:

- the area of the most intensive peak and it's error (it is square root of the sum of the peak area and twice the background under the peak including the contributions of other elements, too),
- the sensitivity limit (three times the square root of the background calculated at 1 FWHM),
- the concentration and it's error (calculated from the errors of the peak area, the accumulated charge, and the solid angle of the detector),
- the sensitivity limit for concentration

Is the quantification in terms of concentrations integrated with the fitting of the peaks or not?
Yes.

What ions can be used for excitation? In what energy ranges? In principle ion of any atomic number and energy can be used for excitation. Practical limitation is due to the validity of the ECPSSR theory in the case of K and L shell ionization [31].
In the case of M shell ionization by proton excitation, in the energy range of 0.06–2.0 MeV for Z=54–92 atomic numbers, ionization cross sections are calculated by DHSM model with interpolation of data of the table [32].
In the case of excitation by other ions, or other energy or atomic number range, also ECPSSR theory is used [33,34].

Output possibilities/report formats?
The program in ASCII format creates two result files: (i) the first is containing detailed results, including input data, values of all fitted parameters and their errors; (ii) the second is a table including only the spectrum name, the normalized value of χ^2 , values of concentrations and their errors, and sensitivity limits.

What spectrum file formats are accepted? ASCII file, its format is 10F8.0, file created by Nucleus PCA-II card, Oxford type binary file created by Oxford Microbeam setup.

Can spectra be manipulated (added, subtracted, filtered, ...) and then saved to file again? No

What QA/QC measures does the software take? For example, does the program offer special options for handling reference material results, monitoring stability of time, etc.? Does it report χ_r^2 of fits, resolution parameters etc. that help in assessing the quality of the results? Detailed result file includes the value of normalized χ^2, and root mean square, as well as values of all fitted parameters and their errors. The quality of the fit can be classified by these data and the figure shown on the screen.

Is there on-line help? A manual? A web page? Manual.

All data provided by: G. Szabó and I. Borbély-Kiss ,Institute of Nuclear Research of the HAS, Debrecen, Hungary.

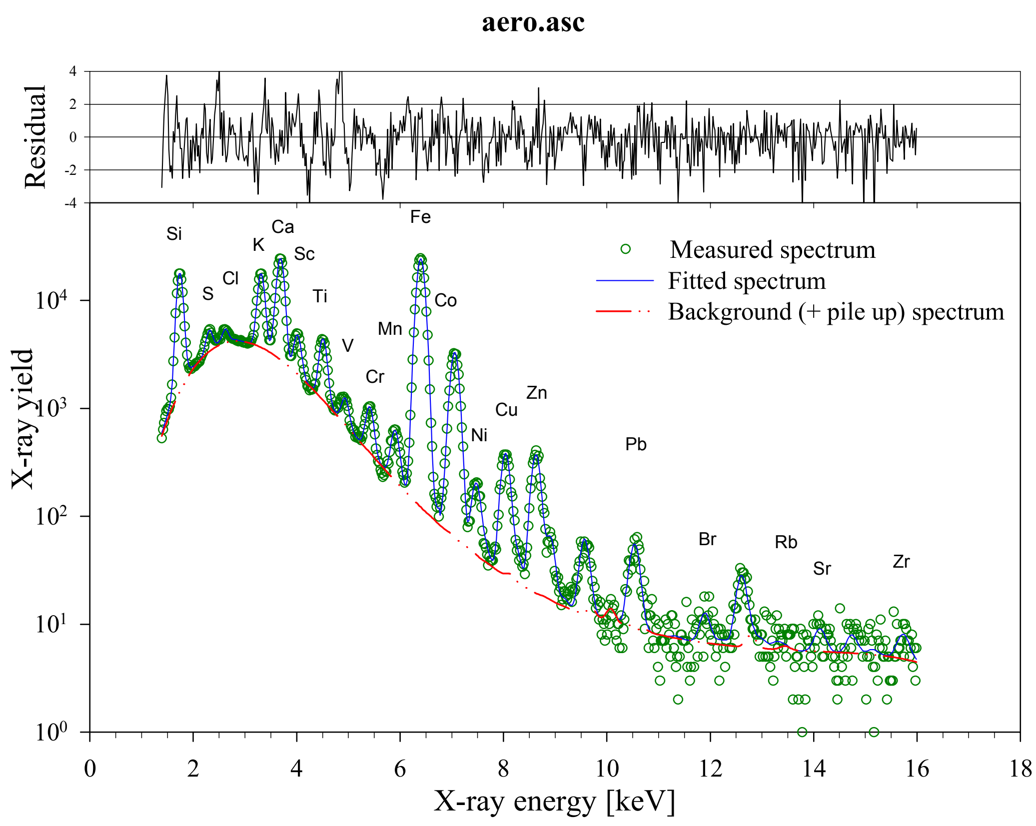

FIG. 12. PIXEKLM fit of the aero test spectrum.

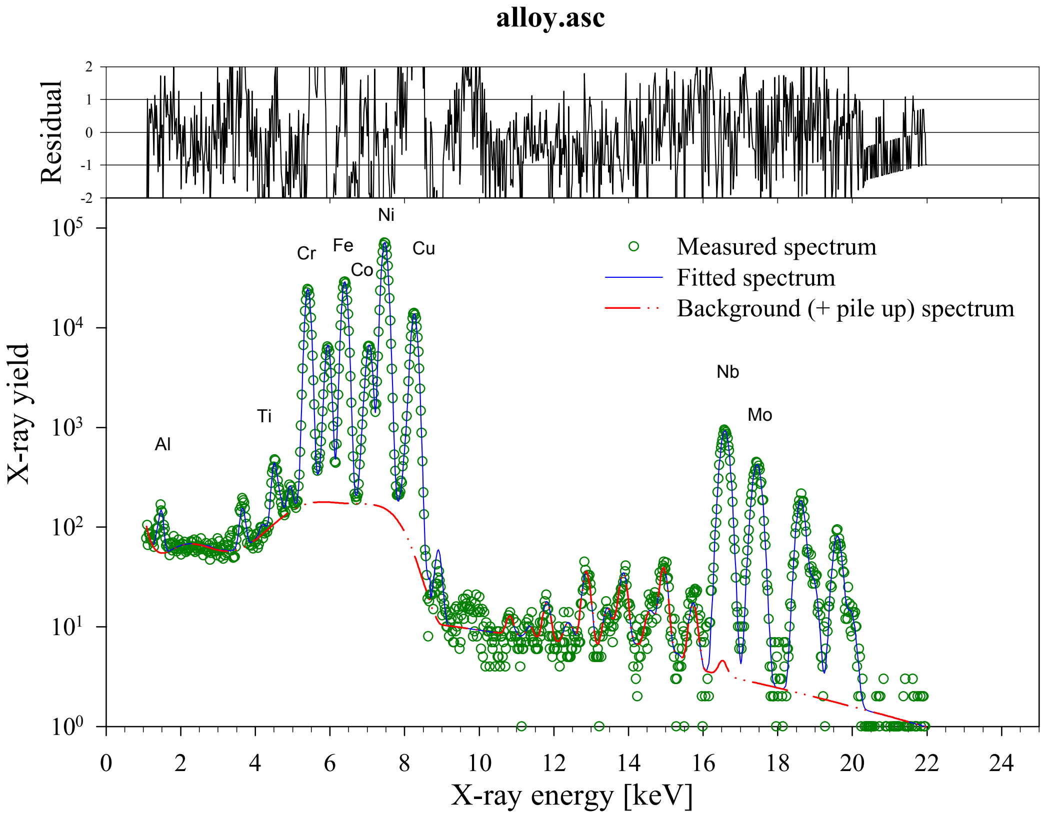

FIG. 13. PIXEKLM fit of the alloy test spectrum.

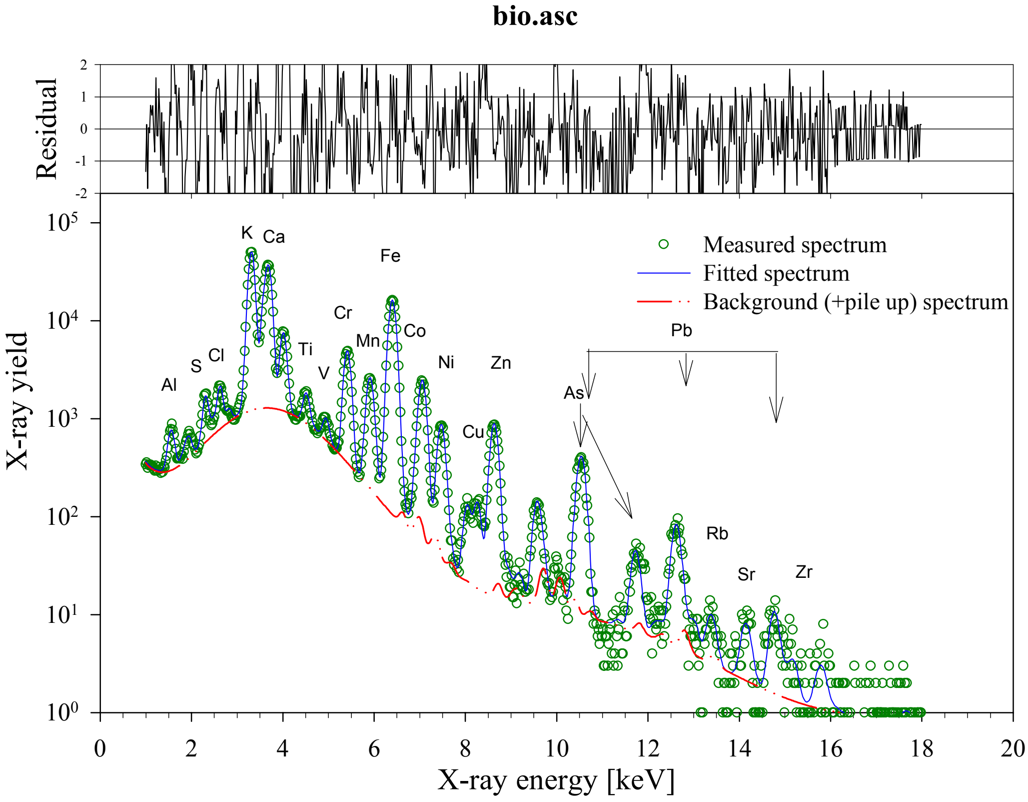

FIG. 14. PIXEKLM fit of the bio test spectrum.

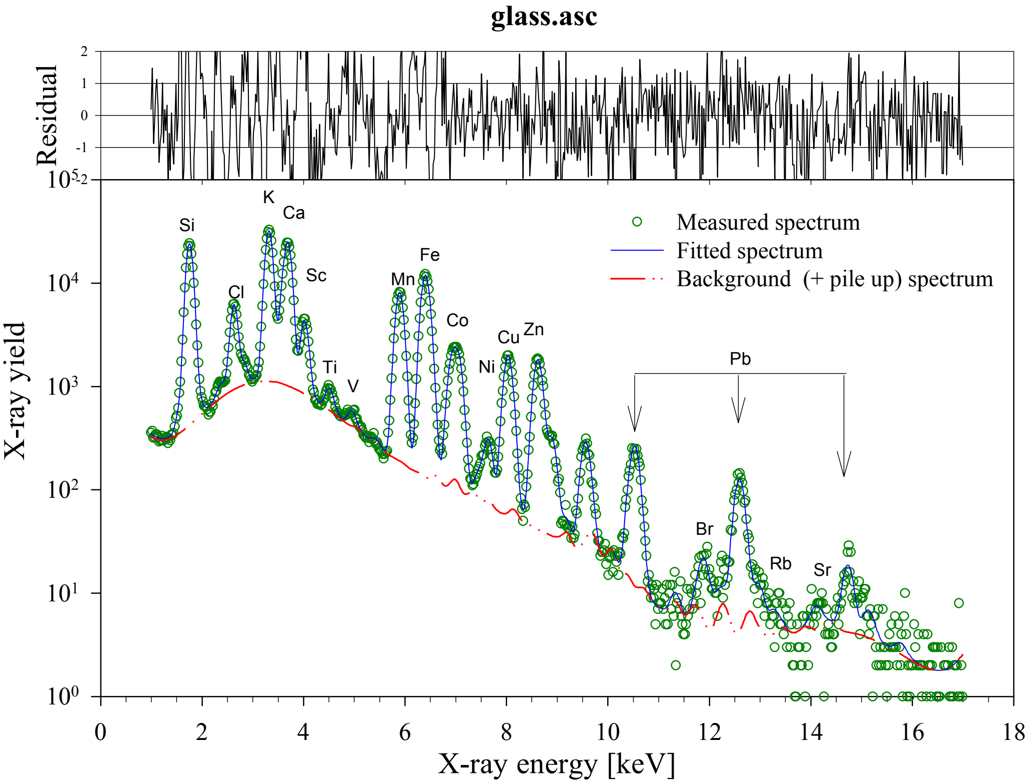

FIG. 15. PIXEKLM fit of the glass test spectrum.

4.5. SAPIX

What operating system/ computer type does the software require? MS-DOS, General Windows machine, Quick-basic execution programs.

Are graphical representation of spectra, fits, residuals, and calibration available?

energy calibration	Yes ☒	No ☐	spectra	Yes ☒	No ☐
FWHM calibration	Yes ☒	No ☐	fits	Yes ☒	No ☐
efficiency calibration	Yes ☐	No ☒	residuals	Yes ☐	No ☒

Are Ka Kb etc. treated as singlets or as multiplets?

singlets ☒ multiplets ☒ i.e. both options are possible (selectable).

Energy calibration: linear, quadratic, other…?

Linear ☒ quadratic ☐ other __________________________

Appropriate calibration can be chosen for each energy region.

What expression is used for FWHM calibration? It is expressed as Gaussian functions drawn in the spectrum.

What expression is used for efficiency calibration? No expression. Efficiency of the detecting system is determined directly by our own method and program, which is not included in SAPIX but in the combined program.

What expression is used for peak shape function? Expressed as response functions or Gaussians. Response functions are determined experimentally.

What phenomena are taken into account?

escape peaks	Yes ☒	No ☐	pile up treatment	Yes ☐	No ☒
radiative Auger	Yes ☐	No ☒	other satellites	Yes ☒**	No ☐
exponential tails	Yes ☒	No ☐ If Yes, how many? 2 (see *)			
short steps	Yes ☐	No ☒ If Yes, how many? ________________			
shelf	Yes ☐	No ☒			

* peak tails are approximated by two Gaussians which have different FWHM

** satellites can be included into peak response

Are user-defined peak shapes allowed?

Yes ☐ No ☒ Only selection of single Gaussian and response function is allowed.

What fitting algorithm is used?

Non-linear least squares ☐ Marquardt ☒ (modified Marquardt)

Other ____

What background functions are used? User define functions possible? User can create the background shape by combination of exponential and polynomial functions. User-define functions are not available, but the user-made background is available.

What matrix correction methods (thick target correction for X ray intensities) are used? No correction. Matrix correction is not included in SAPIX, and some matrix effects, such as X ray absorption in the target, is corrected using other programs.

What database of X ray line intensities is used?

Ionization cross sections for K-,L- and M-shell, for various projectiles and for a wide range of incident energy, can be prepared easily by our computer code ICPER, based on the ECPSSR theory. For physical quantities (fluorescence yields, radiative widths etc.) we use values given by W.Bambynek et al. [35]. X ray production cross sections for all elements are calculated and tabulated for some practical incident energies.

What lines are available for analysis (K,L,M,) for what atomic number ranges?
K lines atomic number range: 10–60. L lines atomic number range: 30–90. M lines are not available. (Though we prepared X ray production cross sections for M-shell, we have not used them for quantitative analysis since physical parameters (fluorescence yields, radiative widths, Coster-Kronig coefficients etc.) are not well known and produce large errors.

What database is used for detection system efficiency computations? Data base for detection system efficiency prepared by means of our original method and the computer codes [36].

- **Can the user edit that database?**
  Yes ☒ No ☐
  Each user has his own detection system and he/she must modify the database.

Can a set of elements to be determined be specified
(or does the program look for all elements in the region.)? Yes ☒ No ☐
It is selectable according to the sort of samples.

What information is given in the report (peak areas and what kinds of associated uncertainties, concentrations and what kinds of associated uncertainties, what kind of detection limit)? Sample name, users name, run number, date, live time, integrated beam currents, detector number, X ray absorber are given at the top of the report. The X ray peak name, peak counts and associated errors estimated by the error matrix of the modified Marqurdt method, concentrations and their errors, follow. The latter errors contain errors of the X ray production cross sections and systematic errors coming from uncertainties of the detection efficiency and X ray transmission of the X ray absorber. Detection limits are not estimated at the report.

Is the quantification in terms of concentrations integrated with the fitting of the peaks or not? No. The combined program "KEI" performs quantification.

What ions can be used for excitation? In what energy ranges? Since we prepared the data base for quantification for p, d, 3He, alpha particles, and for incident energies ranging from 0.1 to 40 MeV, they are all available. Of cause, the validity of the ECPSSR theory for incident energies below 1 MeV has not been confirmed.

Output possibilities/ report format? The reports are printed out or saved into the data file. In the latter case, two kinds of reports, detailed and simplified, are saved. The counts for each separated peak and backgrounds can be saved as a text file which can be read by Microsoft-Excel. (In addition, graphic hard copies can be printed out at any time.)

What spectrum file formats are accepted? Four binary data types (CANBERRA, SEIKO EG&G, etc.) and all kinds of text data. Transformation from a text file into a binary file is allowed.

Can spectra be manipulated (added, subtracted, filtered) and then saved to file again? Yes, different spectra are normalized by each other and can be subtracted/added and saved as a new file.

What QA/QC measured does the software take? For example, does the program offer special options for handling reference material results, monitoring stability of time, etc? Does it report χ^2 of fits resolution parameters etc. that help in assessing the quality of the results? In SAPIX, χ^2 and a computing time are always expressed throughout the course of iteration.

Is there on-line help? A manual? A web page? For on-line help, no. (We are now planning to rewrite SAPIX so as to run on Windows 98. In that case, on-line help must be prepared.) For operating manual, there is a manual written in English for the version 3. But for a new version (ver.4), it has not been written. We don't have a web page.

All data provided by: K. Sera, Cyclotron Research Center, Iwate Medical University, Iwate, Japan.

