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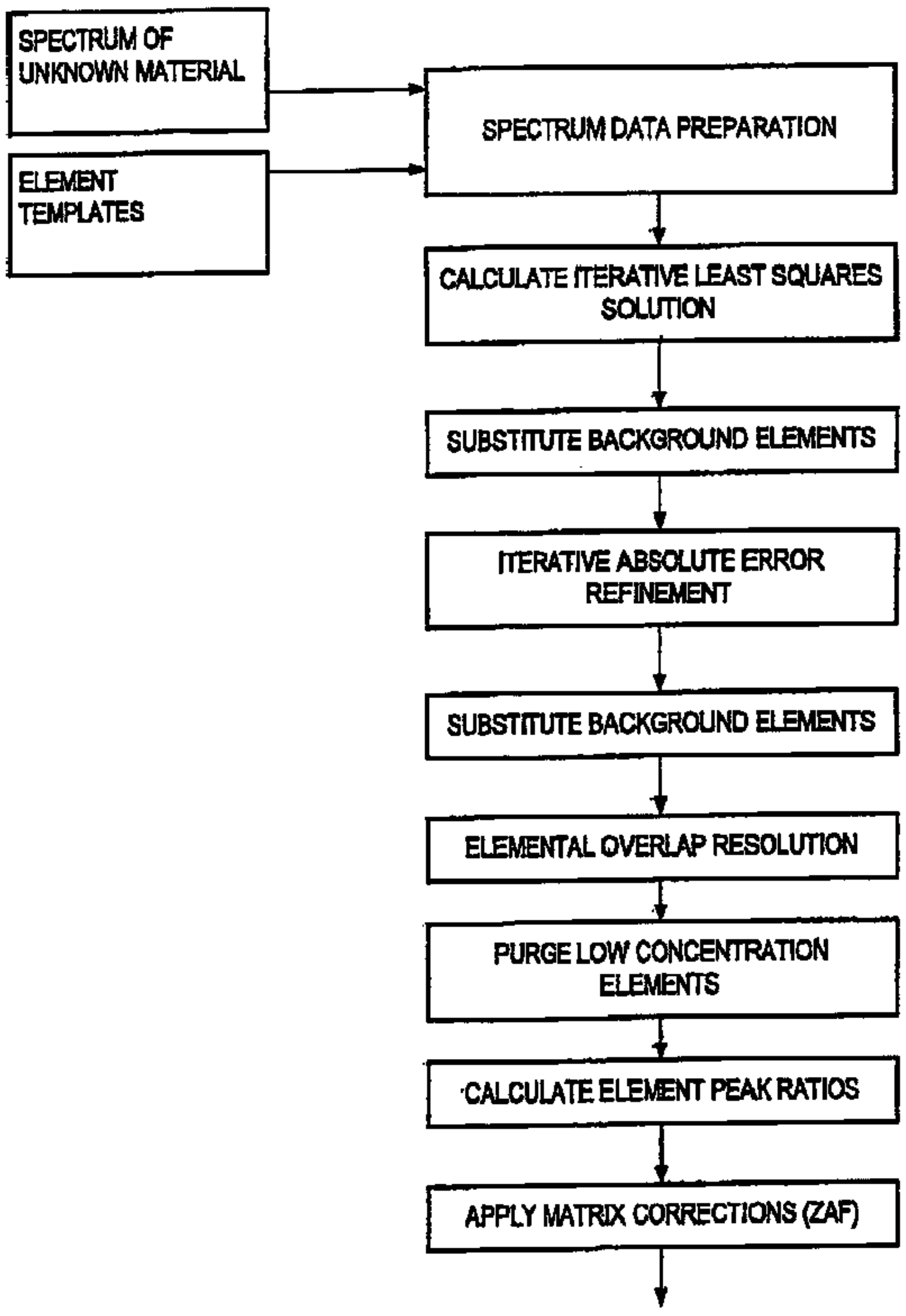

High Level Iterative Least Squares Algorithm

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A method and system for spectrum data analysis. The method comprises the steps of collecting a spectrum of an unknown material; providing a set of element data templates; calculate optical least squares weights for the element data templates in approximating the spectrum; removing one or more of the templates having negative weights in approximating the spectrum; and re-calculating an approximation of the spectrum with said one or more templates removed.

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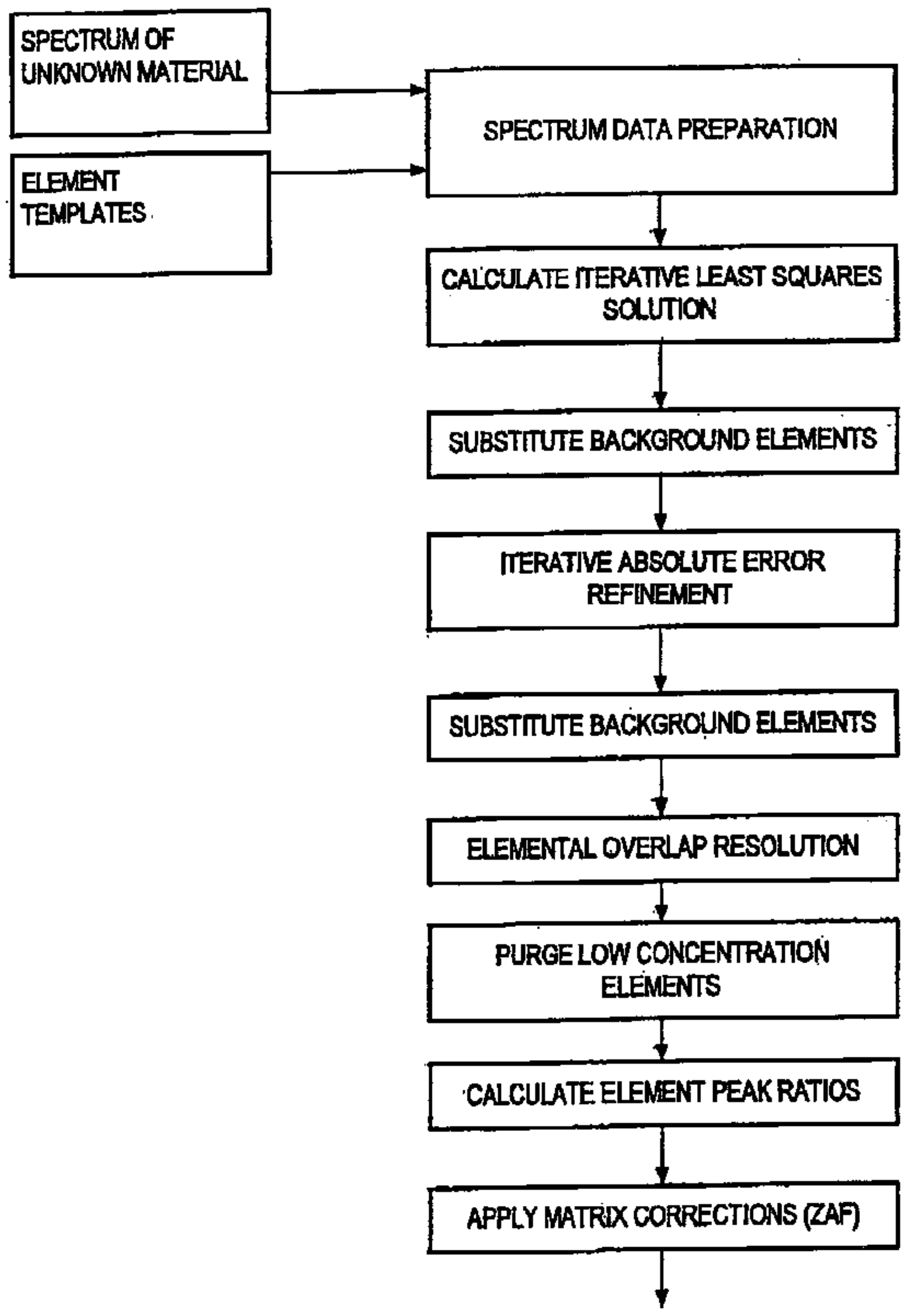

FIG. 15
High Level Iterative Least Squares Algorithm

(57) Abstract: A method and system for spectrum data analysis. The method comprises the steps of collecting a spectrum of an unknown material; providing a set of element data templates; calculate optical least squares weights for the element data templates in approximating the spectrum; removing one or more of the templates having negative weights in approximating the spectrum; and re-calculating an approximation of the spectrum with said one or more templates removed.

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A METHOD AND SYSTEM FOR SPECTRUM DATA ANALYSIS

FIELD OF INVENTION

[0001] The present invention relates broadly to a method and system for spectrum data analysis

BACKGROUND

[0002] In many applications, information about a sample is determined by accumulating radiation from the sample over a period of time. A characteristic of the radiation, such as its energy profile or its diffraction pattern, can often be correlated to the type of material present in the sample. For example, when bombarded by electrons, a sample gives off characteristic x-rays whose energy correlates to the elements in the sample. Similarly, when bombarded with x-rays, crystals produce a characteristic diffraction pattern, and the frequency spectrum of gamma rays and other radiation are used by astronomers to learn about the composition of universe. The term “sample” is used broadly herein to include an object under observation.

[0003] In one widely used application, a scanning electron microscope can be used to determine the elemental composition of an unknown material. The scanning electron microscope (SEM) sends high-energy electrons smashing into material. When these electrons enter an atom, they can knock electrons out of the material. In the process, the first electron looses some energy, but can go on to smash into other atoms until it no longer has enough energy to continue doing so.