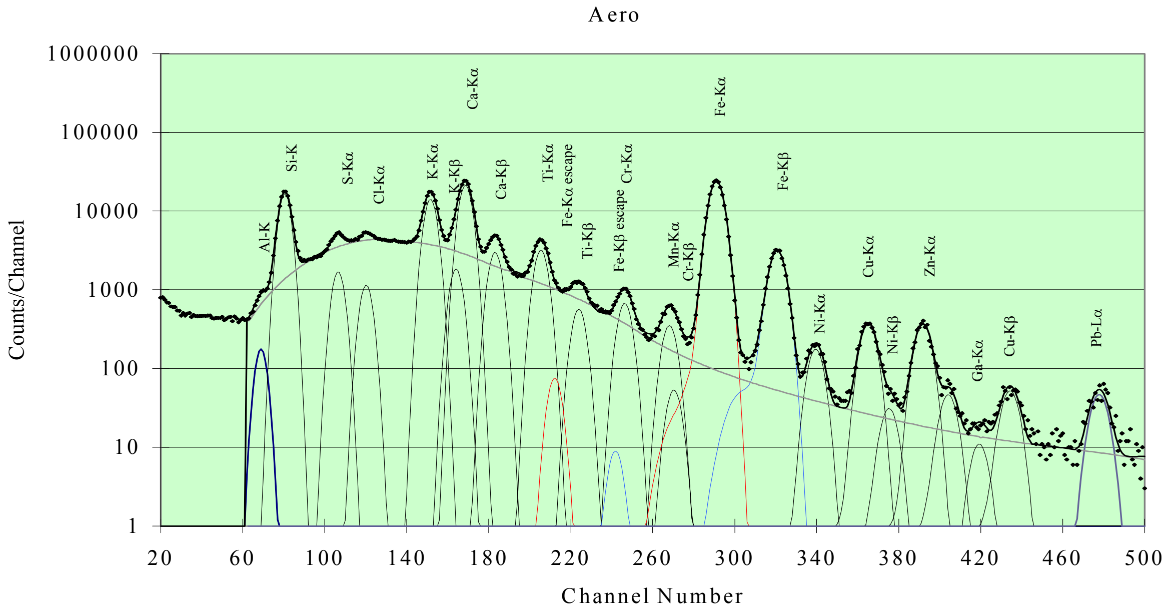

FIG. 16. SAPIX fit of the aero test spectrum.

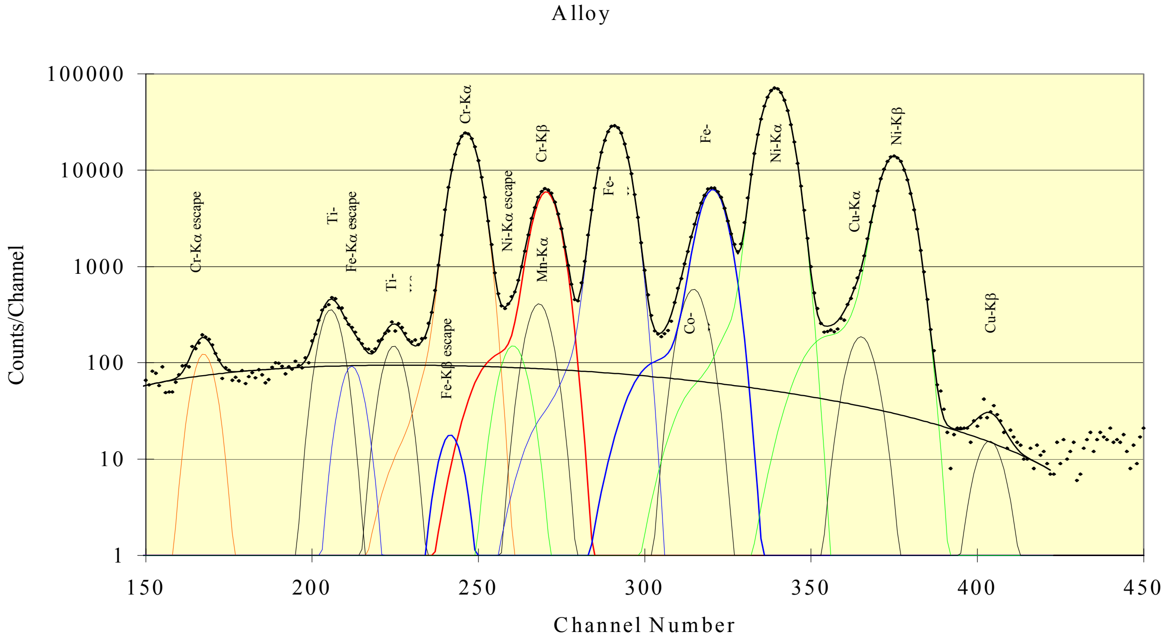

FIG. 17. SAPIX fit of the first part of the alloy test spectrum.

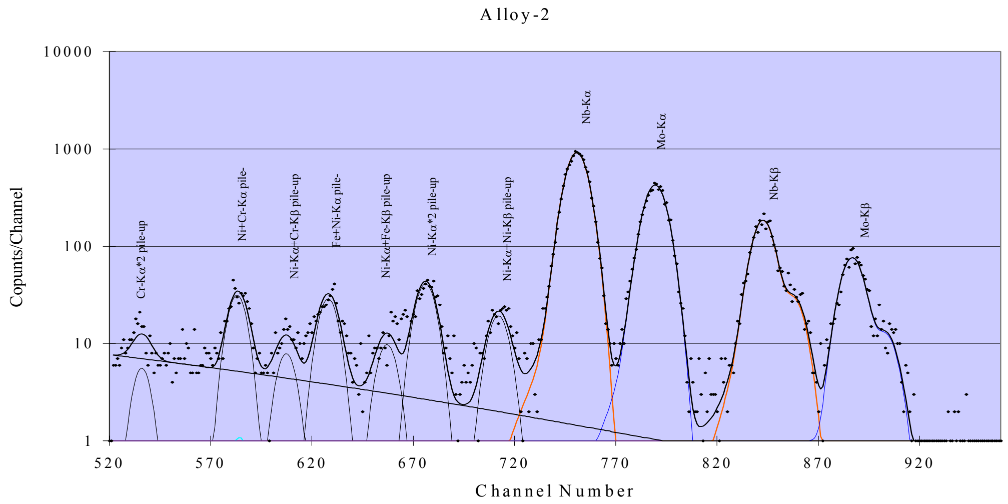

FIG. 18. SAPIX fit of the second part of the alloy test spectrum.

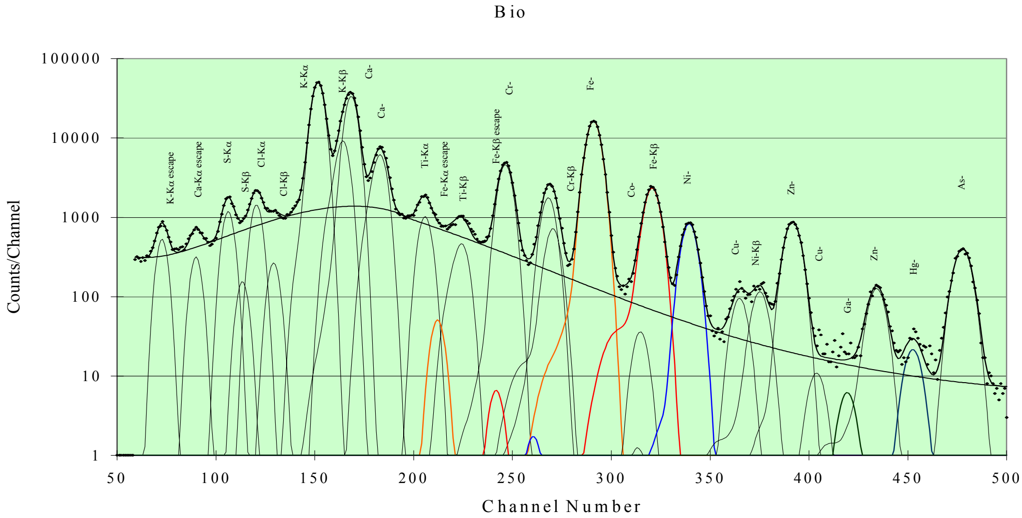

FIG.19. SAPIX fit of the bio test spectrum.

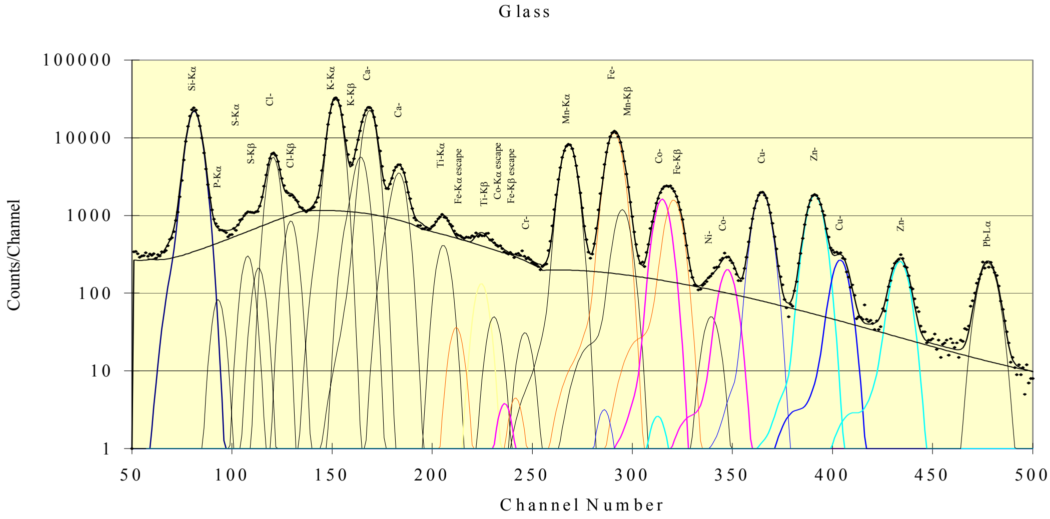

FIG. 20. SAPIX fit of the glass test spectrum.

4.6. WinAxil

Operating system/Computer type. Windows96–98–2000 – NT.

Graphics representations. Spectrum and fit included fitted continuum.

Graphics/Zoom/Color. The program is written as a MS-Windows multi-document interface, each spectrum has it's own window with standard resize capabilities. In each spectrum window the y-axis can be set to linear, logarithmic or square root scale; the x-axis can be set to channels, eV or keV. Zooming and panning of the spectrum is possible with the mouse. A "rubber band" can be used to select (zoom) a portion of the spectrum. Colors are fixed

Are Kα, Kβ etc. treated as singlets or as multiplets? Under control of the user, e.g. he can select to have all K lines as one multiplet or fit them separately as Kα and Kβ, The same applies to L lines and even for the entire KL spectrum.

Energy-calibration. Linear: $E(i) = \text{ZERO} + \text{GAIN} \times i$

What expression is used for FWHM calibration?

$$s^2 = \left(\frac{\text{NOISE}}{2.3548}\right)^2 + 3.85 \times \text{FANO} \times E_j$$

What expression is used for efficiency calibration? Accounting for any attenuation in the path (air, He or vacuum) and the filters between sample and detector, including the "funny" filter and the attenuation by the detector windows.

$$T(E) = T_{Det}(E).T_{Path}(E).T_{filt}(E)$$

$$T_{\text{Det}}(E) = e^{-\mu_{\text{Be}}(\rho d)_{\text{Be}}} e^{-\mu_{\text{Au}}(\rho d)_{\text{Au}}} e^{-\mu_{\text{Si}}(\rho d)_{\text{Si}}} \left(1 - e^{-\mu_{\text{Be}}(\rho D)_{\text{Be}}}\right)$$

$$T_{\text{Path}}(E) = e^{-\mu_{\text{air}}(\rho d)_{\text{air}}}$$

$$T_{\text{Filt}}(E) = e^{-\mu_f(\rho d)_f} \left[h + (1-h) e^{-\mu_{ff}(\rho d)_{ff}}\right]$$

What expression is used for peak shape function? A numerical peak shape correction is applied to the Gaussian. This correction is determined from reference spectra. The correction is adjusted (interpolated) to mach the energy and resolution calibration of the spectrum. *C(i)* is the peak shape correction at channel *i* for a certain element

$$y_P(i) = A\left\{R'_{K\alpha}\left[G(i, E_{K\alpha}) + C(i)\right] + \sum_{j=2}^{N_P} R'_j G(i, E_j)\right\}$$

What phenomena are taken into account?

escape peaks Yes ☒ No ☐ pile up treatment Yes ☒ No ☐
radiative Auger Yes ☐ No ☒* other satellites Yes ☐ No ☒
exponential tails Yes ☒ No ☒** If Yes, how many? ________________
short steps Yes ☒ No ☐ If Yes, how many? ________________
shelf Yes ☐ No ☒***

* indirectly via numerical peak shape correction
** indirectly via numerical peak shape correction
*** indirectly via numerical peak shape correction

Are user-defined peak shapes allowed? In principle not, can be done by manipulating the database, i.e. giving fake energies to a seldom-used element (not recommended).

What fitting algorithm is used?
Non-linear least squares, Marquardt algorithm, modified to include "soft constraints".

What background functions are used? User defined functions possible? Linear; exponential; bremsstrahlung (exponential x efficiency); filter (iterative peak stripping); orthogonal polynomial. No user defined function, but number or parameters in each of the models can be adjusted by the user

What matrix correction methods (thick target correction for X ray intensities) are used? None.

What database of X ray line intensities is used? Microsoft Access database (WinAxil.mdb).

- Can the user edit that database?

Yes ☒* No ☐

*using MS-Access or via separate program (WaxLibMan).

What lines are available for analysis (K,L,M,) for what atomic number ranges? Depends on data in the database, default is:

K lines → range: B-Ba L lines → range: Fe-U M lines → range: Not available

What database is used for detection system efficiency computations? Parameters of the system (data in Filters, Be-window, etc) is stored in the database WinAxil.mdb. Mass attenuation coefficients are based on McMaster tables (not in database, but hard coded in DLL).

- Can the user edit that database?

Yes ☒ No ☐

Can a set of elements to be determined be specified
(or does the program look for all elements in the region.)? Yes ☒* No ☐

*Users has to enter the elements to be fitted clicking on a periodic table.

What information is given in the report (peak areas and what kinds of associated uncertainties, concentrations and what kinds of associated uncertainties, what kind of detection limit)? There are two reports: short and full. The short report gives: the fitting region, begin and end channel, Chi-square, continuum type, and for each element, the name of the element, the line (Kα, Lα), the energy (keV), area, standard deviation and chi-square of the peak. Only info on so called "analytical" lines, Kα, Lα or Mα are given. The full report gives: fitting region, energy and resolution calibration (initial and estimated parameters), continuum parameters; and for each line used the element name, energy, peak position in channels, peak FWHM in eV, relative intensity of that line in the multiplet (line ratio corrected for absorption), peak area, its standard deviation, chi-square of the peak.

Is the quantification in terms of concentrations integrated with the fitting of the peaks or not?
Not integrated, only as a separate program and only for XRF (Fundamental parameters).

What ions can be used for excitation? In what energy ranges? Any information can be entered, but is not used explicitly.

Output possibilites/ report format? Short and full report. Saved as text or rich text format. Graphical output via Windows metafile format. Copy and past of all data between WinAxil and any other MS-Window application (Excel, Word...)

What spectrum file formats are accepted? Native WinAxil: *.WAX; DOS Axil: *.SPE; Canberra CAM: *.cnf; Nuclear Data Accuspec (*.dat); Canberra S100 (*.MCA); Ortec ACE (*.chn); Aptec Version 4.3 (*.s0); Tracor SpecTrace 5000; Nucleus (*.spm); PGT IMIX (*.spt); plain ascii (*.*).

Can spectra be manipulated (added, subtracted, filtered) and then saved to file again? No.

What QA/QC measures does the software take? Report of overall chi-square and chi-square per peak. In full output all estimated parameters and their uncertainty are listed. All data used to perform the fit as well as all relevant data on the sample and the measurement conditions are stored in the spectrum file (*.WAX) as well as all the results of the fit.

Is there on-line help? A manual? A web page? On-line help YES. Manual YES.

All data provided by: P. Van Espen, MiTAC, University of Antwerp, Antwerp, Belgium.

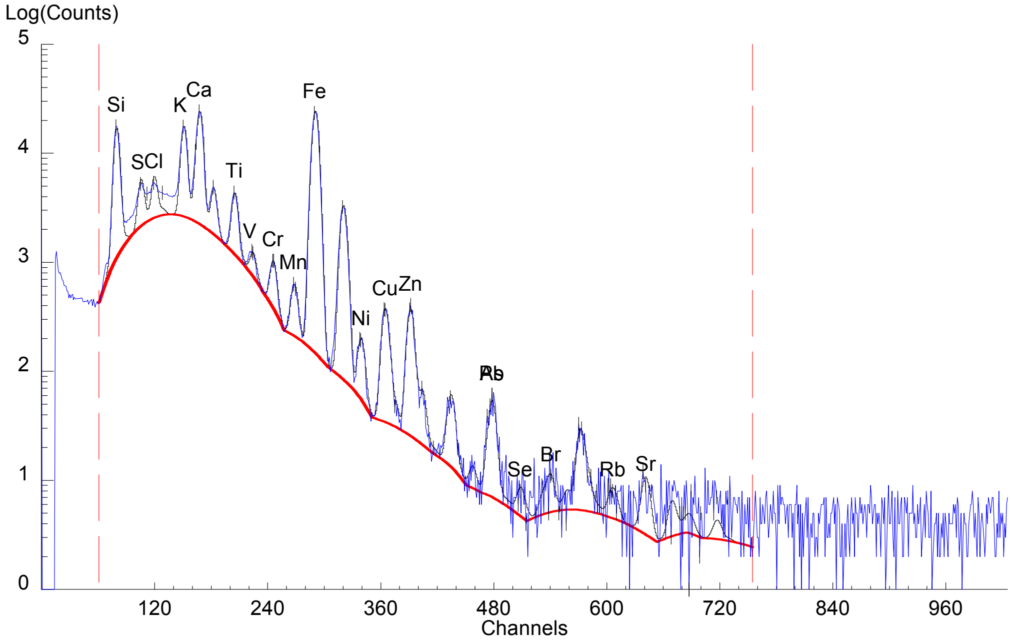

FIG. 21. WinAxil fit of the aero test spectrum by the Method 1.

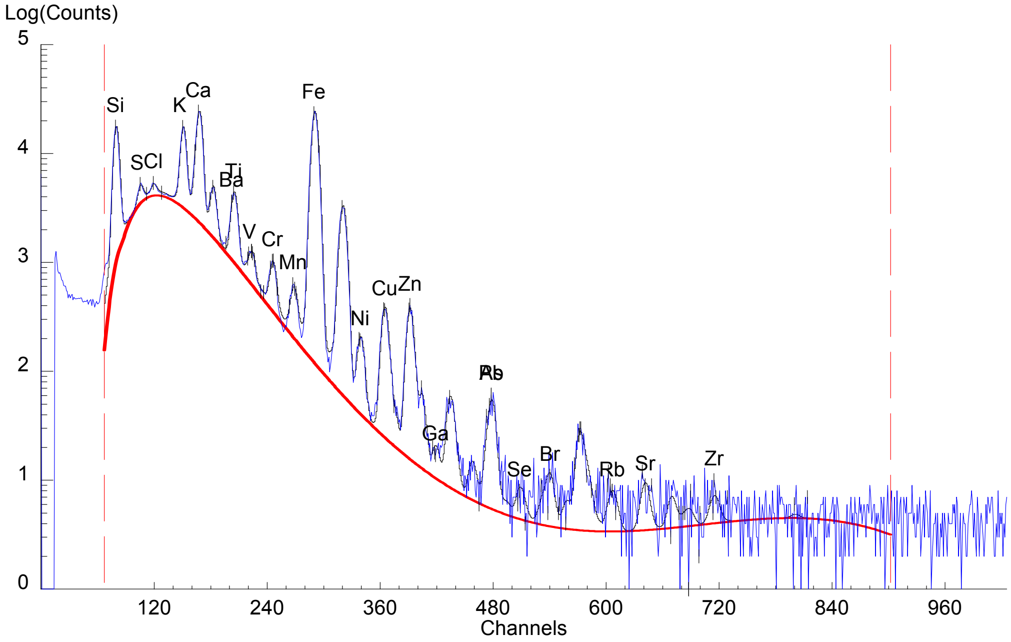

FIG. 22. WinAxil fit of the aero test spectrum by the Method 2.