[0004] Figure 1 shows an atom with electrons bound to the K, L, and M energy levels. An electron from the SEM is fired into this atom at a very high energy, dislodging one of the electrons from the atom. A very short time later, an electron from a higher energy level will fall into the created gap. In the process of falling into the lower energy K shell, it emits a single x-ray to balance the overall energy. The energy of the emitted x-ray depends on the initial location of the electron. If the electron originates from the L shell, then the radiation is designated as Kα radiation. If it originates from the M shell, then the radiation is designated as Kβ radiation, which has a higher energy than Kα radiation.

[0005] Alternatively, if an electron was dislodged from the L energy level, then a different set of x-rays may be omitted, depending from where the electron that will fill in the emptied position originates. Figure 1 shows that an electron falling from the M shell to the L shell is associated with the emission of Lα radiation.

[0006] The emitted x-rays are dependent on the specific starting and finishing energy levels. By analyzing the energy of the emitted x-ray, the type of the emitting atom can be determined. Each element in the periodic table has a specific set of energies corresponding to these x-ray energies. For example, the energy of the Kα radiation for carbon is 277eV, compared to 523eV for oxygen, or 98434eV for uranium. If the electron from the SEM has a lower energy than this binding energy, then it is unable to dislodge the electron from the atom.

[0007] A complete list of binding energies for each element can be seen at http://xdb.lbl.gov/Section1/Table_1-2.pdf.

[0008] Alternatively, the electrons from the SEM may not enter an atom, but may be deflected away from an atom. This is caused by the negative electric charge on the electron being repelled by the negative charge of the electron cloud around the atoms.

[0009] Figure 2 shows that the path of the electron is deflected away from an atom due to mutual electrostatic repulsion. The deflection of the path causes a small drop in energy of the high energy electron. This generates the Bremsstrahlung radiation. This effect occurs at lower intensities than the emission of x-rays seen in Figure 1. However, it also occurs at all energy levels, rather than at discrete energy levels. The Bremsstrahlung radiation is an artefact of using an electron beam from a SEM. It must be taken into account when calculating the elemental composition. The shape of the Bremsstrahlung radiation depends on the average density of the material being analyzed, and is also affected by the standard based spectral analysis.

Standard Based Spectral Analysis

[0010] Standard based spectral analysis is a term used to describe the process of comparing the spectrum of an unknown mineral or element with a set of known spectra to determine the composition of the unknown spectrum in terms of the known spectra. This approach generates a solution that represents a multiplication factor for each of the known templates, which are then added together to synthesize the unknown spectrum.

[0011] Figure 3 shows the spectrum of pyrite (FeS_2). The spectrum comprises several peaks, and some regions of Bremsstrahlung radiation. There are some additional smaller peaks in this plot that are due to carbon (at 277eV), and the iron Lα peak at 705eV.

[0012] If one measures a sample of pure iron and pure sulphur, the spectra of these elements can be overlaid onto the spectrum of pyrite appropriately. The result is shown in

Figure 4. In particular, Figure 4 shows that scaling the iron spectrum 44 to 42.0% and the sulphur spectrum 46 to 41.5% allows them to fit the peaks in the pyrite spectrum 42. These numbers are the peak ratios of these elements, because they represent the ratio of the area of each peak relative to a pure sample of the element. They do not represent the weight percentage of the material.

Matrix corrections

[0013] The peak ratios obtained previously can be converted to a weight percentage using a standard matrix correction algorithm such as ZAF corrections. ZAF corrections account for differences in the atomic number (Z) of the elements, the absorption factor (A) of x-rays travelling through the material, and fluorescence (F) of x-rays from elements stimulating the emission of x-rays from other elements.

Issues with standards-based spectral analysis

[0014] In order to use standard-based spectral analysis, the operating conditions of the SEM must be determined. The factors that influence spectral analysis are the beam voltage, x-ray detector angles and beam current. The beam voltage affects the peaks that are stimulated and produce x-rays. As discussed previously in the text, if the beam voltage is lower than a particular binding energy for an elemental peak, then the peak is not present in the spectrum. In addition, the peaks that have a significantly lower binding energy are stimulated far more than peaks with binding energy close to the beam voltage. This results in the spectrum containing very large peaks in the low energy range, and very small peaks in the high energy range.

[0015] The x-ray detector angle affects the calculations for ZAF corrections, because it models the length of the path that the x-rays traverse through the material before reaching the detector.

[0016] The beam current affects the rate at which x-rays are generated. The standards need to be collected at the same current as the analysis is performed.

Overlapping Spectra

[0017] Some elemental spectra have peaks that overlap other element peaks. For instance, sulphur, lead and molybdenum have a peak at 2307eV, 2342eV and 2293eV respectively. The elements have other peaks at different energies, but these spectra look very similar because the SEM beam voltage is too low to excite the molybdenum K peaks significantly (at 17481eV). In addition, the lead K peaks are not excited at all because their energy is too high (74989eV). This causes difficulties trying to resolve minerals that contain lead, sulphur or molybdenum. This is particularly difficult for galena which contains both lead and sulphur.

[0018] Figure 5 shows the spectrum 52 for galena, and the scaled spectra 54 for lead and sulfur 56. The peaks for lead and sulfur overlap significantly, which makes the analysis of galena more difficult than pyrite. There are other elements whose elemental peaks overlap strongly and, thus, elemental artefacts may occur if one of these elements is present in the mineral. Figures 6 to 12 show further examples of such overlapping elements.

[0019] In particular, Figure 7 shows that the platinum spectrum 74 and the zirconium spectrum 72 have an overlapping peak at 2.04keV (channel 102). This causes problems in the analysis because it can incorrectly introduce zirconium to the analyzed composition if platinum is present. Figure 8 shows the same type of overlapping peaks for the sodium spectrum 82 and the zinc spectrum 84. This causes sodium artefacts to be reported in minerals containing zinc. Figure 9 shows that this type of overlap is also present for the aluminium spectrum 92 and the bromine spectrum 94. Figure 10 shows the overlapping peak of the cadmium spectrum 102 and the uranium spectrum 104, which are very similar and could be confused at low concentration.

[0020] Figure 11 shows the close overlap of the peaks of the silver spectrum 112 and the thorium spectrum 114. This close overlap causes problems at low count because the only difference between the spectra of these elements is the small peak at channel 648, which is invisible for low count spectra. This causes the identification of minerals containing either thorium or silver to incorrectly include the other element because of this overlap. Finally, Figure 12 shows the overlapping peaks of the Yttrium spectrum 122 and the Iridium spectrum 124. Even such a relatively small overlap seems to cause problems for zirconia.

Low count spectral analysis

[0021] The calculation of the constituent elements from a spectrum is not particularly difficult if high count spectra are used. For instance, Figure 13 shows the spectrum of the mineral Albite ($NaAlSi_3O_8$) with the peaks shown very smoothly. The total number of x-rays collected to generate this spectrum was one million. In contrast, Figure 14 shows the same mineral where the total number of x-rays collected was three hundred. In this figure, the jagged plot 142 shows the spectrum of the mineral, while the smooth plot 144 shows a fit of elemental spectra to the mineral. In the second example there is significant noise in the spectra and the peaks are not smooth. The elements reported for the low count spectra contain a number of artefacts that appear to be present based on the spectra, but are not present in the mineral. The task of analyzing spectra at low counts is more difficult because there is far more variability in the underlying spectrum, and the peaks of each element are not Gaussian. Therefore, the techniques used by existing approaches are unsuitable for low count spectral analysis for mineral identification, because they generally assume a smooth spectrum.

[0022] On the other hand, the accuracy of element quantification is lower for low-count spectra. If the elements shown in Figure 13 and Figure 14 are compared, it is apparent that the quantities of the four elements O, Na, Al and Si are slightly inaccurate at 300 counts.

SUMMARY

[0023] It is an object of the present invention to substantially overcome, or at least ameliorate, one or more disadvantages of existing arrangements; or to provide a useful alternative.

According to an aspect of the present disclosure, there is provided a method of spectrum data analysis, the method comprising the steps of:

collecting a spectrum of an unknown material;

providing a set of element data templates;

approximating the spectrum with the element data templates by calculating least squares weights for the element data templates;

removing one or more of the element data templates having negative weights;

calculating an approximation of the spectrum with said one or more element data templates removed, said approximation including an initial error estimate;

iteratively removing an element data template from the calculated approximation of the spectrum and calculating new approximations of the spectrum with new weights for the remaining element data templates, said new approximations including new error estimates;

identifying a new approximation of the spectrum having a smallest new error estimate that is less than the initial error estimate; and

determining from the new element data template weights in the identified new approximation and properties of corresponding elements the relative abundance of the elements in the unknown material.

According to another aspect of the present disclosure, there is provided an electron beam system programmed to perform the above-method.

According to another aspect of the present disclosure, there is provided a method of spectrum data analysis of a sample, the method comprising:

collecting a spectrum of an unknown material;

providing a set of data templates, each data template corresponding to a spectrum of a specific material;

determining a first set of weighting factors to be applied to the data templates to approximate the spectrum, the weighting factors being determined by minimizing an error factor between the weighted data templates and the spectrum of the unknown material;

removing one or more of the data templates having a negative weighting factor;

calculating an approximation of the spectrum with said one or more data templates removed, said approximation including an initial error estimate;

iteratively removing a data template from the calculated approximation of the spectrum and calculating new approximations of the spectrum with new weighting factors from the remaining data templates, said new approximations including new error estimates;

identifying a new approximation of the spectrum having a smallest new error estimate that is less than the initial error estimate; and

determining from the new data template weighting factors for the identified new approximation and the properties of corresponding materials the relative abundance of the materials present in the unknown material.