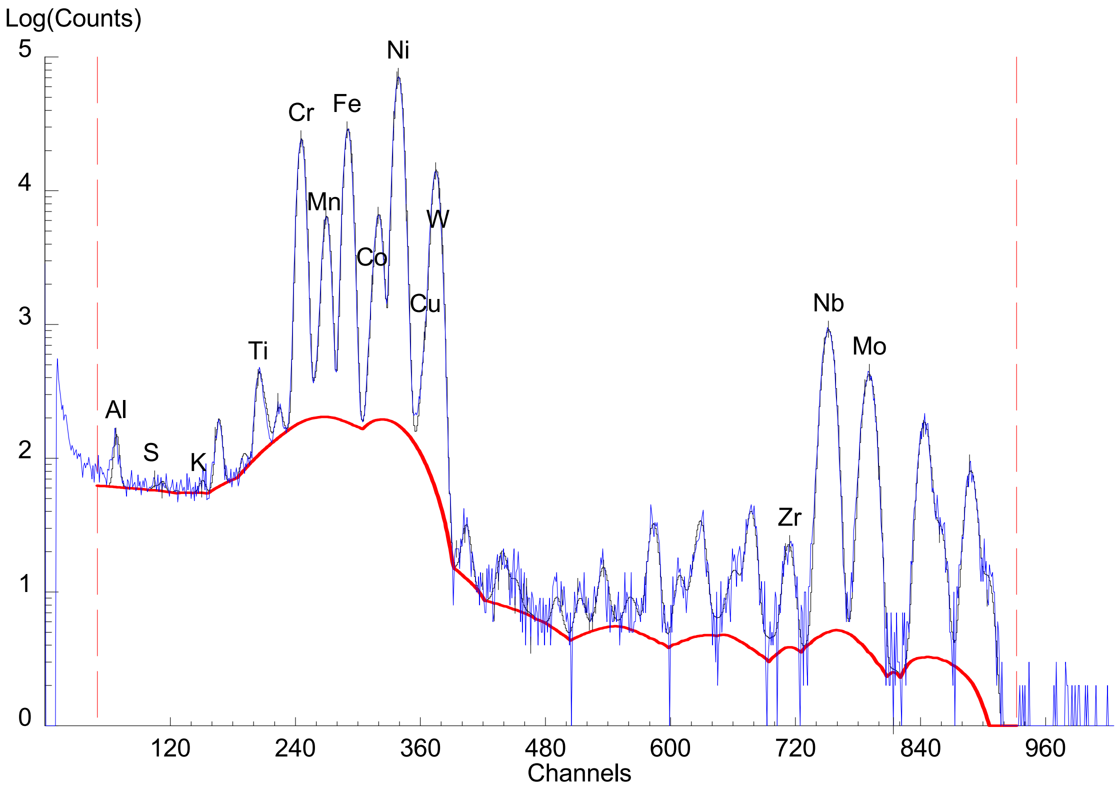

FIG. 23. WinAxil fit of the alloy test spectrum by the Method 1.

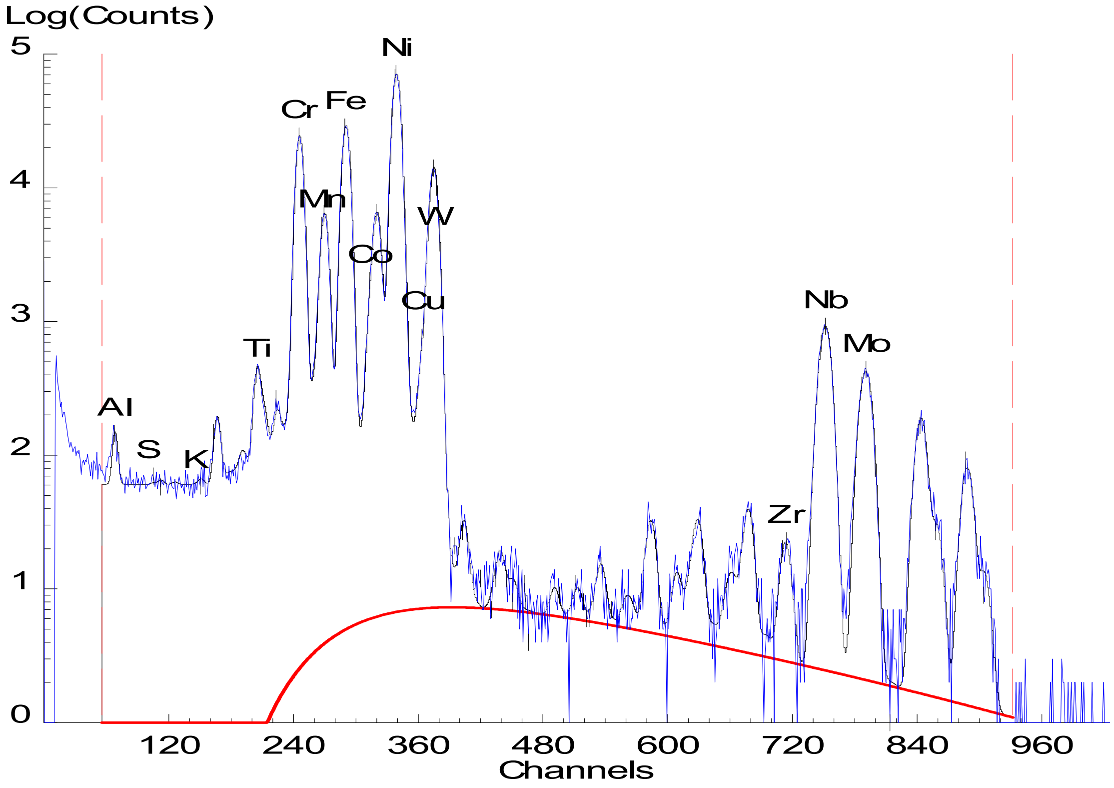

FIG. 24. WinAxil fit of the alloy test spectrum by the Method 2.

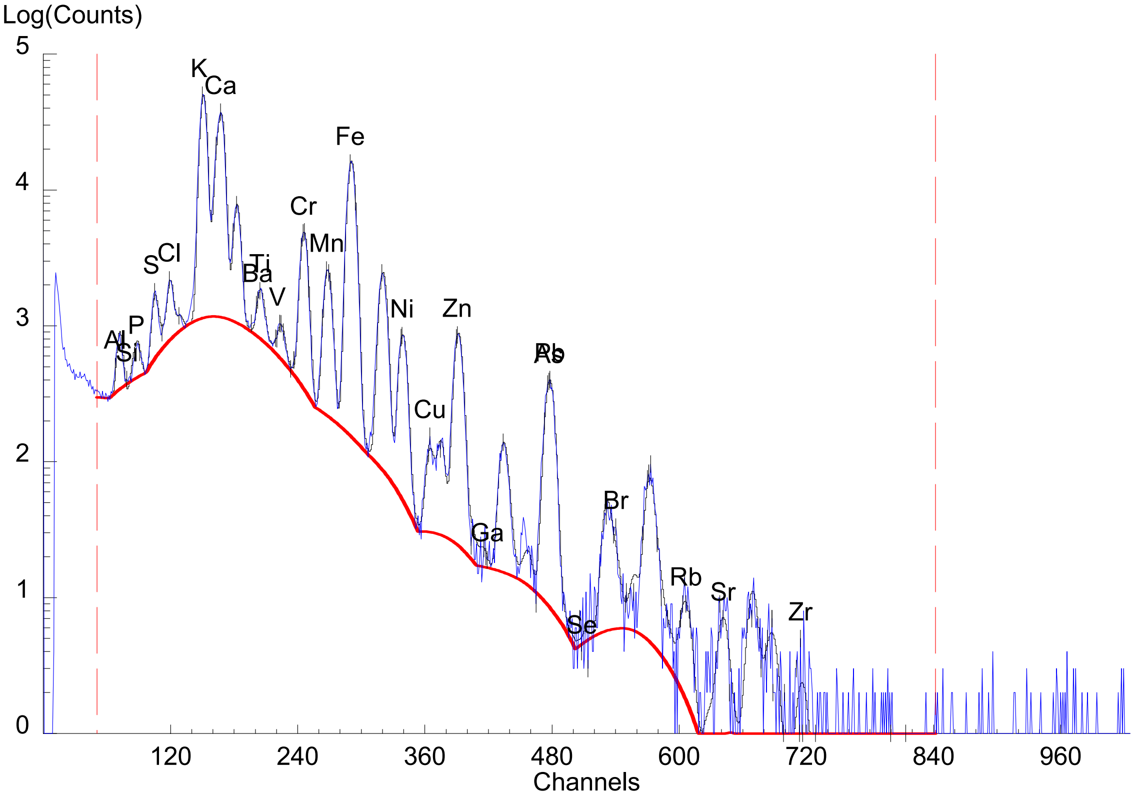

FIG. 25. WinAxil fit of the bio test spectrum by the Method 1.

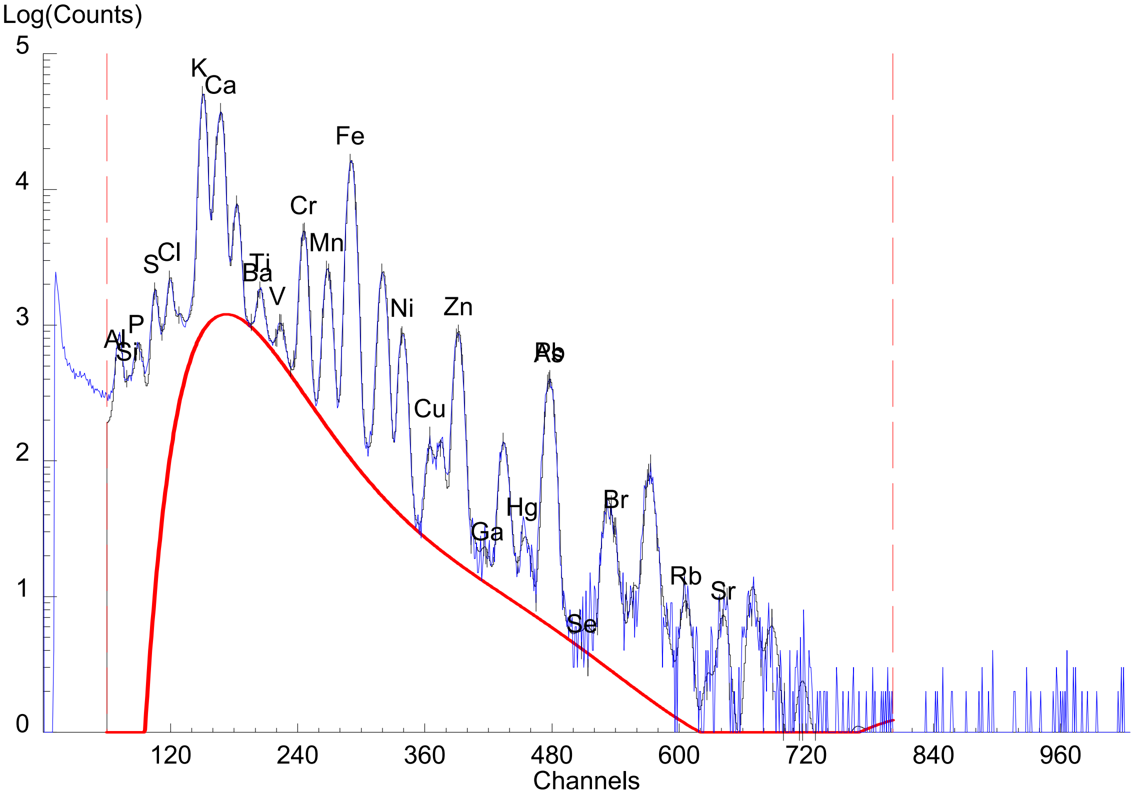

FIG. 26. WinAxil fit of the bio test spectrum by the Method 2.

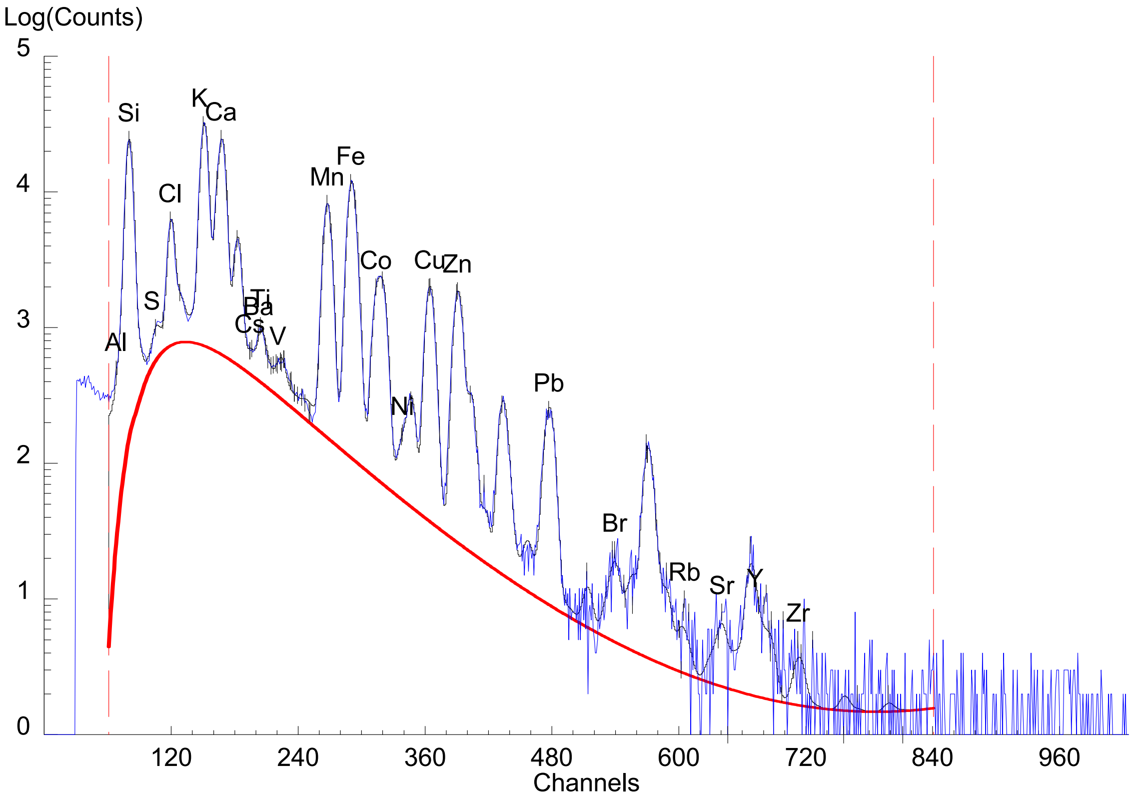

FIG. 27. WinAxil fit of the glass test spectrum by the Method 1.

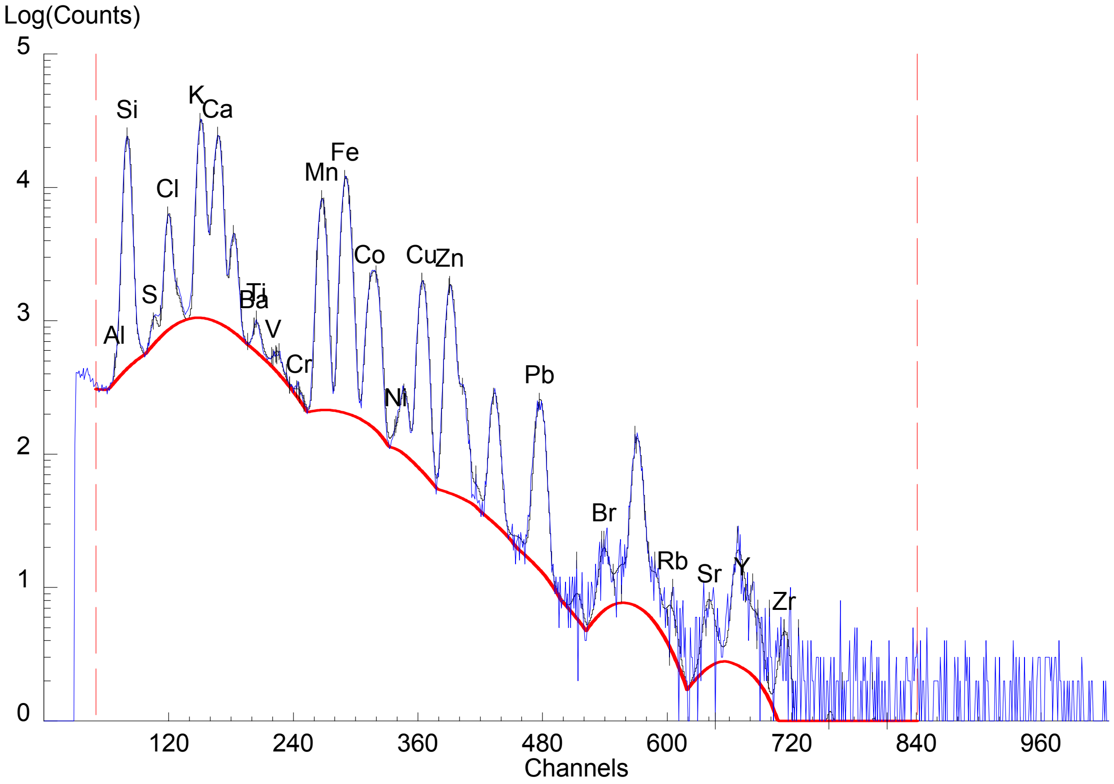

FIG. 28. WinAxil fit of the glass test spectrum by the Method 2.

4.7. WitsHex

What operating system/computer type does the software require? Windows or Dos.

Are graphical representations of spectra, fits, residuals, and calibrations available?

energy calibration	Yes ☐	No ☒	spectra	Yes ☒	No ☐
FWHM calibration	Yes ☐	No ☒	fits	Yes ☒	No ☐
efficiency calibration	Yes ☐	No ☒	residuals	Yes ☐	No ☒

What Graphics/Zoom/Color setting options are offered? Lots — full graphical display during fitting and complete log, square root or linear display of any part of the spectra post fitting, raw, background and fit displayed.

Are Kα, Kβ, etc. treated as singlets or as multiplets?
singlets ☐ multiplets ☒

Energy calibration: linear, quadratic, other…?
linear ☒ quadratic ☐ other ________________________________

What expression is used for FWHM calibration?
FWHM = a +Eb; a and b fitted parameters from user defined initial estimates.

What expression is used for efficiency calibration?
high energy → linear
low energy → parabolic

What expression is used for peak shape function?
Gaussian with low energy tail.

What phenomena are taken into account?

escape peaks	Yes ☒	No ☐	pile up treatment	Yes ☐	No ☒
radiative Auger	Yes ☐	No ☒	other satellites	Yes ☐	No ☒
exponential tails	Yes ☐	No ☒	If Yes, how many? _______________		
short steps	Yes ☐	No ☒	If Yes, how many? _______________		
shelf	Yes ☒	No ☐			

Are user-defined peak shapes allowed?
Yes ☐ No ☒

What fitting algorithm is used?
non-linear least squares ☐
Marquardt ☒
other ____

What background functions are used. User define functions possible?

- Rolling ball (Kneen, M. A., *Computational Aspects of Environmental Air Pollution Analysis, Data Handling and Interpretation*, Dissertation submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the Degree of Master of Science).
- Parabolic [37]
- Parameter — traditional HEX [38]
- User defined functions are not possible.

What matrix correction methods (thick target corrections for X ray intensities) are used? No thick target corrections currently operational.

What database of X ray line intensities is used? Library file protected from editing within the program can be edited in test editor if required.

- **Can the user edit that database?**
  Yes ☒ No ☐

What lines are available for analysis (K,L,M,...) for what atomic number ranges?
K lines → atomic number range: 6–46
L lines → atomic number range: 25–100
M lines → atomic number range: 57–100

What database is used for detection system efficiency computations? Calibration can be done automatically from standards.

- **Can the user edit that database?**
  Yes ☒ No ☐

Can a set of elements to be determined be specified
(or does the program look for all elements in the region)? Yes ☒ No ☐

What information is given in the report (peak areas and what kinds of associated uncertainties, concentrations and what kinds of associated uncertainties, what kind of detection limit). Full report includes: Fitting parameters, peak areas, peak transmissions, concentrations and errors — as proportion of concentration as well as mean detection limit for each element.

Is the quantification in terms of concentrations integrated with the fitting of the peaks? Yes.

What ions can be used for excitation? In what energy ranges? Protons normally using parameter driven backgrounds — others including electrons and X rays using "rolling ball" background.

Output possibilities/report formats? Three levels of text files including all or part of the complete list of possibilities.

What spectrum file formats are accepted? Only defined internal format. Details are given on how to create the required ASCII file.

Can spectra be manipulated (added, subtracted, filtered, ...) and then saved to file again? No. Please use excel or similar program.

What QA/QC measures does the software take? For example, does the program offer special options for handling reference material results, monitoring stability of time, etc.? Does it report χ_r^2 of fits, resolution parameters etc. that help in assessing the quality of the results? The program plots the fits as they are calculated so problems can be identified visually. It reports χ_r^2 of fits, and of each element fitted. Reference samples are used to calibrate the system and later samples can be used to check stability. Final fits, absolute and relative errors in those fits can be plotted after fitting is completed.

Is there on-line help? A manual? A web page? There is a manual and internal help file.

All data provided by: M. Kneen from University of Witwatersrand, Johannesburg, South Africa.

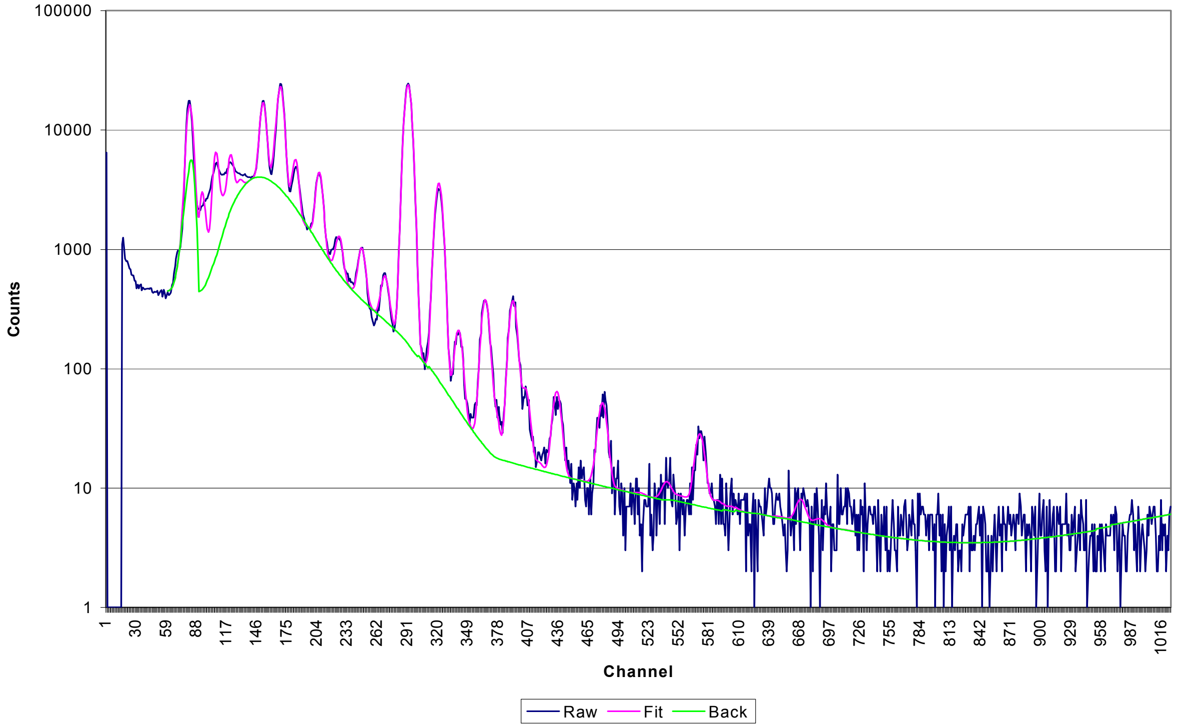

FIG. 29. Witshex fit of the aero test spectrum by using "parametric background"(Witshex1).

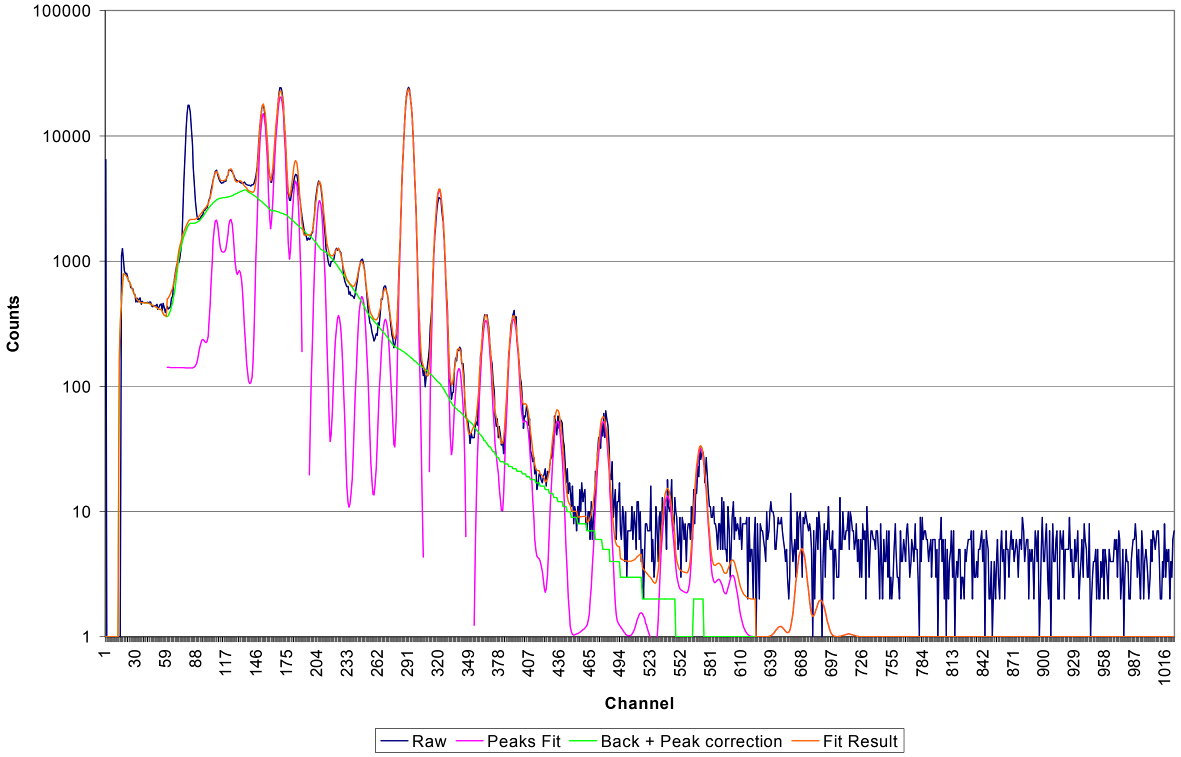

FIG. 30. Witshex fit of the aero test spectrum by using "rolling ball background"(Witshex2).

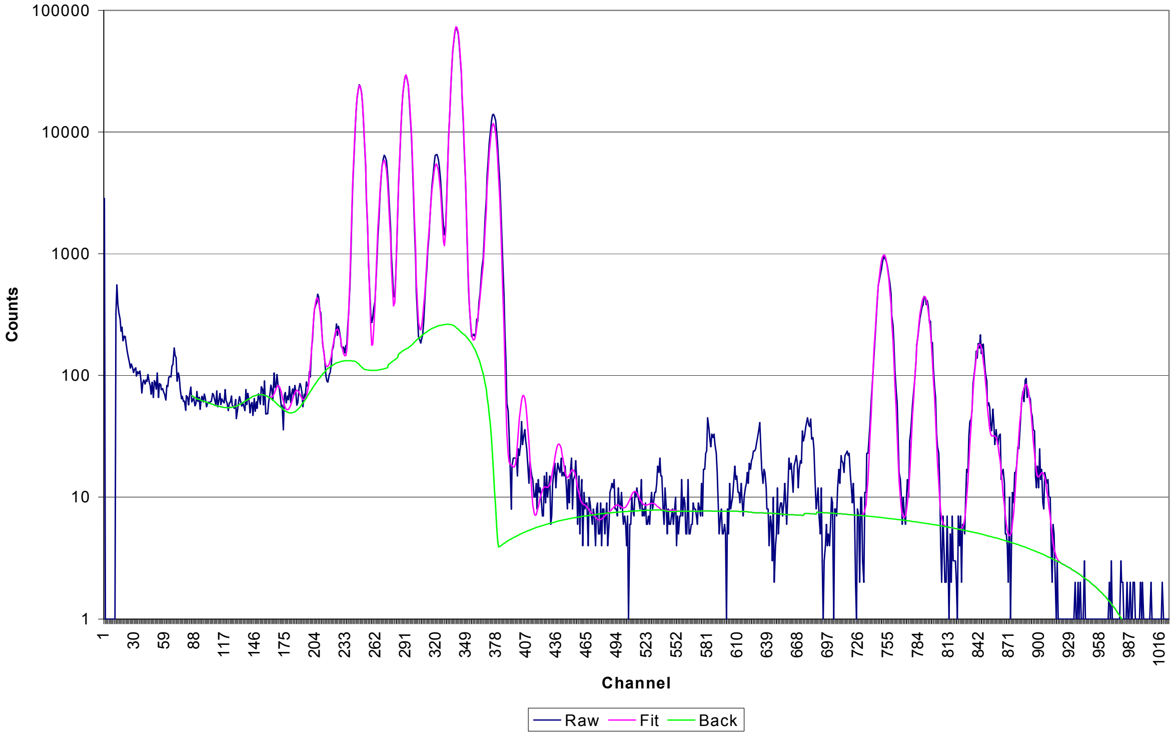

FIG. 31. Witshex fit of the alloy test spectrum by using "parametric background"(Witshex1).

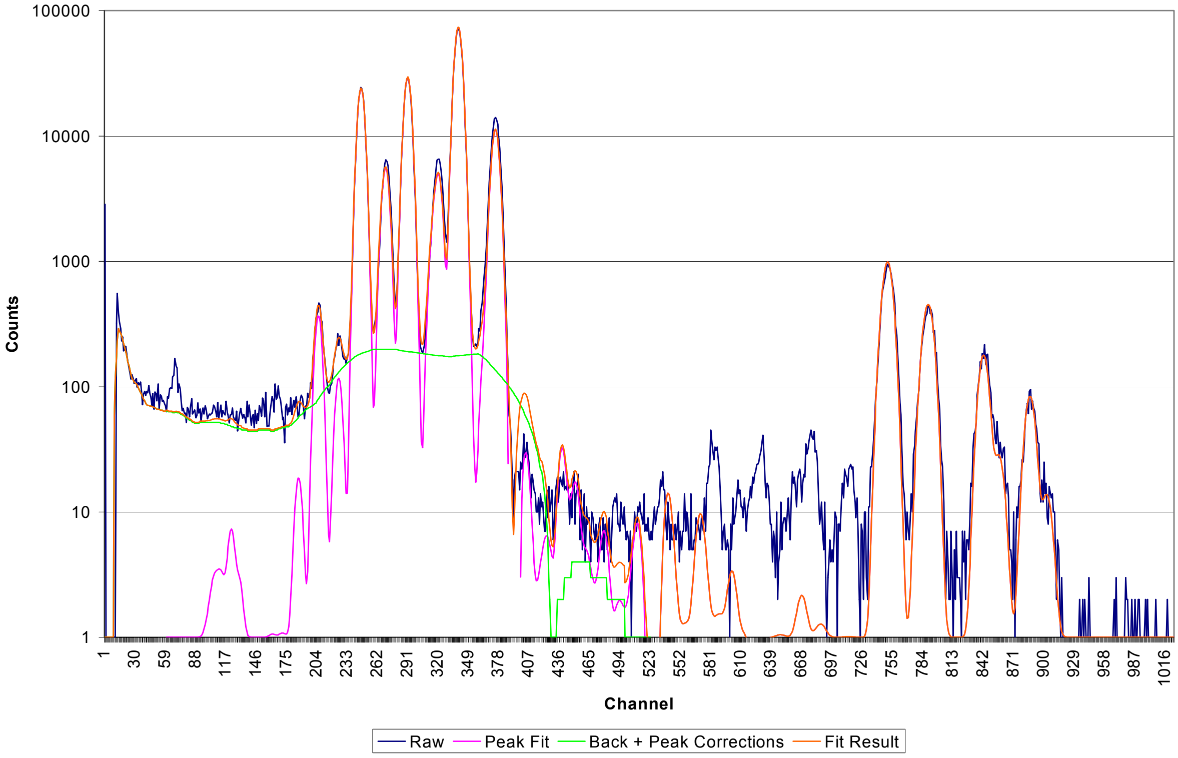

FIG. 32. Witshex fit of the alloy test spectrum by using "rolling ball background"(Witshex2).

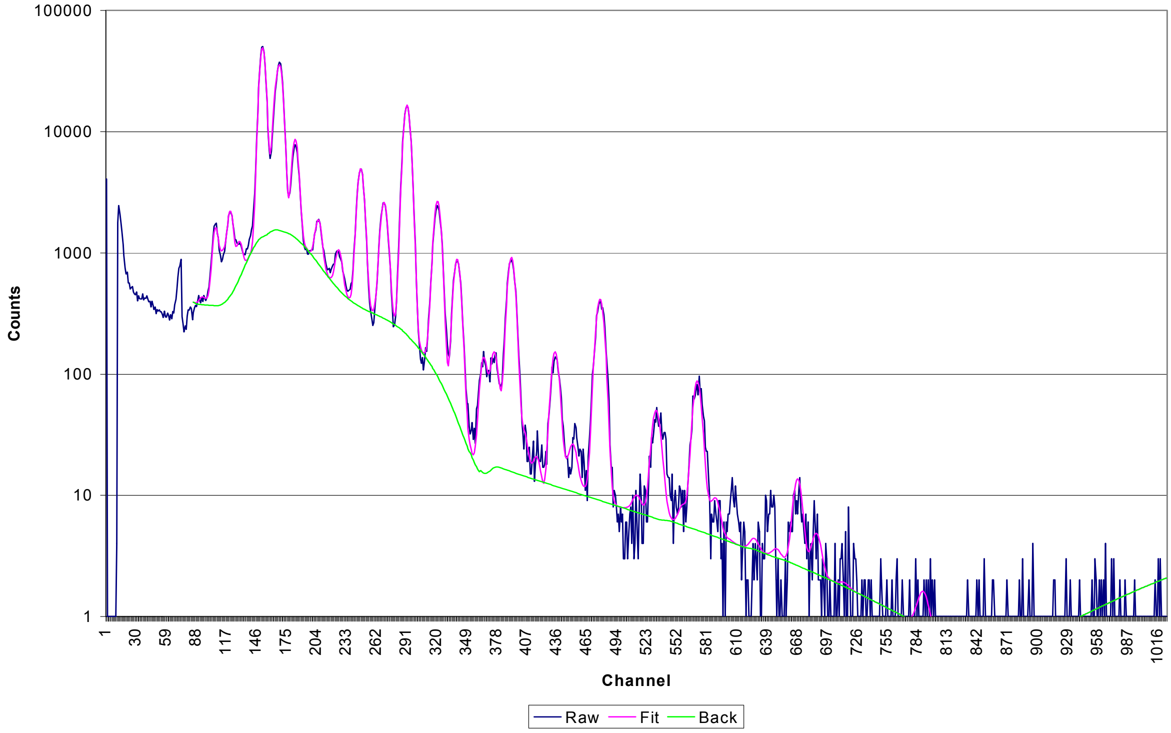

FIG. 33. Witshex fit of the bio test spectrum by using "parametric background"(Witshex1).