According to another aspect of the present disclosure, there is provided an apparatus for determining the elemental composition of a sample, comprising:

a source of an electron beam for impinging on a sample;

an x-ray detector for detecting x-rays emitted from the sample upon impingement of the electron beam;

computer memory for:

accumulating information from the x-ray detector to determine an x-ray spectrum of the sample;

storing data templates corresponding to elements;

storing a computer program including instructions for:

determining a set of first set of weighting factors to be applied to the data templates to approximate the sample spectrum, the weighting factors being determined by minimizing an error factor between the weighted data templates and the sample spectrum;

removing one or more of the data templates having a negative weighting factor in approximating the sample spectrum;

calculating an approximation of the spectrum with said one or more data templates removed, said approximation including an initial error estimate;

iteratively removing an element data template from the calculated approximation of the spectrum and calculating new approximations of the spectrum with new weighting factors from the remaining element data templates, said new approximations including new error estimates;

identifying a new approximation having a smallest new error estimate that is less than the initial error estimate; and

determining from the new weighting factors from the identified new approximation and the properties of elements corresponding to the element data templates in the new approximation the relative abundance of the elements in the sample; and a processor for executing the computer instructions to determine the composition of the sample.

According to another aspect of the present disclosure, there is provided a computer readable media comprising computer readable instructions for:

determining a set of first set of weighting factors to be applied to a set of data templates to approximate a spectrum of an unknown material, the weighting factors being determined by minimizing an error factor between the weighted element data templates and the spectrum;

removing one or more of the templates having a negative weighting factor in approximating the spectrum;

calculating an approximation of the spectrum with said one or more data templates removed, said approximation including an initial error estimate;

iteratively removing a data template from the calculated approximation of the spectrum and calculating new approximations of the spectrum with new weighting factors from the remaining data templates, said new approximations including new error estimates;

identifying a new approximation having a smallest new error estimate that is less than the initial error estimate; and

determining from the new weighting factors from the identified new approximation and the properties of elements corresponding to the data templates in the new approximation the relative abundance of the elements in the unknown material.

[0038] Other aspects of the invention are also disclosed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0039] Some conceptual diagrams and at least one embodiment of the present invention will now be described with reference to the drawings and appendices, in which:

[0040] Figs. 1 and 2 show conceptual energy diagrams and in principal functionality behind the method of standard electron microscopy (SEM).

[0041] Fig. 3 shows the spectrum of mineral pyrite.

[0042] Fig. 4 shows a two-element spectral analysis of pyrite.

[0043] Fig. 5 shows the spectrum of Galena with nearby elements.

[0044] Fig. 6 illustrates the concept of element peak overlap.

[0045] Figs. 7 to 12 show the overlapping peaks of various elements.

[0046] Figs. 13 and 14 show two spectra of Albite obtained on the basis of different count number.

[0047] Fig. 15 shows a high-level flow diagram of the currently described Itterative Least Square Algorithm.

[0048] Fig. 16 shows galena(PbS) before and after non uniform sub-sampling.

[0049] Fig. 17 shows magnified view of sub-sampled region.

[0050] Figs. 18 and 19 show template spectra obtained without and with non-uniform sub-sampling, respectively.

[0051] Fig. 20 shows interative least squares initialization block diagram.

[0052] Fig. 21 shows albite spectrum ($NaAlSi_3O_2$).

[0053] Fig. 22 shows raw template multipliers for albite after 1st iteration.

[0054] Fig. 23 shows scaled templates for albite.

[0055] Fig. 24 shows magnified portion of scaled templates.

[0056] Fig. 25 shows background element substitution algorithm.

[0057] Fig. 26 shows interative absolute error refinement.

[0058] Fig. 27 shows simple two element spectral analysis of nickel silicide.

[0059] Fig. 28 shows Ni_2Si spectrum.

[0060] Fig. 29 shows monazite.

[0061] Fig. 30 shows portions of the spectrum used to calculate the nickel K peak ratio.

[0062] Fig. 31 shows peak ratio calculation block diagram.

[0063] Fig. 32 shows average processing time.

[0064] Figs. 33 to 47 show the compositions of various minerals calculated by way of the algorithm of the present invention.

[0065] Fig. 48 shows a typical electron beam system embodying the present invention.

DETAILED DESCRIPTION

[0066] Embodiments of the invention are particularly well suited for determining sample characteristics using a relatively small number of "counts," that is, a relatively small amount of detected radiation. The radiation can be, for example, an x-ray spectrum for an electron microscope, an x-ray spectrum from X-ray fluorescence, an x-ray diffraction pattern, a light, microwave, or gamma ray spectra from an astronomical object, or a mass spectrum from a mass spectrometer. While the prior art interprets a smooth spectrum produced by a large number of counts, embodiments of the invention are suitable for determining materials from a rough, noisy spectrum having, for example, fewer than 100,000 counts, fewer than 10,000 counts, fewer than 1,000 counts, or fewer than 500 counts. Because it takes time to accumulate counts, embodiments of the invention allow for more rapid characterization of materials compared to the prior art. Embodiments of the invention can be used to determine, for example, the elemental composition of a sample in an x-ray spectroscopy embodiment, the mineral composition of a sample in an x-ray diffraction embodiment, or the mass composition of a sample, in a mass spectroscopy embodiment.

[0067] In an embodiment in which the invention is used to determine the elemental composition of a sample using x-ray spectroscopy, the standard operating conditions of the SEM configuration used in obtaining at least some of the results presented in the present description include 25keV beam voltage, 5nA beam current, and 35 degree x-ray detector angle. The beam voltage is too low to dislodge the electrons for uranium in the K shell, which require nearly four times that energy. However, it is high enough to dislodge the M shell electrons for uranium because they require 3165eV.

[0068] Some portions of the description which follows are explicitly or implicitly presented in terms of algorithms and functional or symbolic representations of operations on data within a processor or a computer memory. These algorithmic descriptions and functional or symbolic representations are the means used by those skilled in the data processing arts to convey most effectively the substance of their work to others skilled in the art. An algorithm is here, and generally, conceived to be a self-consistent sequence of steps leading to a desired result. The steps are those requiring physical manipulations of physical quantities, such as electrical, magnetic or optical signals capable of being stored, transferred, combined, compared, and otherwise manipulated.

[0069] Unless specifically stated otherwise, and as apparent from the following, it will be appreciated that throughout the present specification, discussions utilizing terms such as “scanning”, “calculating”, “determining”, “replacing”, “generating”, “initializing”, “outputting”, or the like, refer to the action and processes of a computer system, or similar electronic device, that manipulates and transforms data represented as physical quantities within the computer system into other data similarly represented as physical quantities within the computer system or other information storage, transmission or display devices.

[0070] Thus, the present specification discloses both a method and an apparatus for performing the operations of the method. Such apparatus may be specially constructed for the required purposes, or may comprise a general purpose computer or other device selectively activated or reconfigured by a computer program stored in the computer. The algorithms and displays presented herein are not inherently related to any particular computer or other apparatus. Various general purpose machines may be used with programs in accordance with the teachings herein. Alternatively, the construction of more specialized apparatus to perform the required method steps may be appropriate. The structure of a conventional general purpose computer will appear from the description below.

[0071] In addition, the present specification also implicitly discloses a computer program, in that it would be apparent to the person skilled in the art that the individual steps of the method described herein may be put into effect by computer code. The computer program is not intended to be limited to any particular programming language and implementation thereof. It will be appreciated that a variety of programming languages and coding thereof may be used to implement the teachings of the disclosure contained herein.

Moreover, the computer program is not intended to be limited to any particular control flow.

[0072] Furthermore, one or more of the steps of the computer program may be performed in parallel rather than sequentially. Such a computer program may be stored on any computer readable medium. The computer readable medium may include storage devices such as magnetic or optical disks, memory chips, or other storage devices suitable for interfacing with a general purpose computer. The computer readable medium may also include a hard-wired medium such as exemplified in the Internet system, or wireless medium such as exemplified in the GSM mobile telephone system. The computer program when loaded and executed on such a general-purpose computer effectively results in an apparatus that implements the steps of the preferred method.

[0073] The invention may also be implemented as hardware modules. More particular, in the hardware sense, a module is a functional hardware unit designed for use with other components or modules. For example, a module may be implemented using discrete electronic components, or it can form a portion of an entire electronic circuit such as an Application Specific Integrated Circuit (ASIC). Numerous other possibilities exist. Those skilled in the art will appreciate that the system can also be implemented as a combination of hardware and software modules.

[0074] Embodiments of the invention use one or more mathematical algorithms to approximate a measured property, such as an x-ray spectrograph, by using known data templates corresponding to various materials, and weighting factors that correlate to the relative abundance of those materials in the sample. Weighting factors are determined that produce, in combination with the data templates, a spectrum, diffraction pattern, or other pattern, that closely matches the measured pattern. The difference between the measured pattern and the combination of the data templates and weighting factors, is referred to an error value. Mathematical algorithms are used to minimize the error value. One preferred algorithm to find weighting factors that minimize the error value is an iterative least squares method, and is described in detail below. The invention is not limited to any particular algorithm.

Iterative Least Squares Algorithm

[0075] The iterative least squares analysis is a technique which uses standard linear least squares curve fitting to find the optimal weights for each template in order to synthesise the spectrum of an unknown material. It builds a list of candidate elements and uses various conditions to detect which elements are artefacts and which elements are in the solution.

[0076] The spectral analysis algorithm disclosed here is presented in Figure 15. The algorithm is directed at analysing low-count spectra (typically 1000 counts), but can also be applied for analysing high count spectra. It performs element identification and quantification simultaneously to compute the peak ratios of each element. It also applies real-world knowledge to address various minor deficiencies and to minimize the chance of reporting artefact elements that appear to be in the spectrum but are not actually present.

Spectrum Data preparation

[0077] The raw spectrum data is altered to improve the discrimination ability between similar elements. When spectrum data is acquired, the data tends to have larger peaks at lower energy, and if any peaks are present at high energy they are generally far smaller in magnitude. This presents a problem for discriminating between similar elements (see Figure 4 for example).