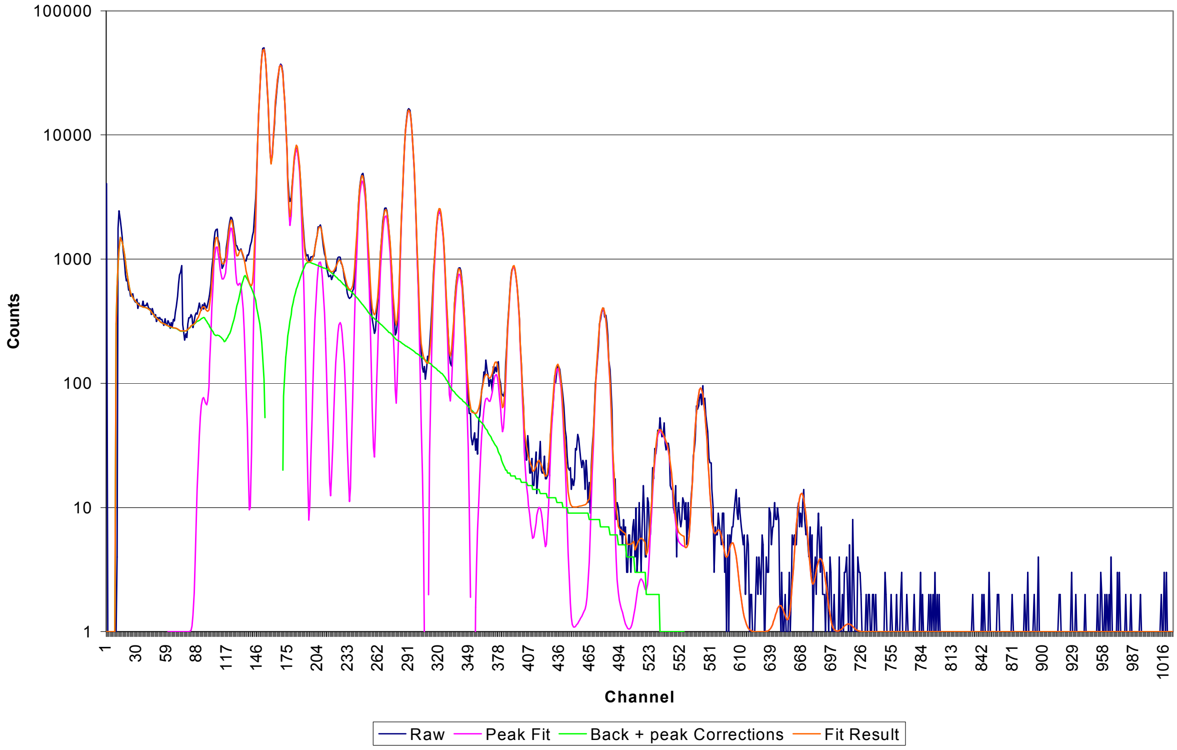

FIG. 34. Witshex fit of the bio test spectrum by using "rolling ball background"(Witshex2).

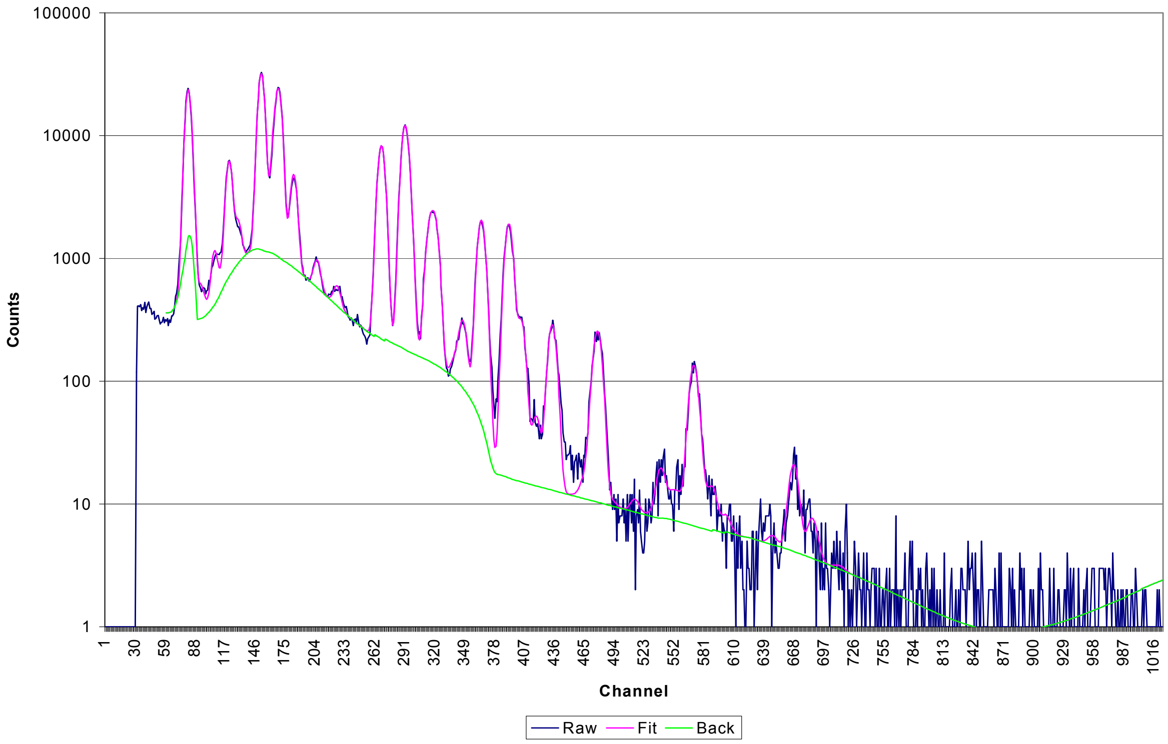

FIG. 35. Witshex fit of the glass test spectrum by using "parametric background"(Witshex1).

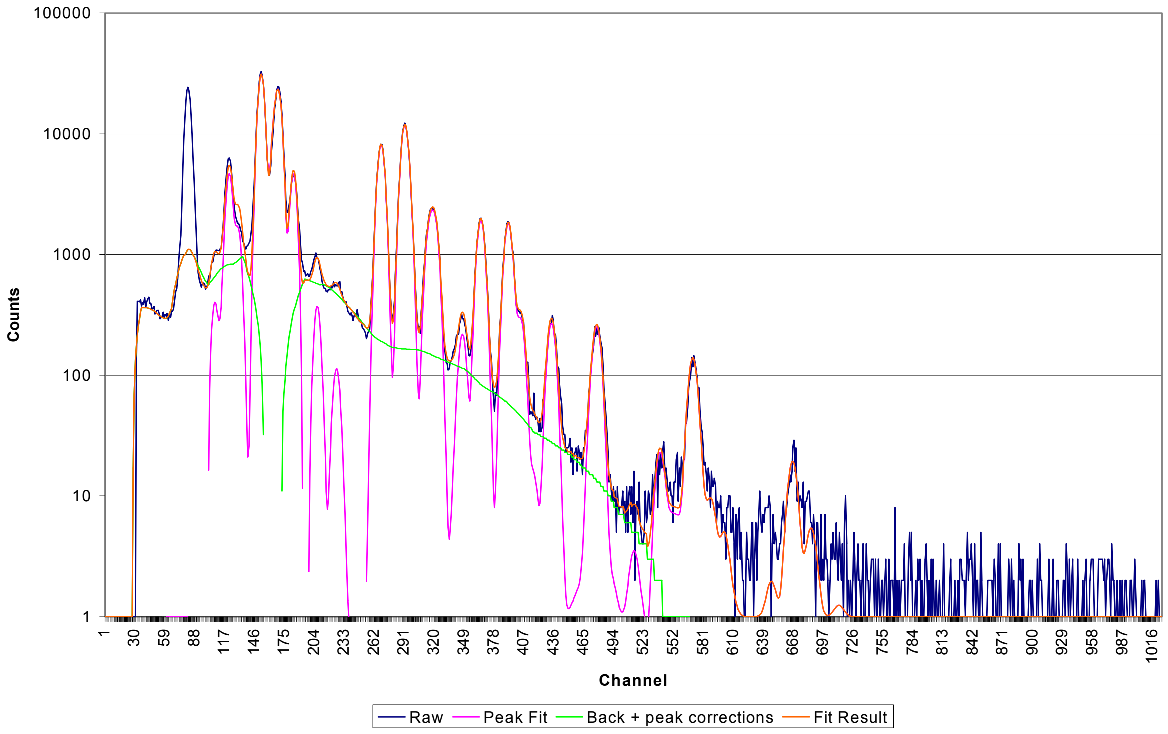

FIG. 36. Witshex fit of the glass test spectrum by using "rolling ball background"(Witshex2).

5. Results and discussion

Tables 3 through 6 show z_{rep} scores for all hits, as reported by the participating programs for all four test spectra. Tables 7 through 10 show corresponding z_{ref} scores. Tables 11 to 20 show the χ_r^2 values calculated by taking into consideration the corresponding z-scores. These tables will be used as a basis for further discussion related to the reported peak area ratios, related uncertainties and peak discrimination.

5.1. Peak area ratios

The intercomparison results of primary interest are, of course, the peak area ratios reported by the participating programs. Because of the inherent uncertertainties in the peak areas, a perfect match to the reference ratios cannot be expected and the results are tested in the statistical sense.

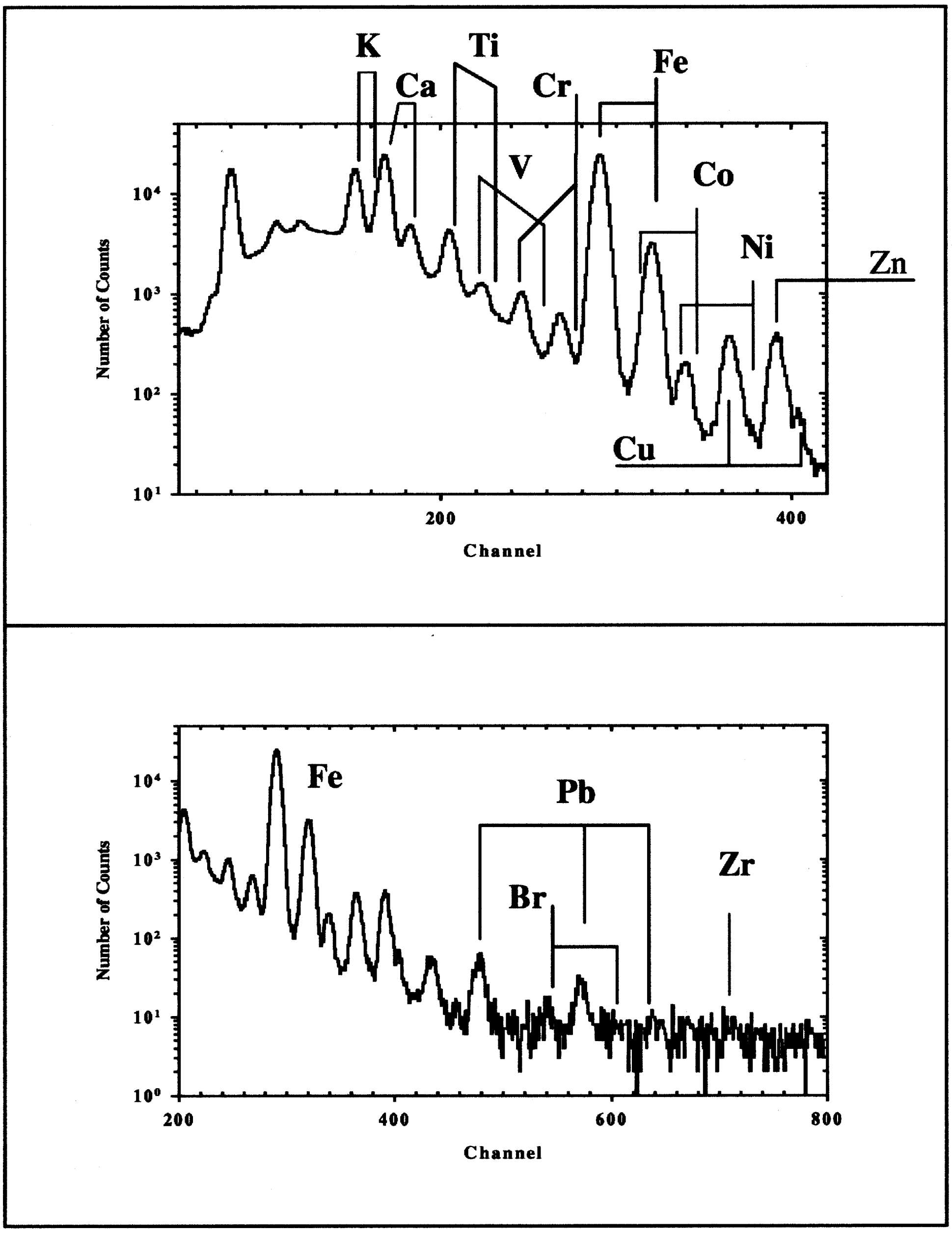

FIG. 37. The zoomed "Aero" test spectrum, showing X ray peak positions and intensities.

The “Aero” test spectrum has 8 high-precision and 10 low precision ratios. Table 3 shows that most of the ratios reported are not statistically different from the reference values. In case of the high-precision ratios, there is statistical disagreement between the Ca reported and reference value for most of the programs. The reason for observed differences may be due to the overlapping Ca-Kα and K-Kβ peaks with the high background in the area of these two peaks in the “Aero” test spectrum (see Figure 37). There is also a level of statistical disagreement between the Ni ratios. The reason may be due to the overlapping of Co-Kβ and Cu-Kα peaks. Among the low-precision ratios, three programs have not reported the V ratio and the others show statistical disagreement. The reason for this may be due to the peak overlaps between the Ti, V and Cr with the relatively high background. The peak area ratios for Co and Zr have been reported by only one program. A difficulty with the Co ratios may be due to the Fe, Co and Ni peak overlaps, while the Zr-Kα is very noisy peak, almost invisible.

The “Alloy” spectrum has 5 high-precision and 5 low precision ratios (two of them being dubious). All high-precision ratios reported by the participants are in relatively good statistical agreement with the reference values (Table 4). Regarding the low-precision ratios, two programs have not reported the W ratio, and one of the programs reported the ratio in statistical disagreement with the corresponding reference value. The reason for these problems may be in the W-Lα and Ni-Kβ peak overlap, the W-L$_l$ and Ni-Kα overlap, and interference of the W-Lβ/Lγ peaks with the pile-up area of the spectrum (between channels 420 and 550, see Figure 38). The two dubious ratios, for Mn and Cu, have not been reported by any program.

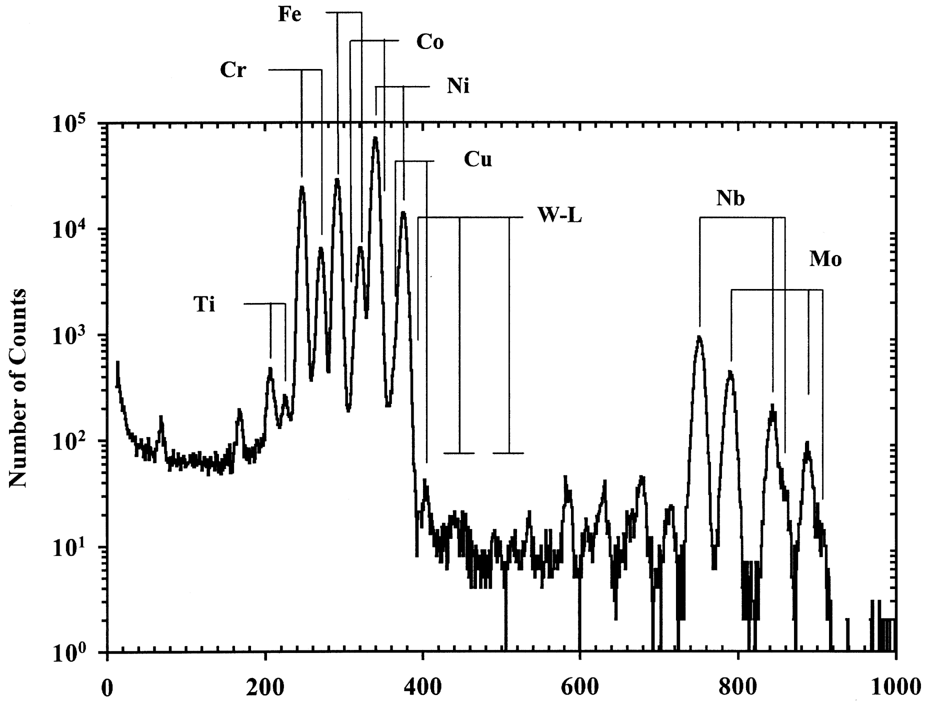

FIG. 38. The “Alloy” test spectrum, showing X ray peak positions and intensities.

The “Bio” spectrum has 9 high-precision and 10 low precision ratios (one of them being dubious). Table 5 shows good statistical agreement between reported and reference ratios for almost all the programs and the reported ratios. In case of the low-precision ratios, there is some statistical disagreement for the Br, Hg and Pb ratios (see Figure 39). Three programs have not reported the Hg peak ratio. In case of Br, it may be due to the Br-Kα overlap with the As-Kβ and Br-Kβ overlap with the Rb-Kα. In case of Pb, the Pb-Lα overlaps with the As-Kα. Regarding Hg, its Lα peak is in the noisy area between the Zn-Kβ and As-Kα peaks, and the group of its Lβ peaks overlap with the As-Kβ and Br-Kα.

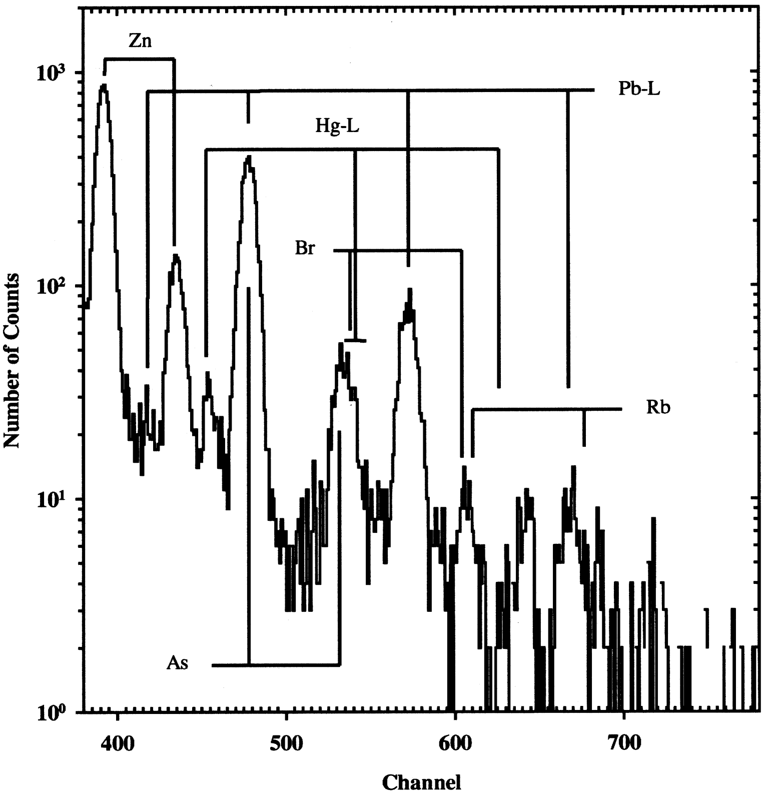

FIG. 39. The zoomed "Bio" test spectrum, showing X ray peak positions and intensities. The unmarked peaks round the channels 640 and 720 correspond to the Sr Kα and Kβ peaks respectively.