Non uniform spectra sub-sampling

[0078] In the non-uniform spectra sub-sampling phase, the spectrum is sub-sampled non uniformly. Such sampling preserves the resolution of the low energy portion of the spectrum, while increasing the peak signal-to-noise ratio at high energy at the expense of peak resolution. This trade-off is acceptable for two reasons – firstly the tiny high energy peaks become more important, and secondly the Energy-Dispersive Spectroscopy (EDS) x-ray detector has a resolution that is significantly worse at high energy compared to low energy.

[0079] The non-uniform sub-sampling is implemented as follows:

[0080] 1. Retain the original spectrum for all channels below 8keV. The purpose is to preserve the high resolution obtained by the x-ray detector for these channels. It also fits with the fact that elements have a higher count rate (i.e. rate at which x-rays are generated) at lower energy compared to higher energy. This arbitrary threshold was selected based on the spectra of nickel and copper, where the K-L ratio changes from greater-than-1 for nickel to a value of less-than-1 for copper. The copper K-alpha peak occurs at 8040eV, and will be magnified accordingly.

[0081] 2. For the remaining data (i.e. above 8keV), accumulate six consecutive channels to form a new channel. This has the effect of increasing the height of all data within this region, and will reinforce peaks while leaving the noise spread out. Figure 16 shows the original Galena (lead-sulphide) mineral before and after this processing. In standard operating conditions of the described system, the processing changes the number of channels in a spectrum from 1024 to 504. Figure 17 shows the channels for 8keV – 25keV for the original and sub-sampled spectra. The original Galena mineral peak at channel 527 is approximately 3000 photons, compared to 45,000 photons for the peak at channel 117. After processing, this peak has increased in height to 20,000 photons (approximately a factor of 6), while decreasing the number of channels in this region by a factor of 6. This assists in the discrimination between similar elements because the small peaks suddenly become far more important in the least squares fitting. It also reduces the processing time significantly because fewer channels are processed.

Low Count Channel Optimization

[0082] The algorithm optimizes the analysis by reducing the number of channels analyzed for the spectrum based on the templates used and the number of photons in the spectrum. For example, low count spectra generally have no peaks at higher energies because there aren't enough photons detected at those energies to create a statistically meaningful peak. Figure 18 shows an overlay of 45 million count spectra for the elemental templates. If a random spectrum is analyzed which contains only 1000 counts, then any peaks below the thick horizontal line are unlikely to be created because the probability that a photon will be detected there is less than 1/1000. Therefore, it isn't necessary to analyze all 1024 channels for a 1000 count analysis, and thus the number of channels analyzed can be reduced to about 800. This range is dynamically generated based on the templates used for analysis, and increases the computation speed for each iteration. The low count channel optimization is performed after the non-uniform sub-sampling. This reduces the upper channel from about 800 to about 480 for a 1000 count analysis, as shown in Figure 19.

Calculate iterative least square solution

Iterative Least Squares Initialization

[0083] Figure 20 shows the block diagram for a proposed algorithm for iterative least squares initialization. The purpose is to quickly remove artefact elements from the solution by purging elements whose concentration is negative. When the elemental concentration is calculated, there are no restrictions on the weights calculated for each element. Thus, this algorithm uses the fact that elements can't have negative concentration as the rule to remove elements. Once there are no negative concentration elements then the stage has completed. The calculation to generate the optimal weights uses the standard linear least squares algorithm. The least squares algorithm solves an over-determined system of linear equations of the form

[0084] $Ax = b$ (**Equation 1**: Linear equation to be solved)

[0085] where:

[0086] A is the matrix of known data points;

[0087] b is final solution; and

[0088] x is the set of unknowns which linearly scale the known matrix A to generate the vector b.

[0089] In the presently disclosed approach, A represents the known element templates, b represents the spectrum being analyzed, and x is the multiplication factor applied to each template to generate the spectrum. This is solved as follows

[0090] $X=(A^TA)^{-1}A^Tb$ (**Equation 2**: Least squares solution)

[0091] This calculates the optimal set of weights that minimize the squared error

[0092] $e = II\ Ax - b\ II^2$ (**Equation 3**: Error term minimized by Equation 2)

[0093] In Figure 21 the spectrum of the mineral albite is shown. The four peaks are generated by the elements oxygen, sodium, aluminium and silicon respectively. The "concentration" of each element is calculated to minimize the squared error, not to calculate the composition of the mineral. Thus, they are not concentrations but actually represent a multiplier with respect to the reference spectrum for each element. These multipliers are not guaranteed to lie between 0 and 100% but could be any value. In addition, some elements may have negative concentrations, because they are creating "anti-peaks" which are in turn used to offset artefact peaks of other elements that aren't present. This effect is demonstrated in Figure 22, Figure 23 and Figure 24.

[0094] Figure 23 shows each of the element templates after they've been scaled by the values shown in Figure 22. The four main elements, oxygen, sodium, aluminium and silicon, stand out quite strongly for this mineral. Figure 24 shows that some of the peaks introduced into the solution are being cancelled out by the presence of anti-peaks. If the elements which generate the anti-peaks are removed, the template multipliers for the remaining elements can be improved. In order to reduce the artefact elements, all elements with concentrations below 0.0 are removed and the solution is re-calculated. This process is repeated until there are no more negative concentrations. This removes most of the artefact elements from the mineral. The entire process can be summarised as follows:

[0095] 1. Generate the matrix A from the set of templates (accounting for template spectra live time)

[0096] 2. Solve for the optimal weights for x

[0097] 3. If any negative concentrations are present in x, remove those corresponding templates from A, or equivalently, set the weight corresponding to those elements to zero, and go back to step 1.

Substitute background elements

[0098] This phase of the processing analyzes the solution and substitutes a pre-defined set of overlapping elements for each element in the solution. The purpose of this phase is to determine whether an element has been removed from the solution prematurely and to restore it if so. The algorithm outline is shown in Figure 25.

[0099] This phase scans through each element and verifies whether any of the elements is listed with overlapping elements. If so, each overlapping element is added to the composition, one at a time, and the composition is re-computed. The algorithm also tries substituting each of the overlapping elements for the original element. It tests whether the composition has improved by examining the absolute error of the synthesised spectrum given by the composition against the original. A list of overlapping elements is shown in Table 1.

Reference Element	Overlapping element 1	Overlapping element 2	Overlapping element 3	Overlapping element 4
Fluorine	Manganese	Iron		
Sodium	Zinc			
Aluminium	Bromine			
Silicon	Strontium	Tungsten	Tantalum	Rubidium
Phosphorous	Zirconium	Platinum	Iridium	Yttrium
Sulfur	Molybdenum	Lead		
Chlorine	Rhodium	Rubidium		
Potassium	Indium			
Calcium	Antimony			
Vanadium	Oxygen			
Chromium	Vanadium	Manganese		
Manganese	Fluorine	Europium		
Iron	Manganese	Cobalt	Fluorine	
Cobalt	Iron	Nickel		
Nickel	Cobalt			
Zinc	Sodium			
Bromine	Aluminium			
Rubidium	Silicon	Tungsten	Tantalum	
Strontium	Silicon	Tungsten		
Yttrium	Osmium	Phosphorous		
Zirconium	Platinum	Phosphorous	Iridium	
Niobium	Mercury			
Molybdenum	Sulfur	Lead		
Ruthenium	Chlorine			
Rhodium	Chlorine			
Silver	Thorium			
Cadmium	Uranium			
Indium	Potassium			
Antimony	Calcium			
[illegible]	[illegible]			
Praseodymium	Lanthanum			
Neodymium	Cerium			
Europium	Manganese			
Terbium	Iron			
Dysprosium	Iron			
Tantalum	Silicon	Tungsten	Rubidium	Copper
Tungsten	Silicon	Strontium	Tantalum	Rubidium
Osmium	Yttrium			
Iridium	Zirconium	Platinum	Phosphorous	
Platinum	Zirconium	Phosphorous	Iridium	
Mercury	Niobium			
Lead	Sulfur	Molybdenum		
Thorium	Silver			
Uranium	Cadmium			

Table 1

Purge oxygen below 5%

[00100] This is an optional single processing step which can be implemented either at this stage of the algorithm, or in the stage of purging trace elements, described later in the text. In particular, this step removes oxygen if the concentration is below 5%. This arbitrary threshold was reached after analysing all 76 minerals and elements and determining that this threshold was appropriate to retain oxygen that was indeed present in the minerals. At the same time the chosen concentration also allowed to successfully remove from the calculations oxygen that was merely an artefact. This reduces the amount of trace oxygen reported for all results. The purpose of this stage is to reduce the complexity of the results reported.

Iterative Absolute Error Refinement

[00101] Figure 26 shows the block diagram for the iterative absolute error refinement stage. The purpose of this stage is to remove element artefacts from the composition by minimising the absolute error between the synthesised spectrum and the source spectrum. It iterates through the elements and removes each element one at a time. It then recomputes the concentrations of the remaining elements and checks if the absolute error has decreased. This is repeated for all elements. It then removes the element that had the largest decrease in error, and repeats the process iteratively.

Element Overlap Resolution

[00102] This is a final processing stage which represents a set of rules for removing certain elements if their overlapping element (see Table 2) is also present. The stage is designed to remove elements that may appear to be in the spectrum, but are usually the result of matrix effects distorting the mineral spectrum and altering the relative intensity of element peaks. For example, the synthetic mineral nickel silicide (Ni_2Si) consists of nickel (plot 274) and silicon (plot 276). If the relative heights of the nickel K and L peaks are compared for Ni_2Si and pure nickel, the Ni_2Si Lα peak 272 (851eV) is significantly taller than expected, as shown in Figure 27.