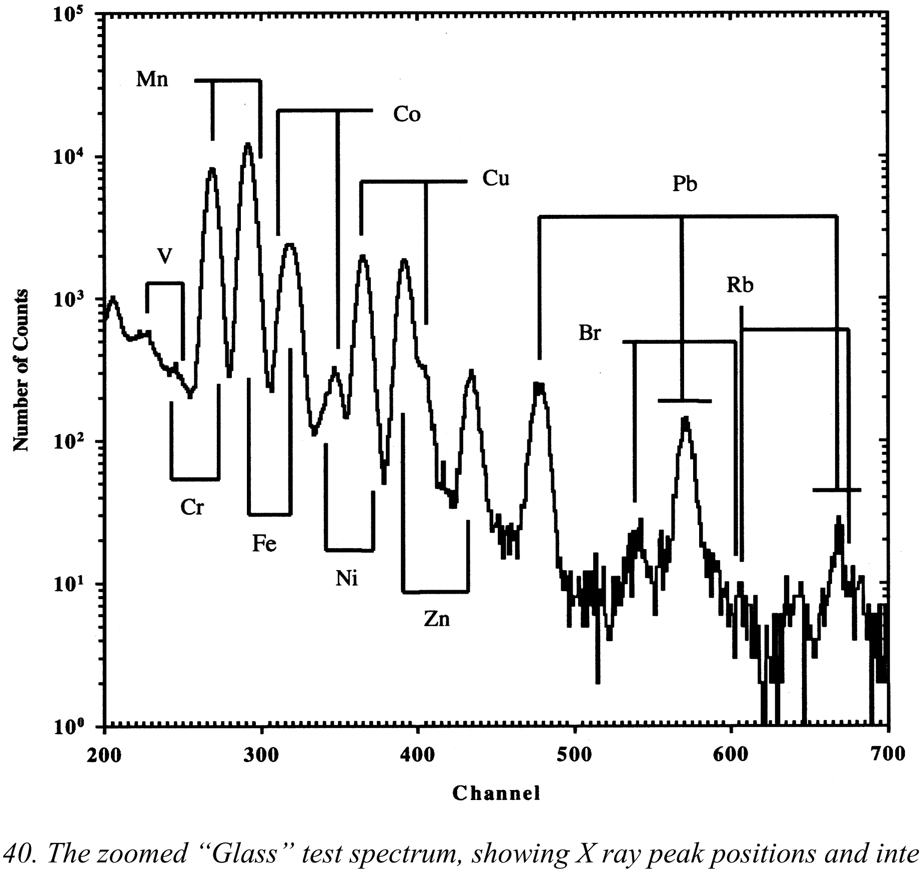

FIG. 40. The zoomed "Glass" test spectrum, showing X ray peak positions and intensities.

TABLE 3. z_{rep} SCORES FOR HITS RELATED TO AERO SPECTRUM. EMPTY CELL MEANS THAT THE PROGRAM WAS NOT REPORTING ANY PEAK (WHILE IT WAS REPORTED IN THE REFERENCE FILE). HIGH PRECISION RATIOS ARE MARKED WITH H RIGHT TO THE ELEMENT SYMBOL. LOW PRECISION RATIOS ARE MARKED WITH L.

	z_{rep}								
El	1	2	3	4	5	6	7	8	9
Si (H)	–1.3	0.3	–0.5	–0.4	0.7	1.4	1.6	–10.9	
S(L)	–0.6	–0.7	0.3	–2.1	0.9	6.3	–1.4	35.7	4.4
Cl(L)	–2.3	–0.8	1.9	–0.2	1.0	6.4	–2.3	21.7	6.2
K(H)	–2.1	0.2	–6.8	–1.0	2.5	10.4	3.7	–2.0	22.5
Ca(H)	–3.0	–0.2	–12.3	–6.0	1.1	5.4	5.8	–6.0	–15.4
Ti(L)	0.5	0.9	–0.4	–0.4	0.4	0.7	0.6	3.0	1.0
V(L)	–3.4		–5.3	–3.9				–5.3	
Cr(H)	0.9	0.4	–2.1	–1.3	–0.1	0.0	–1.6	–0.1	–4.5
Mn(L)	0.2	0.1	0.7	–0.6	–0.2	–0.2	–3.3	–4.8	–5.8
Fe(H)	0.2	–0.2	–2.9	0.6	0.5	–0.2	–1.0	–1.9	–5.3
Co(L)				0.8					
Ni(H)	–4.5	–2.9	–4.9	–1.7	–2.0	–3.6	–1.8	–1.7	–6.8
Cu(H)	–1.8	–1.5	–2.5	–0.2	0.0	–1.6	0.3	0.5	–2.6
Zn(H)	–0.4	0.4	–2.2	0.4	0.4	–0.8	1.0	0.7	–1.4
Br(L)	–0.4		–1.6	–0.6	–1.1		3.1	–2.7	3.9
Sr(L)	0.4		0.0	–0.1		2.3	1.4		
Zr(L)			0.6						
Pb(L)	0.4	0.4	–0.5	0.8	1.9	–2.8	–3.2	0.2	4.7

1=Geopixe, 2=Gupix, 3=Pixan, 4=Pixeklm, 5=Sapix, 6=Winaxil1, 7=Winaxil2, 8=Witshex1, 9=Witshex2.

TABLE 4. z_{rep} SCORES FOR HITS RELATED TO ALLOY SPECTRUM. EMPTY CELL MEANS THAT THE PROGRAM WAS NOT REPORTING ANY PEAK (WHILE IT WAS REPORTED IN THE REFERENCE FILE). DUBIOUS PEAKS ARE MARKED WITH *. HIGH PRECISION RATIOS ARE MARKED WITH H RIGHT TO THE ELEMENT SYMBOL. LOW PRECISION RATIOS ARE MARKED WITH L.

	z_{rep}								
El	1	2	3	4	5	6	7	8	9
Ti (L)	–3.2	0.2	–0.2	–3.4	–2.2	–2.5	–1.6	–0.1	1.1
Cr (H)	–1.0	–0.2	–0.6	–4.1	–1.3	–1.9	–0.8	5.9	5.3
*Mn (L)									
Fe (H)	–1.5	0.8	10.4	–1.6	0.6	–2.1	–0.5	8.8	10.1
Co (L)	–2.3	0.0		0.0	–1.7	0.5	0.9	1.7	4.2
Ni (H)	1.0	–0.1	6.2	1.5	0.8	0.7	0.9	3.9	4.3
*Cu (L)									
Nb (H)	–1.2	–1.9	–0.6	1.5	0.2	0.2	0.1	–0.9	0.1
Mo (H)	–0.6	–3.2	–1.5	–0.8	0.0	–0.3	–0.4	–2.5	–0.9
W (L)	–1.8		0.5	–0.1		–0.1	–0.2	5.5	–4.3

1=Geopixe, 2=Gupix, 3=Pixan, 4=Pixeklm, 5=Sapix, 6=Winaxil1, 7=Winaxil2, 8=Witshex1, 9=Witshex2

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TABLE 5. z_{rep} SCORES FOR HITS RELATED TO BIO SPECTRUM. EMPTY CELL MEANS THAT THE PROGRAM WAS NOT REPORTING ANY PEAK (WHILE IT WAS REPORTED IN THE REFERENCE FILE). DUBIOUS PEAK IS MARKED WITH *. HIGH PRECISION RATIOS ARE MARKED WITH H RIGHT TO THE ELEMENT SYMBOL. LOW PRECISION RATIOS ARE MARKED WITH L.

	z_{rep}								
El	1	2	3	4	5	6	7	8	9
S (L)	1.1	–0.2	–2.5	–2.7	–0.9	–1.9	1.9	1.9	2.5
Cl (L)	0.9	1.4	0.0	–1.8	–0.6	–1.3	2.1	3.4	4.2
K (H)	1.3	0.2	4.6	1.2	2.4	2.1	1.4	4.2	10.4
Ca (H)	1.4	0.9	24.6	–1.2	0.8	0.9	0.3	–4.5	12.4
Ti (L)	1.2	0.4	–1.8	–1.4	–0.3	–0.1	–1.1	1.1	0.2
V (L)	0.7	–0.4	0.2	–0.2		–0.2	0.7	2.7	–3.4
Cr (H)	–2.3	2.0	–2.4	–1.0	1.6	1.2	3.7	0.8	–1.8
Mn (H)	–1.9	–1.7	–2.1	–1.7	–3.5	–1.2	0.6	–10.1	–9.3
Fe (H)	–1.1	–0.3	–0.7	0.8	2.4	–1.5	–0.5	–4.7	–2.1
*Co (L)									
Ni (H)	–1.5	–0.3	–4.1	–0.7	–0.4	–1.3	0.0	–1.3	–5.3
Cu (H)	–2.6	0.1	–3.3	0.2	–2.3	–1.6	–0.7	2.4	–7.0
Zn (H)	–0.1	–1.4	–1.3	0.0	0.8	–0.8	1.1	–1.0	0.6
As (H)	0.7	0.2		0.2	–1.3	4.3	4.6	0.2	–1.3
Br (L)	–1.6	1.7	–0.3		3.8	0.3	–0.4		6.2
Rb (L)	0.6	0.1	–0.3	–0.1	1.6	–0.7	–0.2		
Sr (L)	–0.2	1.0	–1.3	–0.2	–0.7	–0.3	–0.3		
Hg (L)	2.2				3.7		–0.6	–0.5	
Pb (L)	–7.7	–1.5	–1.9	–0.5	1.3	–9.0	–8.5	–1.8	1.6

1=Geopixe, 2=Gupix, 3=Pixan, 4=Pixeklm, 5=Sapix, 6=Winaxil1, 7=Winaxil2, 8=Witshex1, 9=Witshex2.

TABLE 6. z_{rep} SCORES FOR HITS RELATED TO GLASS SPECTRUM. EMPTY CELL MEANS THAT THE PROGRAM WAS NOT REPORTING ANY PEAK (WHILE IT WAS REPORTED IN THE REFERENCE FILE). HIGH PRECISION RATIOS ARE MARKED WITH H RIGHT TO THE ELEMENT SYMBOL. LOW PRECISION RATIOS ARE MARKED WITH L.

	z_{rep}								
El	1	2	3	4	5	6	7	8	9
Si (H)	–0.3	0.0	0.3	0.0	1.9	–0.7	–0.1	3.1	
S (L)	2.6	–0.2	1.3		0.5	2.3	–0.3	13.9	5.2
Cl (H)	2.4	0.4	0.9	0.3	1.9	2.9	2.2	3.2	–3.8
K (H)	1.1	–0.8	–3.3	–0.7	–0.7	1.2	0.6	6.6	15.0
Ca (H)	1.7	–0.8	2.8	–1.1	2.2	–0.4	2.8	4.0	–3.5
Ti (L)	–0.2	2.2	–1.9	–0.8	–1.1	–0.6	0.6	1.5	3.1
V (L)	2.3		1.8	2.2		2.4	1.1	3.9	–4.3
Cr (L)		0.4	–1.1		1.4				
Mn (H)	–1.9	–0.6	–1.2	–1.8	–2.8	–2.0	–1.5	–0.7	0.9
Fe (H)	0.2	1.6	3.5	2.6	0.1	–1.1	1.1	1.9	1.4
Co (H)	–2.7	–2.5	1.6	0.6	–2.8	–3.1	0.2	–2.2	–7.2
Ni (L)	–3.5	–0.5	–1.7	–0.2	–4.7	–3.9	2.8	–2.9	–10.5
Cu (H)	–3.0	–2.7	–3.0	–1.9	–3.5	–2.9	0.3	–0.5	–4.4
Zn (H)	–0.7	–0.1	–0.8	–0.2	–1.5	–0.5	2.0	3.4	–2.5
Br (L)	0.6	–0.5	0.5	1.6	–2.2	–0.3	–0.7	–0.6	4.5
Rb (L)			–2.2						
Sr (L)	–0.1	–0.3	–0.8	–1.1	–0.2	0.3			
Pb (L)	–0.3	–0.9	–0.7	0.7	0.6	0.2	0.8	0.7	2.0

1=Geopixe, 2=Gupix, 3=Pixan, 4=Pixeklm, 5=Sapix, 6=Winaxil1, 7=Winaxil2, 8=Witshex1, 9=Witshex2.

TABLE 7. z_{ref} SCORES FOR HITS RELATED TO AERO SPECTRUM. HIGH PRECISION RATIOS ARE MARKED WITH H RIGHT TO THE ELEMENT SYMBOL. LOW PRECISION RATIOS ARE MARKED WITH L.

	z_{ref}								
El	1	2	3	4	5	6	7	8	9
Si (H)	–0.5	0.1	–0.2	–0.1	0.2	0.7	0.5	–3.6	–15.8
S(L)	–0.2	–0.3	0.1	–0.8	0.3	5.2	–0.5	11.8	1.4
Cl(L)	–0.8	–0.3	0.6	–0.1	0.3	6.3	–0.8	7.2	2.0
K(H)	–1.3	0.1	–2.8	–0.5	2.2	7.6	1.9	–0.8	8.5
Ca(H)	–2.9	–0.1	–5.8	–2.9	1.4	5.3	2.7	–2.7	–6.5
Ti(L)	0.2	0.3	–0.1	–0.1	0.2	0.3	0.2	1.0	0.3
V(L)	–1.8	–2.9	–2.5	–1.6	–2.9	–2.9	–2.9	–1.9	–2.9
Cr(H)	0.7	0.3	–2.0	–1.3	–0.1	0.0	–1.6	–0.1	–3.2
Mn(L)	0.1	0.1	0.3	–0.3	–0.1	–0.1	–1.7	–1.9	–2.2
Fe(H)	0.2	–0.1	–1.5	0.3	0.4	–0.2	–0.5	–0.9	–2.6
Co(L)	–2.4	–2.4	–2.4	0.7	–2.4	–2.4	–2.4	–2.4	–2.4
Ni(H)	–3.9	–2.6	–5.0	–2.5	–1.5	–4.3	–1.8	–1.3	–4.7
Cu(H)	–0.9	–0.8	–1.2	–0.1	0.0	–0.9	0.2	0.2	–1.1
Zn(H)	–0.4	0.3	–1.6	0.3	0.3	–0.9	1.1	0.5	–0.9
Br(L)	–0.5	–4.0	–1.6	–0.6	–0.7	–4.0	0.2	–2.1	2.9
Sr(L)	0.6	–3.5	0.0	–0.2	–3.5	3.3	1.9	–3.5	–3.5
Zr(L)	–1.7		0.7	–1.7	–1.7	–1.7	–1.7	–1.7	–1.7
Pb(L)	0.5	0.4	–0.3	0.6	1.2	–1.9	–1.7	0.1	2.9

1=Geopixe, 2=Gupix, 3=Pixan, 4=Pixeklm, 5=Sapix, 6=Winaxil1, 7=Winaxil2, 8=Witshex1, 9=Witshex2.

TABLE 8. z_{ref} SCORES FOR HITS RELATED TO ALLOY SPECTRUM. DUBIOUS PEAKS ARE MARKED WITH *. HIGH PRECISION RATIOS ARE MARKED WITH H RIGHT TO THE ELEMENT SYMBOL. LOW PRECISION RATIOS ARE MARKED WITH L.

	Z_{ref}								
El	1	2	3	4	5	6	7	8	9
Ti (L)	–1.5	0.1	–0.1	–1.4	–0.8	–1.0	–0.7	0.0	0.4
Cr (H)	–0.7	–0.1	–0.2	–1.5	–0.5	–0.8	–0.3	2.1	1.9
*Mn (L)									
Fe (H)	–0.9	0.7	4.3	–0.7	0.3	–1.0	–0.2	3.5	4.1
Co (L)	–1.0	0.0	–3.2	0.0	–0.6	0.2	0.3	0.6	1.4
Ni (H)	0.3	0.0	2.0	0.5	0.3	0.2	0.3	1.2	1.4
*Cu (L)									
Nb (H)	–0.5	–0.8	–0.2	0.6	0.1	0.1	0.0	–0.3	0.0
Mo (H)	–0.3	–1.5	–0.6	–0.4	0.0	–0.1	–0.2	–1.0	–0.4
W (L)	–0.8	–2.6	2.7	–0.1	–2.6	–0.1	–0.1	2.9	–1.4

1=Geopixe, 2=Gupix, 3=Pixan, 4=Pixeklm, 5=Sapix, 6=Winaxil1, 7=Winaxil2, 8=Witshex1, 9=Witshex2.

TABLE 9. z_{ref} SCORES FOR HITS RELATED TO BIO SPECTRUM. DUBIOUS PEAK IS MARKED WITH *. HIGH PRECISION RATIOS ARE MARKED WITH H RIGHT TO THE ELEMENT SYMBOL. LOW PRECISION RATIOS ARE MARKED WITH L.

	z_{ref}								
El	1	2	3	4	5	6	7	8	9
S (L)	0.4	–0.1	–0.8	–0.9	–0.3	–0.6	0.6	0.6	0.8
Cl (L)	0.3	0.6	0.0	–0.6	–0.2	–0.4	0.7	1.1	1.3
K (H)	0.4	0.1	1.5	0.4	0.8	0.7	0.4	1.4	3.3
Ca (H)	0.7	0.5	8.6	–0.5	0.4	0.4	0.1	–1.5	4.2
Ti (L)	0.4	0.1	–0.6	–0.5	–0.1	–0.0	–0.4	0.4	0.1
V (L)	0.3	–0.1	0.1	–0.1	–2.3	–0.1	0.2	0.9	–1.1
Cr (H)	–1.9	2.3	–2.0	–0.8	1.3	1.1	2.8	0.6	–1.4
Mn (H)	–1.3	–1.5	–1.4	–1.3	–3.5	–0.8	0.4	–6.5	–5.9
Fe (H)	–1.0	–0.2	–0.4	0.4	1.3	–0.9	–0.3	–2.4	–1.1
*Co (L)									
Ni (H)	–1.0	–0.2	–2.9	–0.6	–0.2	–1.6	0.0	–0.8	–3.2
Cu (H)	–2.3	0.1	–2.6	0.2	–1.5	–1.6	–0.6	1.5	–4.1
Zn (H)	–0.1	–1.1	–0.9	0.0	0.6	–0.5	0.9	–0.7	0.4
As (H)	0.7	0.2	–22.6	0.1	–2.1	5.3	5.4	0.1	–1.0
Br (L)	–1.6	1.8	–0.3	–4.0	3.0	0.4	–0.5	–4.0	4.3
Rb (L)	0.5	0.2	–0.2	–0.1	1.1	–0.6	–0.2	–3.2	–3.2
Sr (L)	–0.1	0.9	–0.9	–0.1	–0.5	–0.3	–0.3	–3.5	–3.5
Hg (L)	2.2	–3.2	–3.2	–3.2	2.3	–3.2	–0.3	–0.3	–3.2
Pb (L)	–3.1	–0.8	–0.8	–0.3	0.8	–3.6	–3.2	–0.7	0.7

1=Geopixe, 2=Gupix, 3=Pixan, 4=Pixeklm, 5=Sapix, 6=Winaxil1, 7=Winaxil2, 8=Witshex1, 9=Witshex2.