[00103] The increase in height is caused by x-rays generated from the silicon interacting with the nickel atoms and generating additional x-rays. This causes the spectral fitting to match poorly for this peak, and other elements may be added to the solution to try to reduce the mismatch. This stage is designed to detect elements that may have been added incorrectly and to remove them.

[00104] During this stage, the solution for pairs of elements is analyzed and, if both elements are found, one of the elements is removed. The relative concentration of each element pair is stored, because some of the elements can occur in minerals together (such as molybdenum and sulphur), but others do not (such as thorium and silver). In the case where they do not occur together, the relative concentration required is 0, which means that the less common element will always be removed if both have been reported in the composition. The higher the relative concentration required, the more difficult it is to remove the potentially overlapping elements. The relative concentrations specified here have been derived empirically from a test set, and may not represent the optimal set of relative concentration thresholds for all minerals.

Table 5-2: Heuristic Elemental Removal Rules

Elements Present	Element Removed	Relative concentration required
Sodium, zinc	Sodium	2
Phosphorous, Yttrium	Phosphorous	4
Phosphorous, Zirconium	Phosphorous	3
Gallium, Sodium	Gallium	0
Aluminium, Bromine	Bromine	0
Strontium, Silicon	Strontium	5
Zirconium, Platinum	Zirconium	5
Molybdenum, Sulfur	Molybdenum	8
Indium, Potassium	Indium	0
Cerium, Vanadium	Cerium	0.6
Cerium, Chromium	Cerium	2.7
Neodymium, Chromium	Neodymium	1
Europium, Manganese	Europium	0.5
Europium, Iron	Europium	0.5
Terbium, Iron	Terbium	0.5
Dysprosium, Iron	Dysprosium	8
Holmium, Iron	Holmium	3
Holmium, Cobalt	Holmium	0.5
Erbium, Iron	Erbium	8
Thulium, Copper	Thulium	0.5
Thulium, Aluminium	Thulium	5
Thulium, Iron	Thulium	10
Ytterbium, Nickel	Ytterbium	5
Ytterbium, Zinc	Ytterbium	4
Hafnium, Silicon	Hafnium	8
Tantalum, Silicon	Tantalum	1
Tantalum, Zinc	Tantalum	0
Tantalum, Copper	Tantalum	3
Tungsten, Silicon	Tungsten	3.5
Rhenium, Zinc	Rhenium	7.0
Osmium, Zirconium	Osmium	10.0
Thorium, Silver	Thorium	2.0

Table 2

Purge trace elements

[00105] This step removes trace elements from the solution and normalises the result. It uses a magic threshold of less than 2.5% as the criteria for retaining elements. The reason is

[00106] that elements of such a low concentration are generally artefacts in the composition rather than being present. The specific threshold for elements being removed in the currently disclosed system and method is approximately 0.5%. The solution is then normalized to 100%.

Calculate element peak ratios

[00107] This stage is required because the element ratios up to this point refer to the optimal set of multiplication factors required to fit the element spectra to the unknown mineral. However, the final output of the spectrum processing must be a weight percentage per element, which requires a matrix correction. The ZAF corrections applied at the end require that the elements are quantified relative to a single peak rather than for the entire spectrum. Therefore, this stage computes the peak ratio of each element and specifies the peak that was used to calculate the percentage.

[00108] The peak for each element is determined, and the ratio for that peak is computed. It is desirable to use higher energy peaks because they are not subject to as many ZAF effects as lower energy peaks. In the presently described method, the highest peak for each element is selected for which the ratio of the beam energy to the peak energy does not exceed 2.5. Therefore, when using a beam voltage of 25kV, the selected highest peak has voltage of 10kV or less. In the case of nickel (in Ni_2Si), this is the K peak at 7477eV (Figure 28).

[00109] However, when overlapping elements are present, the peak ratios cannot be calculated individually because emissions from the other elements are often contributing significantly to a particular peak. Figure 29 shows a portion of the spectrum for the mineral “monazite” (plot 292) which contains several rare earth elements, such as La (plot 294), Ce (plot 296), Pr (plot 297), Nd (plot 298) and Th (plot 299). The spectra 297 for Pr and the spectrum 298 for Nd have been highlighted to illustrate that these cannot be computed in isolation of the other elements because there are significant overlapping portions of the spectra from other elements.

[00110] Fortunately, the existing technique of computing the element concentration can be directly applied to computing the peak ratios by using Equation 2. However, rather than compute the solution for the entire spectrum, the technique uses as much of the spectrum as possible, and removes the other peaks. Figure 30 shows a diagrammatic representation of this computation for computing the nickel K peak ratio. The nickel L peak is omitted from the calculation, but otherwise it directly solves for the peak ratio by solving equation 2.

[00111] A block diagram for this computational algorithm is shown in Figure 31. The algorithm attempts to prevent having to compute the peak ratios for elements that only have one peak (such as magnesium) by reusing the existing result. All elements below Argon (Z=18) have one peak. In addition, in the standard operating conditions of the presently disclosed mehtod, the beam voltage is 25keV. Consequently, the elements Pd, Ag, Cd, In, Sn, Sb, Te and I only have one peak, because the K peak is higher than the beam voltage and they do not have any M peaks. This provides a minor performance optimization by avoiding recomputing the peak ratios for these elements.

[00112] The algorithm also contains a second path which drops elements from the composition if their concentration changes significantly. This is intended to catch elements that have been reported in trace amounts, but whose concentration increases by a factor of 10x, if a single peak is analyzed in isolation.

ZAF corrections

[00113] The peak ratios are corrected using ZAF corrections prior to being reported.

Processing Time

[00114] The processing time for the algorithm was targeted at 10 milliseconds for a 1000 count spectrum. Figure 32 shows the average execution time of the entire spectral analysis engine when analysing the set of minerals from the SPI_MINERALS and Smithsonian standard blocks. The processing time was found to be inversely proportional to the number of counts in the spectrum. This is expected, because the spectrum becomes smoother at higher counts and it is less difficult to establish the correct set of elements, and there are fewer incorrect elements that need refining or exchange.

[00115] The longer than expected processing time may be associated with some programming overhead translating between the managed C# code and the unmanaged C++ spectral analysis engine code. The execution time is also proportional to the number of elements used for analysis. The figures shown in Figure 32 were generated when analysing with 72 elements.

[00116] Whereas convention x-ray spectroscopy analysis uses millions of counts that are accumulated on the order or a second or more, to produce a sufficiently smooth surve for conventional analysis, embodiments of the present invention can use fewer than 100,000 counts, fewer than 50,000 counts, fewer than 10,000 counts, fewer than 3000 counts, fewer than 1000 counts or fewer than 500 counts, depending on the accuracy required. Using a typical silicon drifted x-ray detector in which having a surface area of between 10mm^2 and 30mm^2 and subtending a solid angle of about 0.3 sr, embodiments of the present invention can determine the elements present in a sample in less than one hundred milliseconds, less than a ten milliseconds, and in some embodiments, on the order of a few milliseconds.

Results

[00117] Some composition results of the described method for spectral analysis are shown in Figures 33 to 47. The theoretical composition of each mineral is listed at the bottom of each plot. The mean and standard deviation of each result is reported in the legend of each plot. Each of these analyzes was performed at 1000 counts. The main observations that can be made is that carbon and oxygen vary far more widely than other elements. Secondly, low concentration elements may appear or disappear from the composition if their composition is too small. Finally, artefact elements are present in nearly every composition, but at low concentrations.

Hardware Embodiment

[00118] FIG. 48 shows a scanning electron beam system 200 with an x-ray detector 240 suitable for practicing embodiments of the present invention. A scanning electron microscope 241, along with power supply and control unit 245, is provided with system 200. An electron beam 232 is emitted from a cathode 253 by applying voltage between cathode 253 and an anode 254. Electron beam 232 is focused to a fine spot by means of a condensing lens 256 and an objective lens 258. Electron beam 232 is scanned two-dimensionally on the specimen by means of a deflection coil 260. Operation of condensing lens 256, objective lens 258, and deflection coil 260 is controlled by power supply and control unit 245.

[00119] A system controller 233 controls the operations of the various parts of scanning electron beam system 200. The vacuum chamber 210 is evacuated with ion pump 268 and mechanical pumping system 269 under the control of vacuum controller 232.

[00120] Electron beam 232 can be focused onto sample 202, which is on movable X-Y stage 204 within lower vacuum chamber 210. When the electrons in the electron beam strike sample 202, the sample gives off x-rays whose energy correlated to the elements in the sample. X-rays 232 having energy inherent to the elemental composition of the sample are produced in the vicinity of the electron beam incident region. Emitted x-rays are collected by x-ray detector 240, preferably an energy dispersive detector of the silicon drift detector type, although other types of detectors could be employed, which generates a signal having an amplitude proportional to the energy of the detected x-ray.

[00121] Output from detector 240 is amplified and sorted by the processor 220, which counts and sorts the total number of X-rays detected during a specified period of time, at a selected energy and energy resolution, and a channel width (energy range) of preferably between 10-20 eV per channel. Processor 220 can comprise a computer processor; operator interface means (such as a keyboard or computer mouse); program memory 222 for storing data and executable instructions; interface means for data input and output, executable software instructions embodied in executable computer program code; and display 244 for displaying the results of a multivariate spectral analysis by way of video circuit 242.

[00122] Processor 220 can be a part of a standard laboratory personal computer, and is typically coupled to at least some form of computer-readable media. Computer-readable media, which include both volatile and nonvolatile media, removable and non-removable media, may be any available medium that can be accessed by processor 220. By way of example and not limitation, computer-readable media comprise computer storage media and communication media. Computer storage media include volatile and nonvolatile, removable and non-removable media implemented in any method or technology for storage of information such as computer-readable instructions, data structures, program modules or other data. For example, computer storage media include RAM, ROM, EEPROM, flash memory or other memory technology, CD-ROM, digital versatile disks (DVD) or other optical disk storage, magnetic cassettes, magnetic tape, magnetic disk storage or other magnetic storage devices, or any other medium that can be used to store the desired information and that can be accessed by processor 220.

[00123] Program memory 222 can include computer storage media in the form of removable and/or non-removable, volatile and/or nonvolatile memory and can provide storage of computer-readable instructions, data structures, program modules and other data. Generally, the processor 220 is programmed by means of instructions stored at different times in the various computer-readable storage media of the computer. Programs and operating systems are typically distributed, for example, on floppy disks or CD-ROMs. From there, they are installed or loaded into the secondary memory of a computer. At execution, they are loaded at least partially into the computer's primary electronic memory. The invention described herein includes these and other various types of computer-readable storage media when such media contain instructions or programs for implementing the steps described below in conjunction with a microprocessor or other data processor. The invention also includes the computer itself when programmed according to the methods and techniques described herein.

[00124] An x-ray spectrum obtained as described above can be stored in a portion of memory 222, such as the measured spectra memory portion 223. Data template memory portion 224 stores data templates, such as known spectra of elements or, in some embodiments, known diffraction patterns of materials. Weighing Factor Memory portion 225 stores weighting factor for each of the data templates, the weighting factors combining with the data templates to produce a calculated spectrum approximating the measured spectrum. The weighting factors correlated to the abundance in the sample of the element corresponding to the data template. Processor 220 uses the methods described above to minimize an error value which represents the different between the measured pattern and the combination of the data templates and weighting factors.

[00125] While the embodiment shown includes a scanning electron microscope, related embodiment could use a transmission electron microscope or a scanning transmission electron microscope to generate x-rays from the sample. An x-ray fluorescence system could also be used to generate x-rays from the sample. Other embodiments may detect other characteristic radiation, such as gamma rays, from a sample.

Conclusions

[00126] The compositions reported are affected by a number of factors outside of the algorithm of this engine. The definition of the standards used as pure elements was not defined. Although some elements standards, such as gold or iron can be measured directly, other elements must be derived from minerals because they cannot be measured directly. For example, oxygen is derived by measuring quartz (SiO_2) and silicon, and subtracting a portion of the silicon from the quartz spectrum. This is repeated for a large number of elements to create the full element list. Therefore, these derived elements may not be as accurate in their spectra or lifetime. Consequently, additional work is underway to improve the quality of the standards, irrespective of the algorithm presented here.

[00127] As used herein, the term spectrum includes any property that is represented by an intensity graph including for example, an x-ray or a diffraction pattern.

[00128] The present embodiments are to be considered in all respects to be illustrative and not restrictive.

WHAT IS CLAIMED IS:

1. A method of spectrum data analysis, the method comprising the steps of:

collecting a spectrum of an unknown material;

providing a set of element data templates;

approximating the spectrum with the element data templates by calculating least squares weights for the element data templates;

removing one or more of the element data templates having negative weights;

calculating an approximation of the spectrum with said one or more element data templates removed, said approximation including an initial error estimate;

iteratively removing an element data template from the calculated approximation of the spectrum and calculating new approximations of the spectrum with new weights for the remaining element data templates, said new approximations including new error estimates;

identifying a new approximation of the spectrum having a smallest new error estimate that is less than the initial error estimate; and

determining from the new element data template weights in the identified new approximation and properties of corresponding elements the relative abundance of the elements in the unknown material.

2. The method as claimed in claim 1, further comprising the steps of:

after calculating the approximation of the spectrum with said one or more element data templates having negative weights removed,

selecting one element of the approximation;

replacing said one element with an overlapping element;

calculating a candidate solution with the element data template of the overlapping element instead of the element data template of said one element, said candidate solution including a candidate error estimate;

determining whether the candidate error estimate for the candidate solution is less than the initial error estimate; and

storing the candidate solution as an updated approximation of the spectrum if the candidate error estimate is less than the initial error estimate.

3. The method as claimed in claim 2, wherein said one selected element is iteratively replaced with two or more overlapping elements.

4. An electron beam system programmed to perform the method as claimed in claim 1.

5. A method of spectrum data analysis of a sample, the method comprising:

collecting a spectrum of an unknown material;

providing a set of data templates, each data template corresponding to a spectrum of a specific material;

determining a first set of weighting factors to be applied to the data templates to approximate the spectrum, the weighting factors being determined by minimizing an error factor between the weighted data templates and the spectrum of the unknown material;

removing one or more of the data templates having a negative weighting factor;

calculating an approximation of the spectrum with said one or more data templates removed, said approximation including an initial error estimate;

iteratively removing a data template from the calculated approximation of the spectrum and calculating new approximations of the spectrum with new weighting factors from the remaining data templates, said new approximations including new error estimates;

identifying a new approximation of the spectrum having a smallest new error estimate that is less than the initial error estimate; and

determining from the new data template weighting factors for the identified new approximation and the properties of corresponding materials the relative abundance of the materials present in the unknown material.

6. The method of claim 5 in which determining a first set of weighting factors to be applied to the data templates to approximate the spectrum includes determining weighting factors using a minimal residual method to minimize the error factor.

7. The method of claim 5 in which each of the data templates corresponds to an element, a mineral or a combination of elements.

8. The method of claim 5 in which collecting a spectrum of an unknown material includes collecting an x-ray spectrum using energy dispersive spectroscopy and in which the set of data templates includes the x-ray spectrum for known materials.

9. The method of claim 5 further comprising:

substituting a pre-defined set of data templates corresponding to materials having spectral peaks that overlap spectral peaks of materials in the identified new approximation;

calculating a candidate approximation from the set of data templates with the substituted predefined set of data templates, said candidate approximation including candidate weighting factors and a candidate error estimate;

determining that the candidate error estimate is less than the smallest new error estimate corresponding to the new approximation; and

determining from the candidate weighting factors and the properties of corresponding materials the relative abundance of the materials in the unknown sample.

10. The method of claim 5 further comprising adjusting the weighting factors to remove the data template corresponding to oxygen if the weighting factor corresponding to the oxygen data template indicates that oxygen is present at less than five percent.

11. The method of claim 5 in which collecting a spectrum of an unknown material includes collecting an x-ray spectrum including less than 50,000 counts.

12. The method of claim 5 in which collecting a spectrum of an unknown material includes collecting an x-ray spectrum from an energy dispersive x-ray spectrometer in less than 100 ms.

13. The method of claim 5 further comprising determining whether pre-specified pairs of data templates are present in the new approximation and removing the data template of the pair having the lesser concentration in the new approximation if the lesser concentration is less than a pre-specified value.

14. The method of claim 5 further comprising determining a weight percentage of materials present in the unknown material from ratios of at least one peak of each material.

15. An apparatus for determining the elemental composition of a sample, comprising:

a source of an electron beam for impinging on a sample;

an x-ray detector for detecting x-rays emitted from the sample upon impingement of the electron beam;

computer memory for:

accumulating information from the x-ray detector to determine an x-ray spectrum of the sample;

storing data templates corresponding to elements;

storing a computer program including instructions for:

determining a set of first set of weighting factors to be applied to the data templates to approximate the sample spectrum, the weighting factors being determined by minimizing an error factor between the weighted data templates and the sample spectrum;

removing one or more of the data templates having a negative weighting factor in approximating the sample spectrum;

calculating an approximation of the spectrum with said one or more data templates removed, said approximation including an initial error estimate;

iteratively removing an element data template from the calculated approximation of the spectrum and calculating new approximations of the spectrum with new weighting factors from the remaining element data templates, said new approximations including new error estimates;

identifying a new approximation having a smallest new error estimate that is less than the initial error estimate; and

determining from the new weighting factors from the identified new approximation and the properties of elements corresponding to the element data templates in the new approximation the relative abundance of the elements in the sample; and

a processor for executing the computer instructions to determine the composition of the sample.

16. A computer readable media comprising computer readable instructions for:

determining a set of first set of weighting factors to be applied to a set of data templates to approximate a spectrum of an unknown material, the weighting factors being determined by minimizing an error factor between the weighted element data templates and the spectrum;

removing one or more of the templates having a negative weighting factor in approximating the spectrum;

calculating an approximation of the spectrum with said one or more data templates removed, said approximation including an initial error estimate;

iteratively removing a data template from the calculated approximation of the spectrum and calculating new approximations of the spectrum with new weighting factors from the remaining data templates, said new approximations including new error estimates;

identifying a new approximation having a smallest new error estimate **that is less than the initial error estimate; and**

determining from the new weighting factors from the identified new approximation and the properties of elements corresponding to the data templates in the new approximation the relative abundance of the elements in the unknown material.