TABLE 10. z_{ref} SCORES FOR HITS RELATED TO GLASS SPECTRUM. HIGH PRECISION RATIOS ARE MARKED WITH H RIGHT TO THE ELEMENT SYMBOL. LOW PRECISION RATIOS ARE MARKED WITH L.

	z_{ref}								
El	1	2	3	4	5	6	7	8	9
Si (H)	–0.1	0.0	0.1	0.0	0.6	–0.3	0.0	1.0	–24.3
S (L)	1.2	–0.1	0.4	–2.0	0.2	1.2	–0.2	4.7	1.7
Cl (H)	0.9	0.2	0.3	0.1	0.7	1.0	0.9	1.1	–1.2
K (H)	0.5	–0.4	–1.2	–0.3	–0.4	0.5	0.3	2.4	5.4
Ca (H)	1.5	–0.6	1.3	–0.7	2.1	–0.2	1.5	1.8	–1.5
Ti (L)	–0.1	0.9	–0.7	–0.3	–0.4	–0.2	0.2	0.6	1.1
V (L)	5.0	–5.3	2.0	3.0	–5.3	2.7	2.1	3.4	–3.4
Cr (L)	–1.1	0.2	–0.6	–1.1	0.8	–1.1	–1.1	–1.1	–1.1
Mn (H)	–1.0	–0.2	–0.5	–0.7	–1.0	–0.8	–0.6	–0.3	0.3
Fe (H)	0.3	1.3	2.2	1.7	0.1	–0.7	1.0	1.2	0.9
Co (H)	–6.6	–4.9	3.0	1.3	–4.4	–5.2	0.4	–3.2	–9.6
Ni (L)	–3.1	–0.4	–2.4	–0.4	–3.2	–3.5	2.1	–2.2	–6.4
Cu (H)	–1.4	–1.2	–1.2	–0.8	–1.4	–1.3	0.1	–0.2	–1.7
Zn (H)	–0.6	0.0	–0.5	–0.2	–0.9	–0.5	1.8	1.9	–1.4
Br (L)	0.4	–0.3	0.3	1.1	–1.2	–0.2	–0.6	–0.3	2.3
Rb (L)	–1.4	–1.4	–1.0	–1.4	–1.4	–1.4	–1.4	–1.4	–1.4
Sr (L)	–0.1	–0.3	–0.5	–0.9	–0.3	0.2	–2.6	–2.6	–2.6
Pb (L)	–0.1	–0.4	–0.3	0.3	0.4	0.1	0.3	0.3	0.7

1=Geopixe, 2=Gupix, 3=Pixan, 4=Pixeklm, 5=Sapix, 6=Winaxil1, 7=Winaxil2, 8=Witshex1, 9=Witshex2.

TABLE 11. "AERO" SAMPLE χ^2 RESULTS. THE NUMBER OF HIGH-PRECISION RATIOS IN THE REFERENCE LIST IS 8, OF LOW-PRECISION RATIOS 10.

	aero-high_prec			low_prec			all_matches			false_hits		misses	
	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	χ_r^2	N	χ_r^2
Geopixe	8	5.0	3.4	8	2.3	0.6	16	3.7	2.0	1	4.0	2	4.4
Gupix	8	1.4	1.0	5	0.4	0.1	13	1.0	0.6			5	9.0
Pixan	8	30.9	9.5	9	3.9	1.1	17	16.6	5.0	3	1.3	1	5.9
Pixeklm	8	5.2	2.1	9	2.4	0.5	17	3.7	1.3			1	2.9
Sapix	8	1.5	1.2	6	1.2	0.4	14	1.4	0.8			4	7.4
Winaxil	8	19.5	13.4	6	15.8	13.6	14	17.9	13.5			4	8.2
Winaxil2	8	7.2	2.3	7	4.4	1.5	15	5.9	2.0	2	14.6	3	5.7
Witshex	8	20.9	3.0	7	259	28.9	15	132	15.1	1	13500	3	7.1
Witshex2	7	122	22.0	6	21.5	4.7	13	75.3	14.0	1	28.5	5	55.9

TABLE 12. "AERO" SAMPLE χ^2 RESULTS WITH THRESHOLD UNCERTAINTY SET TO 1 %.

	aero-high_prec			low_prec			all_matches			false_hits		misses	
	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	χ_r^2	N	χ_r^2
Geopixe	8	4.3	2.3	8	2.3	0.6	16	3.3	1.5	1	4.0	2	4.4
Gupix	8	1.4	1.0	5	0.4	0.1	13	1.0	0.6			5	9.0
Pixan	8	11.7	4.9	9	3.9	1.1	17	7.6	2.9	3	1.3	1	5.9
Pixeklm	8	1.6	1.1	9	2.4	0.5	17	2.1	0.8			1	2.9
Sapix	8	1.3	0.5	6	1.2	0.4	14	1.2	0.5			4	7.4
Winaxil	8	14.4	5.6	6	15.8	13.6	14	15.0	9.0			4	8.2
Winaxil2	8	3.0	1.2	7	4.4	1.5	15	3.7	1.3	2	14.6	3	5.7
Witshex	8	16.5	2.0	7	260	28.9	15	130	14.6	1	13500	3	7.1
Witshex2	7	48.9	9.2	6	21.5	4.7	13	36.3	7.1	1	28.5	5	55.9

TABLE 13. "ALLOY" SAMPLE X^2 RESULTS. THE NUMBER OF HIGH-PRECISION RATIOS IN THE REFERENCE LIST IS 5, OF LOW-PRECISION RATIOS 4, WHERE 2 OF THE LATTER WERE FLAGGED AS UNCERTAIN.

	alloy-high_prec			low_prec			all_matches			false_hits		misses	
	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	χ_r^2	N	χ_r^2
Geopixe	5	1.3	0.3	3	6.4	1.2	8	3.2	0.7				
Gupix	5	2.9	0.7	2	0.0	0.0	7	2.1	0.5			1	6.9
Pixan	5	29.8	4.5	2	0.1	3.6	7	21.3	4.3	3	10.8	1	10.0
Pixeklm	5	4.8	0.7	3	3.9	0.7	8	4.5	0.7				
Sapix	5	0.6	0.1	2	4.0	0.5	7	1.5	0.2			1	6.9
Winaxil	5	1.7	0.3	3	2.2	0.4	8	1.9	0.3				
Winaxil2	5	0.4	0.1	3	1.2	0.2	8	0.7	0.1				
Witshex	5	26.8	3.9	3	10.9	2.9	8	20.8	3.6	3	30.9		
Witshex2	5	30.0	4.5	3	12.5	1.3	8	23.4	3.3	3	95.4		

TABLE 14. "ALLOY" SAMPLE X^2 RESULTS WITH THRESHOLD UNCERTAINTY SET TO 1 %.

	alloy-high_prec			low_prec			all_matches			false_hits		misses	
	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	χ_r^2	N	χ_r^2
Geopixe	5	0.8	0.1	3	6.4	1.2	8	2.9	0.5				
Gupix	5	2.8	0.6	2	0.0	0.0	7	2.0	0.4			1	6.9
Pixan	5	10.4	1.1	2	0.1	3.6	7	7.5	1.8	3	10.8	1	10.0
Pixeklm	5	1.7	0.2	3	3.9	0.7	8	2.5	0.4				
Sapix	5	0.2	0.0	2	4.0	0.5	7	1.3	0.2			1	6.9
Winaxil	5	0.4	0.0	3	2.2	0.4	8	1.1	0.2				
Winaxil2	5	0.2	0.0	3	1.2	0.2	8	0.6	0.1				
Witshex	5	7.3	0.8	3	10.9	2.9	8	8.6	1.6	3	30.9		
Witshex2	5	7.0	0.7	3	12.5	1.3	8	9.0	1.0	3	95.4		

TABLE 15. "BIO" SAMPLE χ^2 RESULTS. THE NUMBER OF HIGH-PRECISION RATIOS IN THE REFERENCE LIST IS 9, OF LOW-PRECISION RATIOS 10.

	bio-high_prec			low_prec			all_matches			false_hits		misses	
	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	χ_r^2	N	χ_r^2
Geopixe	9	2.5	1.5	9	7.9	2.0	18	5.2	1.8				
Gupix	9	1.1	1.1	8	1.0	0.6	17	1.1	0.9			1	10.0
Pixan	8	83.4	12.4	8	1.9	0.3	16	42.6	6.4	4	3.2	2	260
Pixeklm	9	0.9	0.4	7	1.9	0.2	16	1.3	0.3			2	12.8
Sapix	9	3.9	2.6	8	4.3	2.1	17	4.0	2.4	1	8.8	1	5.1
Winaxil	9	3.7	4.1	8	10.8	1.7	17	7.1	3.0			1	10.0
Winaxil2	9	4.4	4.2	9	9.2	1.3	18	6.8	2.8	1	114		
Witshex	9	19.0	6.3	6	4.5	0.5	15	13.2	4.0	2	26.1	3	12.7
Witshex2	9	48.3	10.5	6	12.6	3.8	15	34.0	7.8	1	96.7	3	10.8

TABLE 16. "BIO" SAMPLE χ^2 RESULTS WITH THRESHOLD UNCERTAINTY SET TO 1 %.

	bio-high_prec			low_prec			all_matches			false_hits		misses	
	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	χ_r^2	N	χ_r^2
Gupix	9	0.7	0.2	8	1.0	0.6	17	0.9	0.4			1	10.0
Witshex	9	12.0	2.3	6	4.5	0.5	15	9.0	1.6	2	26.1	3	12.7
Witshex2	9	33.5	5.9	6	12.6	3.8	15	25.2	5.0	1	96.7	3	10.8
Sapix	9	2.8	1.3	8	4.3	2.1	17	3.5	1.7	1	8.8	1	5.1
Pixeklm	9	0.6	0.1	7	1.9	0.2	16	1.1	0.2			2	12.8
Geopixe	9	1.8	0.8	9	7.9	2.0	18	4.8	1.4				
Pixan	8	37.7	5.2	8	1.9	0.3	16	19.8	2.8	4	3.2	2	260
Winaxil	9	3.3	3.7	8	10.8	1.7	17	6.9	2.8			1	10.0
Winaxil2	9	3.2	3.4	9	9.2	1.3	18	6.2	2.3	1	114		

TABLE 17. "GLASS" SAMPLE χ^2 RESULTS. THE NUMBER OF HIGH-PRECISION RATIOS IN THE REFERENCE LIST IS 9, OF LOW-PRECISION RATIOS 9.

	glass-high_prec			low_prec			all_matches			false_hits		Misses	
	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	χ_r^2	N	χ_r^2
Geopixe	9	3.4	5.5	7	3.6	5.2	16	3.5	5.4			2	1.5
Gupix	9	2.0	3.1	7	0.9	0.2	16	1.5	1.8			2	14.8
Pixan	9	5.0	2.1	9	2.1	1.4	18	3.6	1.8	3	1.9		
Pixeklm	9	1.7	0.7	6	1.6	1.9	15	1.7	1.2			3	2.3
Sapix	9	4.7	3.2	7	4.3	1.8	16	4.6	2.6	1	24.5	2	14.8
Winaxil	9	3.8	3.5	7	3.8	3.0	16	3.8	3.3			2	1.5
Winaxil2	9	2.3	0.9	6	1.8	1.6	15	2.1	1.1			3	3.3
Witshex	9	11.2	3.0	6	36.8	6.6	15	21.4	4.4	2	360.5	3	3.3
Witshex2	8	41.4	16.4	6	31.5	10.4	14	37.1	13.8			4	150

TABLE 18. "GLASS" SAMPLE χ^2 RESULTS WITH THRESHOLD UNCERTAINTY SET TO 1 %.

	glass-high_prec			low_prec			all_matches			false_hits		Misses	
	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	χ_r^2	N	χ_r^2
Geopixe	9	2.7	0.7	7	3.6	5.2	16	3.1	2.7			2	1.5
Gupix	9	1.5	0.3	7	0.9	0.2	16	1.2	0.3			2	14.8
Pixan	9	2.0	0.3	9	2.1	1.4	18	2.1	0.8	3	1.9		
Pixeklm	9	0.8	0.1	6	1.6	1.9	15	1.1	0.8			3	2.3
Sapix	9	3.4	0.5	7	4.3	1.8	16	3.8	1.1	1	24.5	2	14.8
Winaxil	9	3.0	0.5	7	3.8	3.0	16	3.3	1.6			2	1.5
Winaxil2	9	1.2	0.2	6	1.8	1.6	15	1.5	0.8			3	3.3
Witshex	9	4.6	0.6	6	36.8	6.6	15	17.5	3.0	2	360.5	3	3.3
Witshex2	8	13.9	1.9	6	31.5	10.4	14	21.5	5.5			4	150

TABLE 19. ALL SAMPLES COMBINED χ^2 RESULTS. THE NUMBER OF HIGH-PRECISION RATIOS IN THE REFERENCE LIST IS 31, OF LOW-PRECISION RATIOS 34 (THREE OF THEM BEING DUBIOUS AND NOT CONSIDERED).

	High_prec			low_prec			all_matches			false_hits		Misses	
	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	χ_r^2	N	χ_r^2
Geopixe	31	3.2	3.0	27	5.0	2.3	58	4.0	2.7	1	4.0	4	3.0
Gupix	31	1.7	1.6	22	0.7	0.3	53	1.3	1.0	0		9	10.2
Pixan	30	36.9	7.2	28	2.5	1.1	58	20.3	4.3	13	4.2	4	134
Pixeklm	31	2.9	1.0	25	2.2	0.8	56	2.6	0.9	0		6	5.9
Sapix	31	3.0	2.0	23	3.5	1.4	54	3.2	1.8	2	16.7	8	8.9
Winaxil	31	7.5	5.7	24	8.9	4.9	55	8.1	5.4	0		7	6.5
Winaxil2	31	3.9	2.1	25	5.1	1.3	56	4.4	1.7	3	47.6	6	4.5
Witshex1	31	18.5	4.1	22	95.3	11.5	53	50.3	7.2	8	1800	9	7.7
Witshex2	29	60.9	13.9	21	20.5	5.6	50	43.9	10.4	5	82.3	12	76.1

TABLE 20. ALL SAMPLE χ^2 RESULTS COMBINED WITH THRESHOLD UNCERTAINTY SET TO 1 %.

	alloy-high_prec			low_prec			all_matches			false_hits		Misses	
	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	$\chi_{r,rep}^2$	$\chi_{r,ref}^2$	N	χ_r^2	N	χ_r^2
Geopixe	31	2.5	1.0	27	5.0	2.3	58	3.7	1.7	1	4.0	4	3.0
Gupix	31	1.5	0.5	22	0.7	0.3	53	1.2	0.4	0	1.0	9	10.2
Pixan	30	15.5	3.0	28	2.5	1.1	58	9.2	2.1	13	4.2	4	134
Pixeklm	31	1.1	0.4	25	2.2	0.8	56	1.6	0.6	0	1.0	6	5.9
Sapix	31	2.2	0.7	23	3.5	1.4	54	2.7	1.0	2	16.7	8	8.9
Winaxil	31	5.6	2.7	24	8.9	4.9	55	7.1	3.7	0	1.0	7	6.5
Winaxil2	31	2.1	1.4	25	5.1	1.3	56	3.5	1.3	3	47.6	6	4.5
Witshex	31	10.3	1.5	22	95.3	11.5	53	45.6	5.7	8	1798.3	9	7.7
Witshex2	29	27.2	4.7	21	20.5	5.6	50	24.5	5.0	5	82.3	12	76.1

The "Glass" spectrum has 9 high-precision and 9 low precision ratios. Table 6 shows relatively good statistical agreement between the reported and the reference values for all the high precision peak area ratios except for the Cu ratios. It is not clear why disagreement for the Cu ratios exists, since the Cu-Kα is a clear, high intensity peak (see Figure 40). Its Kβ peak slightly overlaps with the Zn-Kα but this does not seem to be a problem. Regarding the low-precision ratios, the Rb ratio has been reported by only one program. The Rb-Kα is a very low intensity peak close to the high energy side of the group of the higher intensity Pb-Lβ lines. V and Cr ratios were not reported by two (four) programs. Their corresponding peaks are very small and on the relatively high background. The V-Kβ overlaps with the Cr-Kα, and Cr-Kβ is almost lost in the very high intensity Mn-Kα peak. Results for the Ni ratios indicate a level of statistical disagreement between the reported and the reference values. The small Ni-Kα and Co-Kβ peaks are between the high intensity Co-Kα and Cu-Kα peaks. The Ni-Kβ peak is almost lost in the very high intensity Cu-Kα peak.

To test the quality of peak area ratio determination $\chi_{\mathrm{r,ref}}^2$ -values were computed from all z_{ref} scores for all matches in the four test spectra. The calculated z_{ref} scores for all elements and all four test spectra are given in Tables 7–10. Corresponding $\chi_{\mathrm{r,ref}}^2$ -values may be found in Tables 11, 13, 15, and 17. Tables 12, 14, 16 and 18 also show the corresponding χ^2 –values, but calculated by setting the threshold uncertainties to 1%. As expected, a better agreement between the reported and reference ratios is obtained in this case. However, as one may see comparing the tables, the general trend is the same. The results summed for all test spectra are given in Table 19 (while Table 20 gives similar results based on threshold uncertainties set to 1%). The final results for $\chi_{\mathrm{r,ref}}^2$ –values, extracted from Table 19, are shown in Figure 41. In principle: the lower the result, the better. Results smaller than 1 are not expected.

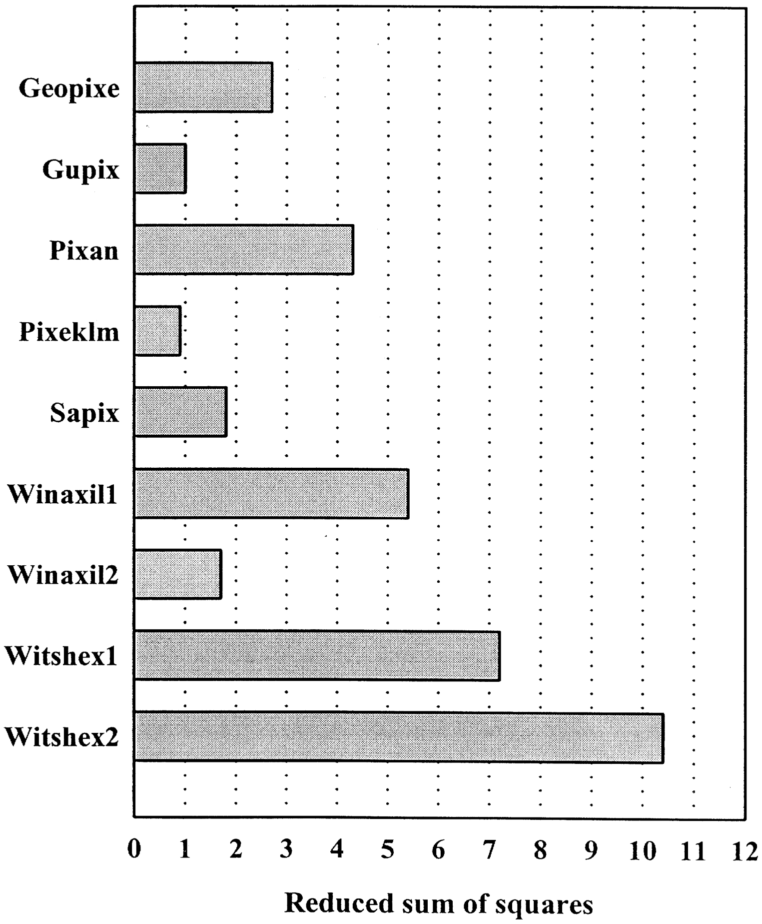

FIG.41. $\chi_{r,ref}^2$ — values, computed from all z_{ref} scores for all matches in four test spectra.