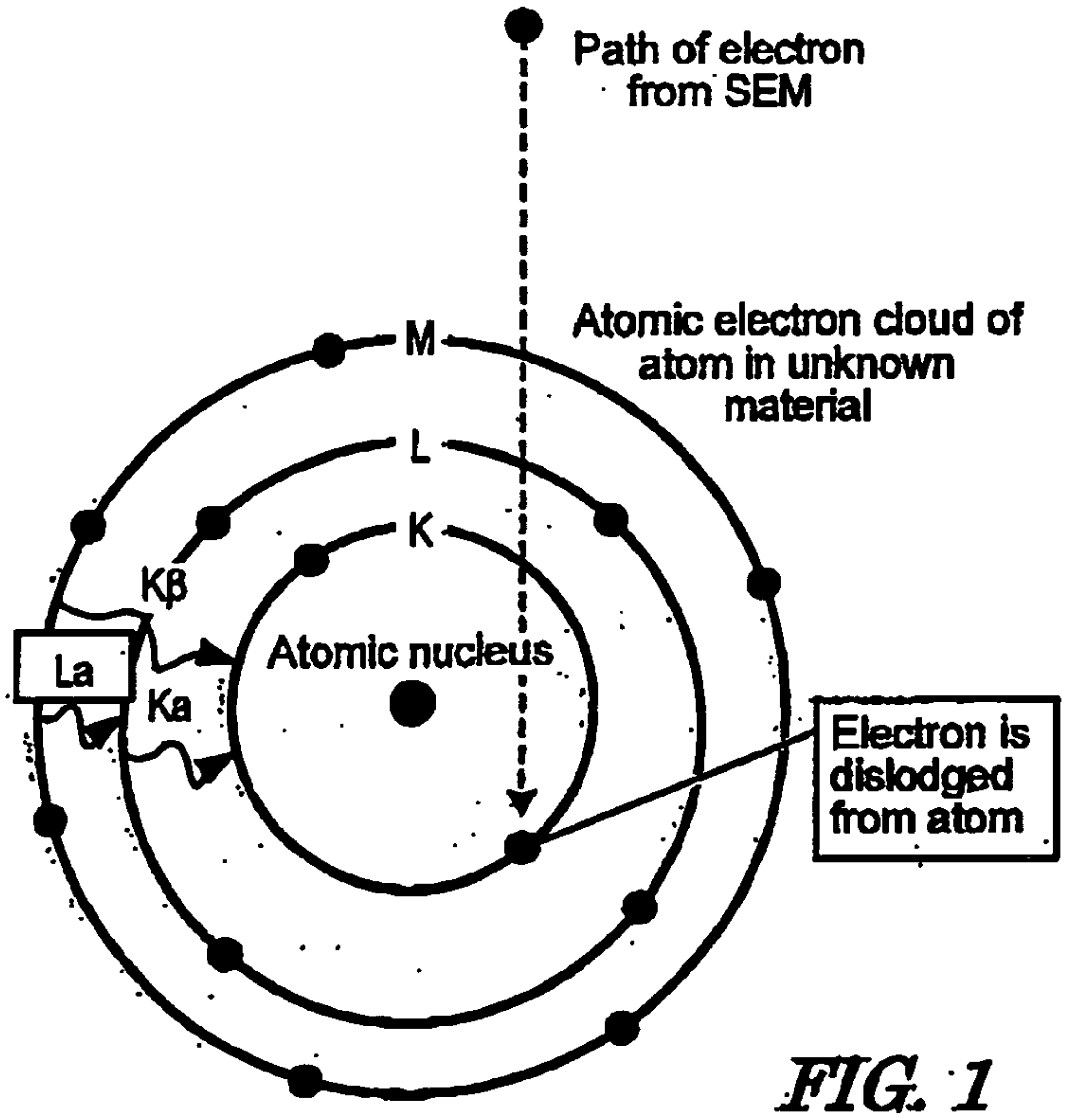

Path of electron from SEM
Atomic electron cloud of atom in unknown material
M
L
K
Kβ
La
Ka
Atomic nucleus
Electron is dislodged from atom

FIG. 1

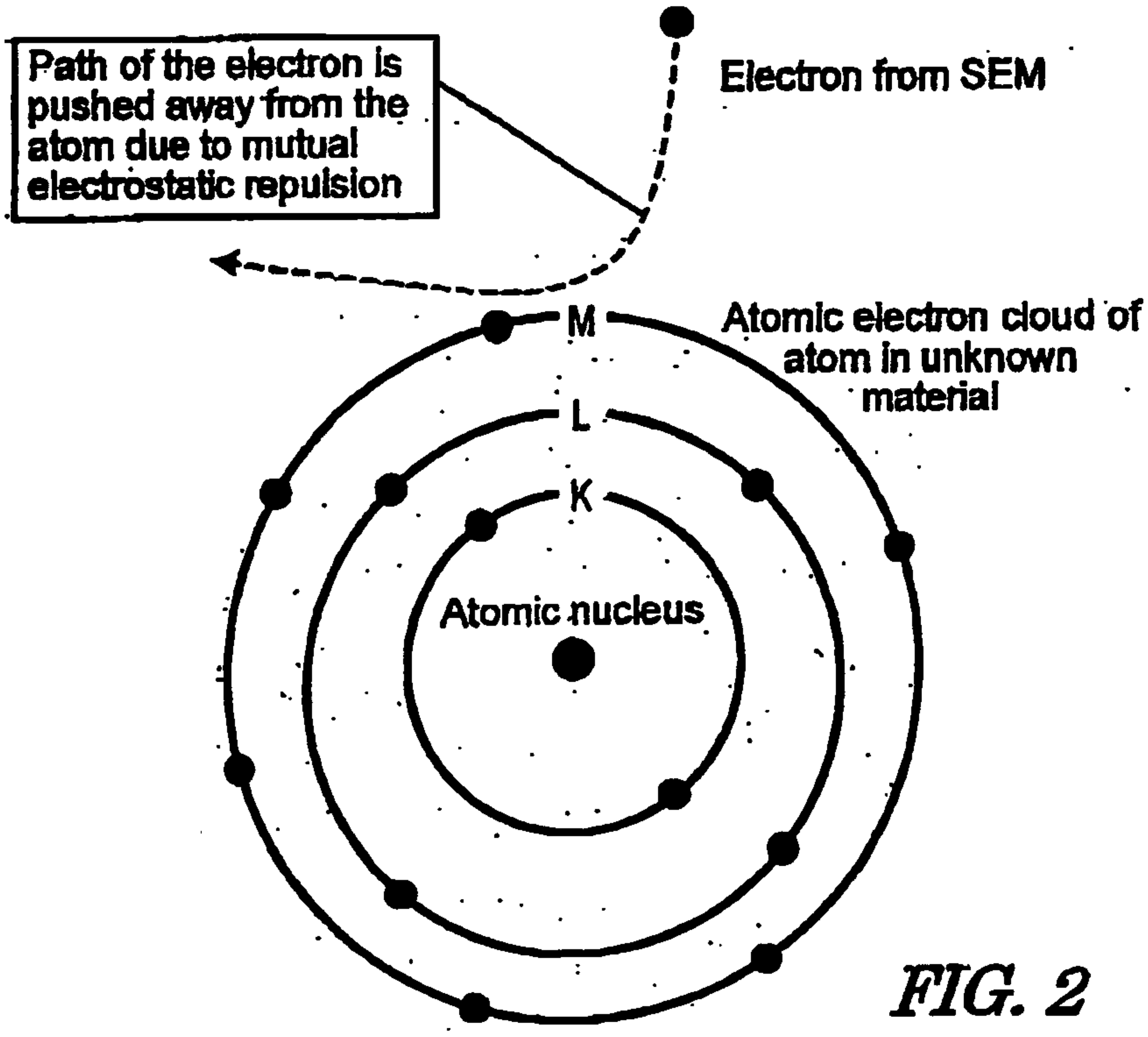

Path of the electron is pushed away from the atom due to mutual electrostatic repulsion
Electron from SEM
Atomic electron cloud of atom in unknown material
M
L
K
Atomic nucleus