5.2. Uncertainties

Except for a very rare exception z_{ref} scores are smaller than the corresponding z_{rep} scores (see Tables 3–6 and compare them with Tables 7–10). As a consequence, almost all the $\chi_{r,ref}^2$ -values are lower than the corresponding $\chi_{r,rep}^2$-values (see Tables 11–20), indicating that participants reported smaller uncertainties in their results than would have been expected from the reference ratio uncertainty values.

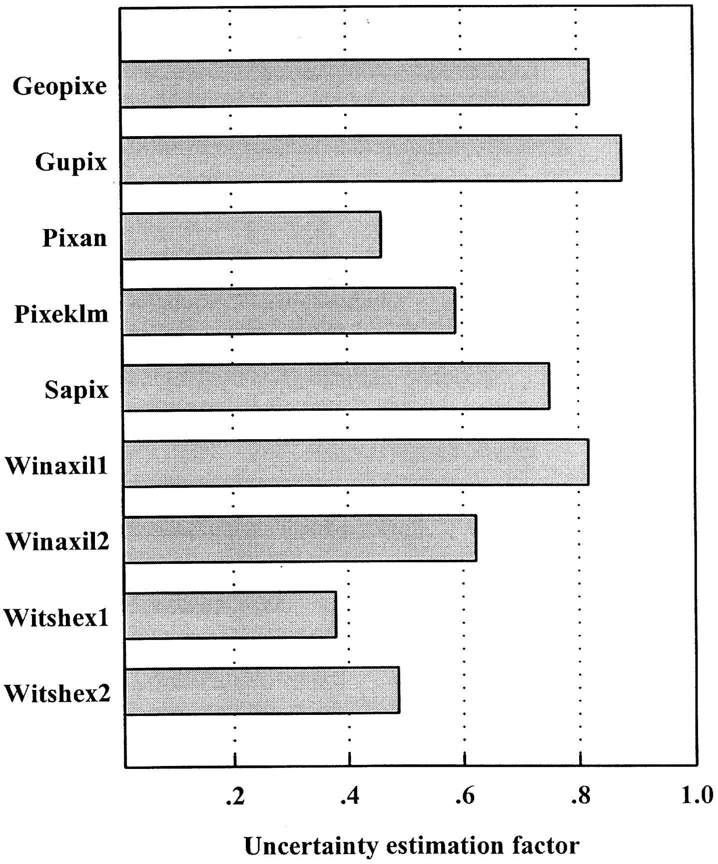

FIG. 42. Estimation of uncertainties. The ideal program would score a factor 1.0. Factor higher than 1 indicates overestimation of uncertainties, and factor lower than 1 indicates underestimation of uncertainties.

The reference ratio uncertainties were not obtained in a rigorous manner and in most cases were estimated on the safe side, i.e. overestimated a little. Still, in most cases, the $\chi_{r,rep}^2$ are much larger than unity, indicating that the reported uncertainties are too small because the reported area ratios did not agree with the reference area ratios to within 1 standard deviation as reported, on average. Uncertainty underestimation factors were therefore computed from the square roots of the combined ratios $\chi_{r,ref}^2/\chi_{r,rep}^2$ for all samples. The results are shown in Figure 42. These underestimation factors appear to be in a reasonable range: Typically, the programs appear to underestimate by a factor of 2. However, taking into account that the reference uncertainties were probably overestimated, the underestimation by the programs is worse than Figure 42 would suggest.

5.3. Peak discrimination

An analysis program is not only expected to report good peak area ratios and uncertainties — it is also expected to report as many as possible without reporting peaks that are not actually present in the spectra. And if a program reports a peak area of a peak that is not really present, it should at least report it with a suitably high uncertainty.

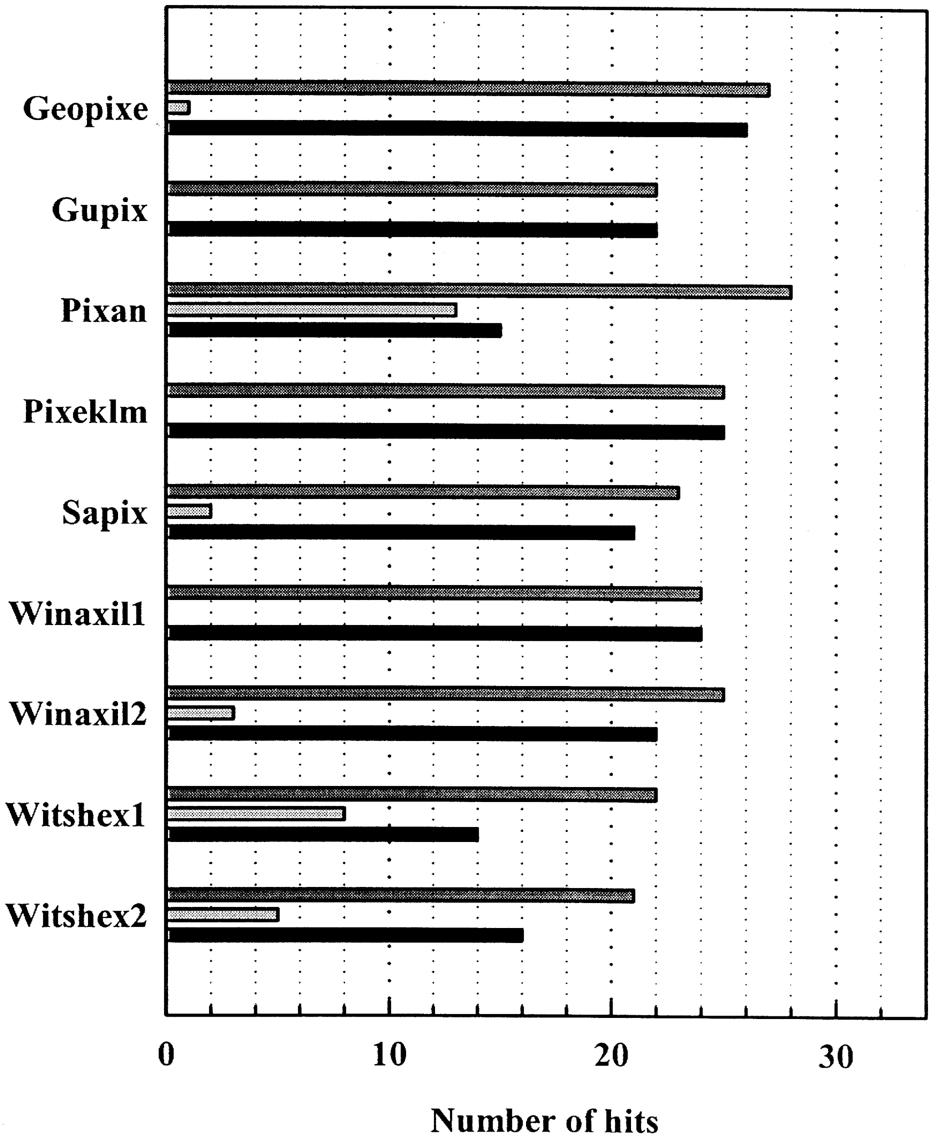

FIG. 43. Peak discrimination ability. The ideal program would detect all 34 low-precision peaks (or 31 if the three dubious peaks from the reference lists are excluded) and report no false hits. Top bar shows number of low-precision peak area ratios reported by the programs. Central bar shows number of "false hits". The third bar shows the difference between the low-precision reported ratios and number of reported "false hits".

As a measure of the ability to distinguish peaks from noise, the difference between the number of detected low-precision peak area ratios and the number of false hits was computed for each program and all samples. The results are shown in Figure 43. In ideal case all 34 low precision peaks (or 31 if we exclude three dubious peaks from the reference lists) would be detected and no false hits reported. In the process of PIXE spectra analysis, during the preparatory stage all X ray peaks to be considered for later analysis by a program are identified and entered as an input to a program by an operator. If an operator overestimates the number of elements (X ray peaks) present in a spectrum, there is a high probability that a larger number of false hits would be reported. Otherwise, if an operator underestimates number of existing elements, a number of misses will occur. Therefore, the role of an operator is essential in struggling with false hits and misses.

The χ_r^2 values associated with false hits are shown in Figure 44. In the ideal case no false hits would be reported. However, if a program reports peak areas of peaks that are not really present with a suitably high uncertainty, the χ_r^2 values will approach unity.

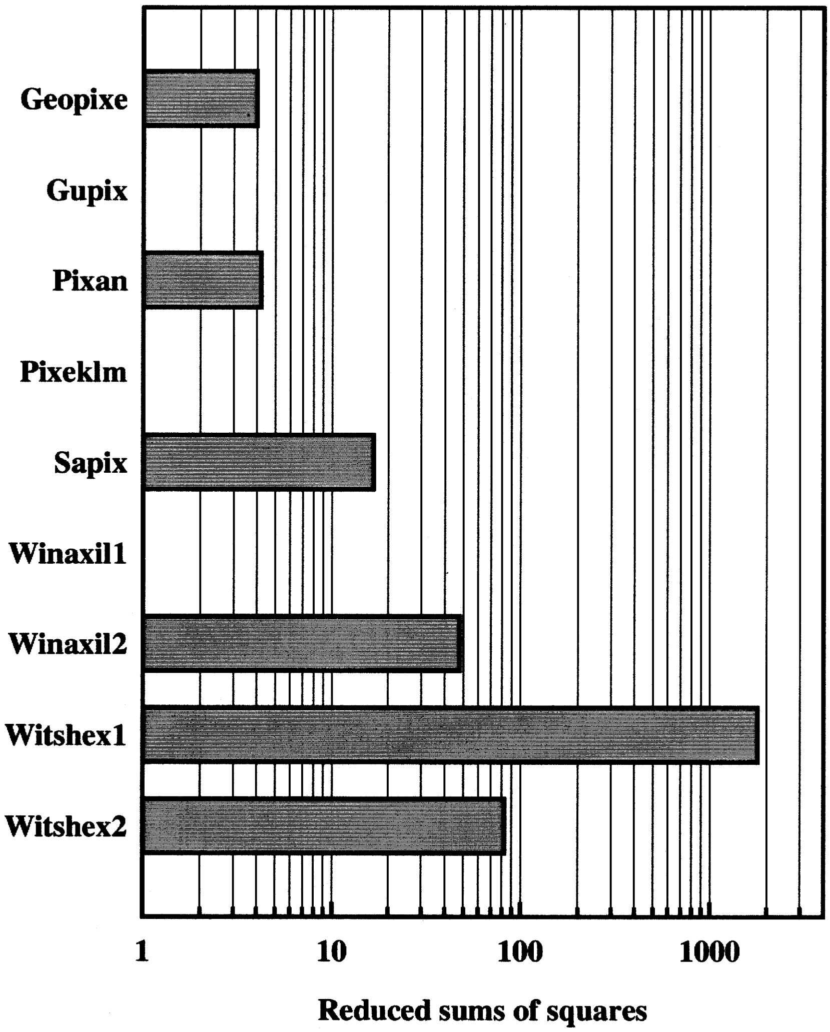

FIG.44. χ_r^2 *values reflecting understimation of uncertainties in "false hit" peak area ratios. The ideal program would not report "false hits" or would have a score of 1.*

6. Conclusions

A set of well characterized test, reference and calibration spectra is produced. They are to be used in an IAEA intercomparison of software packages for analysis of PIXE spectra. All spectra, including originally measured list files of aerosol, alloy, biological and glass samples, with extracted test and reference spectra for 1:9 ratio and 26 single element spectra, are available on request from the IAEA, Physics Section. A companion CD with the complete set of test spectra used for the present intercomparison exercise is attached to this TECDOC. These test spectra may be used in future to test any PIXE spectral analysis software package.

The results of the intercomparison indicate that most of the programs perform reasonably well with respect to peak areas. Some disagreements exist, for example in cases of low precision (intensity) peaks overlapping with or close to high precision (intensity) ones, and when K and L lines overlap.

Except for a very rare exception, the statistical analysis shows that the participants generally reported smaller uncertainties than would have been expected from the reference uncertainty values. The program that generally reported the smallest uncertainties is Witshex.

The results show that all the participants reported a number of statistically significant "false hits" and "misses" in their reports. Here we have to emphasize again that in case of analysis of PIXE spectra by all these programs, the role of an operator is essential in struggling with false hits and misses. If an operator overestimates the number of elements present in a spectrum, there is a high probability that a larger number of false hits would be reported. Otherwise, if an operator underestimates number of existing elements, a number of misses will occur. It is important that, if a program reports a peak area of a peak that is not really present, it should at least report it with a suitably high uncertainty. For example, Figure 43 shows that Pixan reported the highest number of false hits. However, Figure 44 shows that the program reported corresponding peak areas with suitably high uncertainties.

As a final conclusion, it is clear from the results that there is room for further improvements for the developers.

REFERENCES

[1] INTERNATIONAL ATOMIC ENERGY AGENCY, Intercomparison of Gamma Ray Spectrometry Software Packages, IAEA-TECODC-1011, Vienna (1998).

[2] BLAAUW, M., OSORIO FERNANDEZ, V., WESTMEIER, W., Nucl. Instr. and Meth. **A387** (1997) 410–415.

[3] BLAAUW, M., OSORIO FERNANDEZ, V., VAN ESPEN, P., BERNASCONI, G., CAPOTE NOY, R., MANH DUNG, H., MOLLA, N.I., Nucl. Instr. and Meth. **A387** (1997) 416–432.

[4] INTERNATIONAL ATOMIC ENERGY AGENCY, Intercomparison of Alpha Particle Spectrometry Software Packages, IAEA-TECODC-1104, Vienna (1999).

[5] BLAAUW, M., GARCIA-TORAÑO, E., WOODS, S., FAZINIĆ, S., Nucl. Instr. and Meth. **A428** (1999) 317–329.

[6] GARCIA-TORAÑO, E., CRESPO, M.T., WOODS, S., BLAAUW, M., FAZINIĆ, S., Nucl. Instr. and Meth. **A428** (1999) 330–335.

[7] Report on evaluation of interlaboratory comparison for PIXE analysis of fly ash embeded in filters, Internal report IAEA/AL/112, IAEA Laboratories, Seibersdorf (1997).

[8] THOMPSON, M., WOOD, R., Pure & Appl. Chem. **Vol.65, No.9** (1993) 2123–2144.

[9] CAMPBELL, J.L., MAENHAUT, W., BOMBELKA, E., CLAYTON, E., MALMQVIST, K., MAXWELL, J.A., PALLON, J., VANDENHAUTE, J., Nucl. Instr. and Meth. **B14** (1986) 204–220.

[10] FAZINIC, S., JAKSIC, M., CAMPBELL, J.L. , VAN ESPEN, P., BLAAUW, M., ORLIC, I., Nucl. Instr. and Meth. **B183** (2001) 439–448.

[11] BLAAUW, M., CAMPBELL, J.L., FAZINIC, S., JAKSIC, M., ORLIC, I., VAN ESPEN, P., Nucl. Instr. and Meth. **B189** (2002) 113–122.

[12] RYAN, C.G, CLAYTON, E., GRIFFIN, W.L., SIE, S.H., COUSENS, D.R., Nucl. Instr. and Meth. **B34** (1988) 396–402.

[13] RYAN, C.G., COUSENS, D.R., SIE, S.H., GRIFFIN, W.L., Nucl. Instr. and Meth. **B49** (1990) 271–276.

[14] ORLIC, I., SHIJUN ZHOU, SANCHEZ, J.L., WATT, F., TANG, S.M., Nucl. Instr. and Meth. **B150** (1999) 83–89.

[15] MAYER, M., Proceedings of the Fifteenth International Conference on Application of Accelerators in Research and Industry, AIP Conference Proceedings **475** (1999) 541–544.

[16] MAXWELL, J.A., CAMPBELL, J.L., TEESDALE, W.J., Nucl. Instr. and Meth. **B43** (1989) 218.

[17] VEKEMANS, B., JENSENS, K., VINCZE, L., ADAMS, F., VAN ESPEN, P., X-Ray Spectrom. **23** (1994) 278–285.

[18] WOODS, M. J., JEROME, S.M., DEAN, J.C.J., PERKIN, E.M.E., Appl. Radiat. Isot. Vol. **47**, No. 9/10 (1996) 971–979.

[19] CLAYTON, E., PIXAN, The Lucas Heights PIXE Analysis Computer Package, AAEC/M113, 1986.

[20] SZABO, G., BORBELY-KISS, I., Nucl. Instr. and Meth. **B75** (1993) 123.

[21] SERA, K., FUTATSUGAWA, S., Nucl. Instr. and Meth. **B109/110** (1996) 99–104.

[22] LIPWORTH, A.D., ANNEGARN, H.J. , KNEEN, M.A., Nucl. Instr. and Meth. **B75** (1993) 127.

[23] RYAN, C.G., COUSENS, D.R., SIE, S.H., GRIFFIN, W.L., SUTER, G.F., Nucl. Instr. Meth. **B47** (1990) 55.

[24] COHEN, D.D., Nucl. Instr. and Meth. **178** (1980) 481.

[25] AWAYA, T., Nucl. Instr. Meth. **165** (1979) 317.

[26] RYAN, C.G., HEINRICH, C.A., MERNAGH, T.P., Nucl. Instr. Meth. **B77** (1993) 463–471.

[27] COHEN, D.D., HARRIGAN, M., At. Nucl. Data Tables **34** (1986) 393.

[28] KRAUSE, J. Phys. Chem. Ref. Data **8** (1979) 307.

[29] SALEM, S.I., PANOSSIAN, S.L., KRAUSE, R.A., At. Nucl. Data Tables **14** (1974) 91.

[30] CLAYTON, E., Nucl. Instr. and Meth. **218** (1983) 221.

[31] COHEN, D.D., HARRIGAN, M.,Atomic Data and Nuclear Data Tables, **33** (1985) 255.

[32] CHEN, M.H., CRASEMANN, B., Atomic Data and Nuclear Data Tables **41** (1989) 257.

[33] CHOI, B.H., Phys.Rev **A7** (1973) 2056.

[34] GOWDA, R., POWERS, D., Phys. Rev. **A31** (1985) 134.
[35] SERA. K., FUTATSUGAWA, S., MATSUDA, K., Int. J. PIXE **Vol.4 (2 ,3)** (1994) 181.
[36] BAMBYNEK, W., CRASEMANN, B., FINK, R.W., FREUND, H.U., MARK, H., SWIFT, C.D., PRICE, R.E., VENGOPALA RAO, P., Rev. Mod. Phys. **44** (1972) 716.
[37] KAJKOSZ, J., KWIATEK, W.M., Nucl. Instr. and Meth. in Phys. Res. B22 (1987) 78–81.
[38] JOHANSSON G.I., X-ray Spectrometry, **Vol. 11, No 4**, (1982) 194–200.

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