FIG. 2

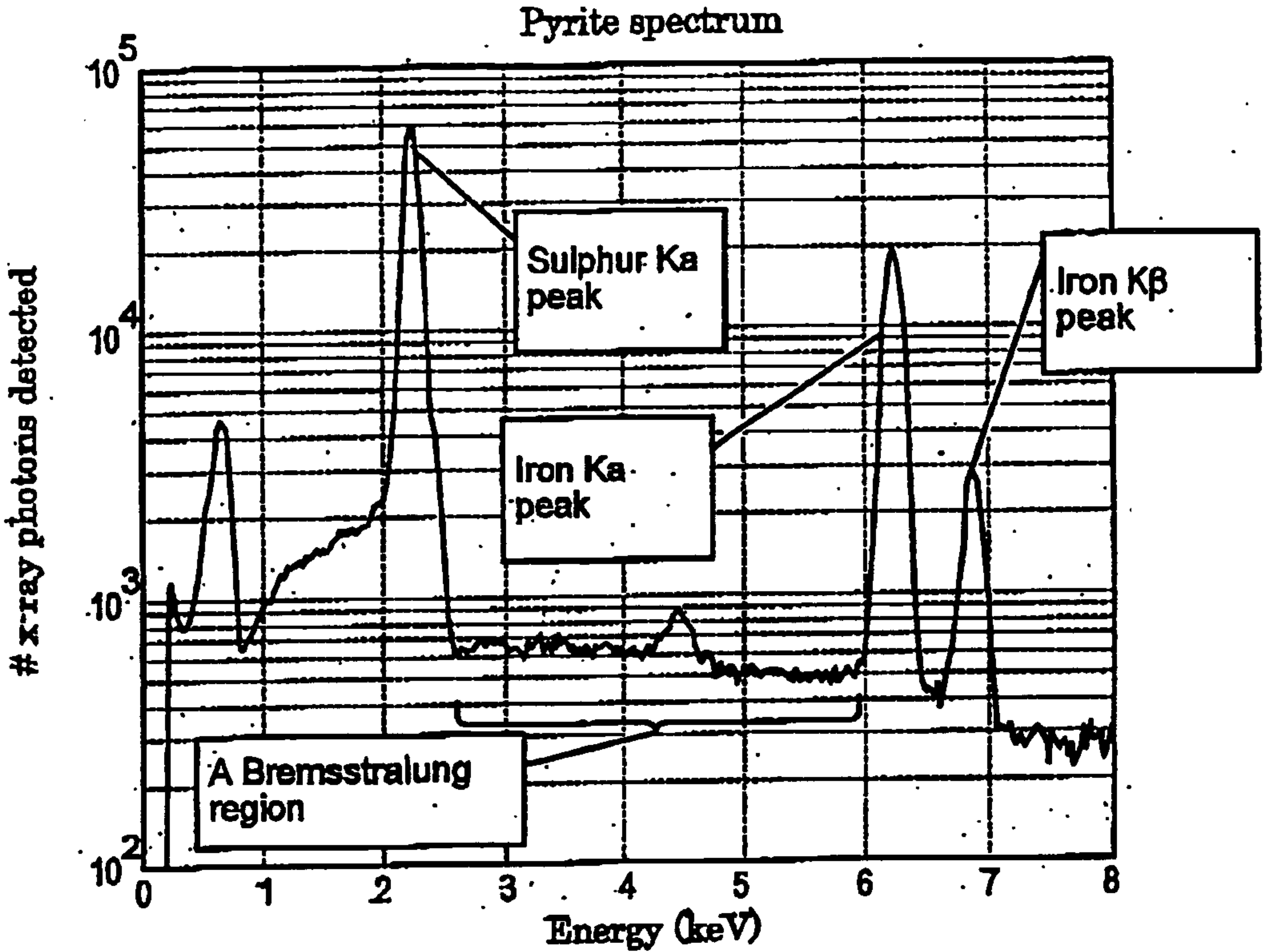

Pyrite spectrum
x-ray photons detected
10^5
10^4
10^3
10^2
0
1
2
3
4
5
6
7
8
Energy (keV)
Sulphur Ka peak
Iron Kβ peak
Iron Ka peak
A Bremsstralung region

FIG. 3

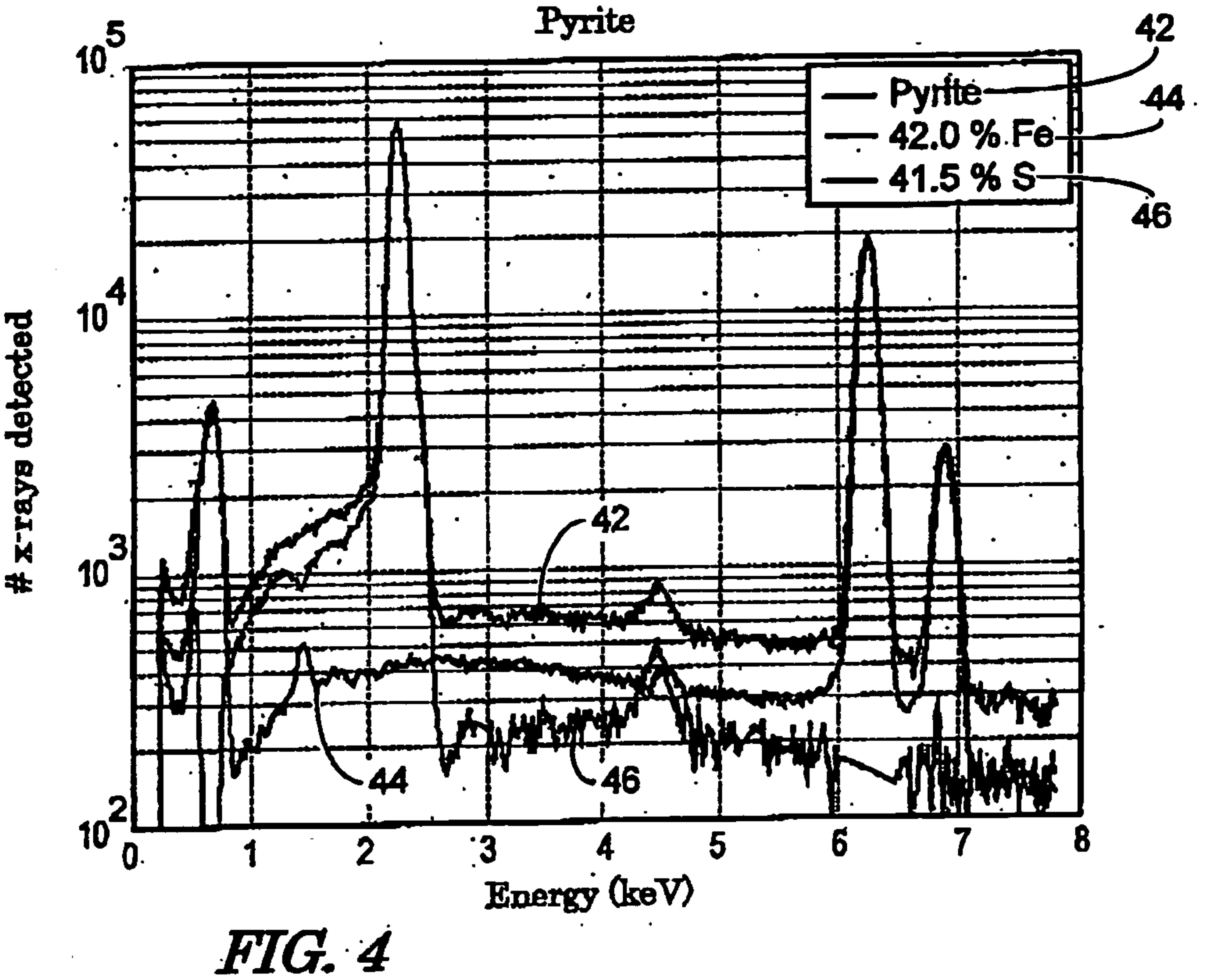

Pyrite
x-rays detected
10^5
10^4
10^3
10^2
0
1
2
3
4
5
6
7
8
Energy (keV)
Pyrite
42.0 % Fe
41.5 % S
42
44
46
42
44
46

FIG. 4

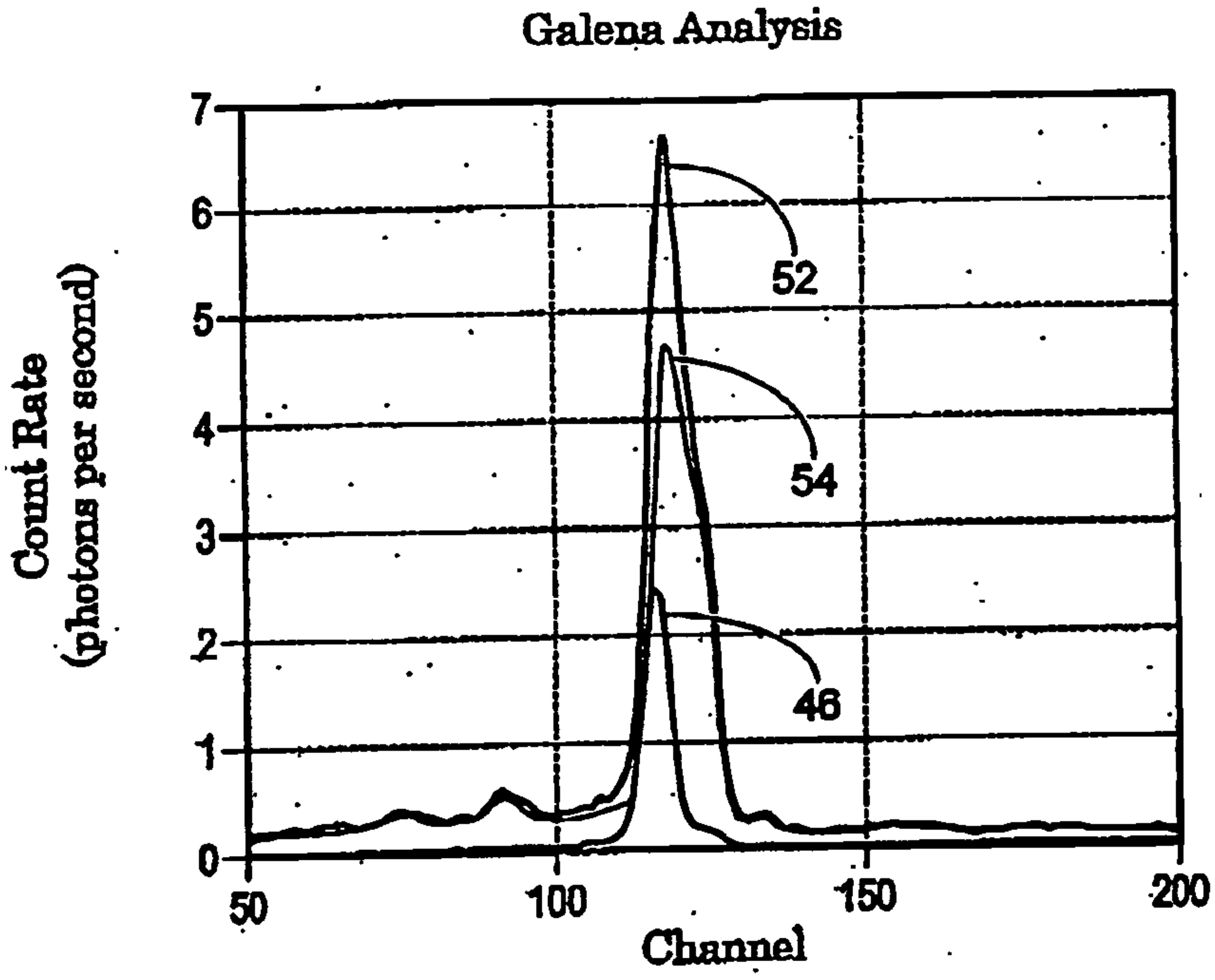

Galena Analysis
Count Rate (photons per second)
7
6
5
4
3
2
1
0
50
100
150
200
Channel
52
54
46

FIG. 5

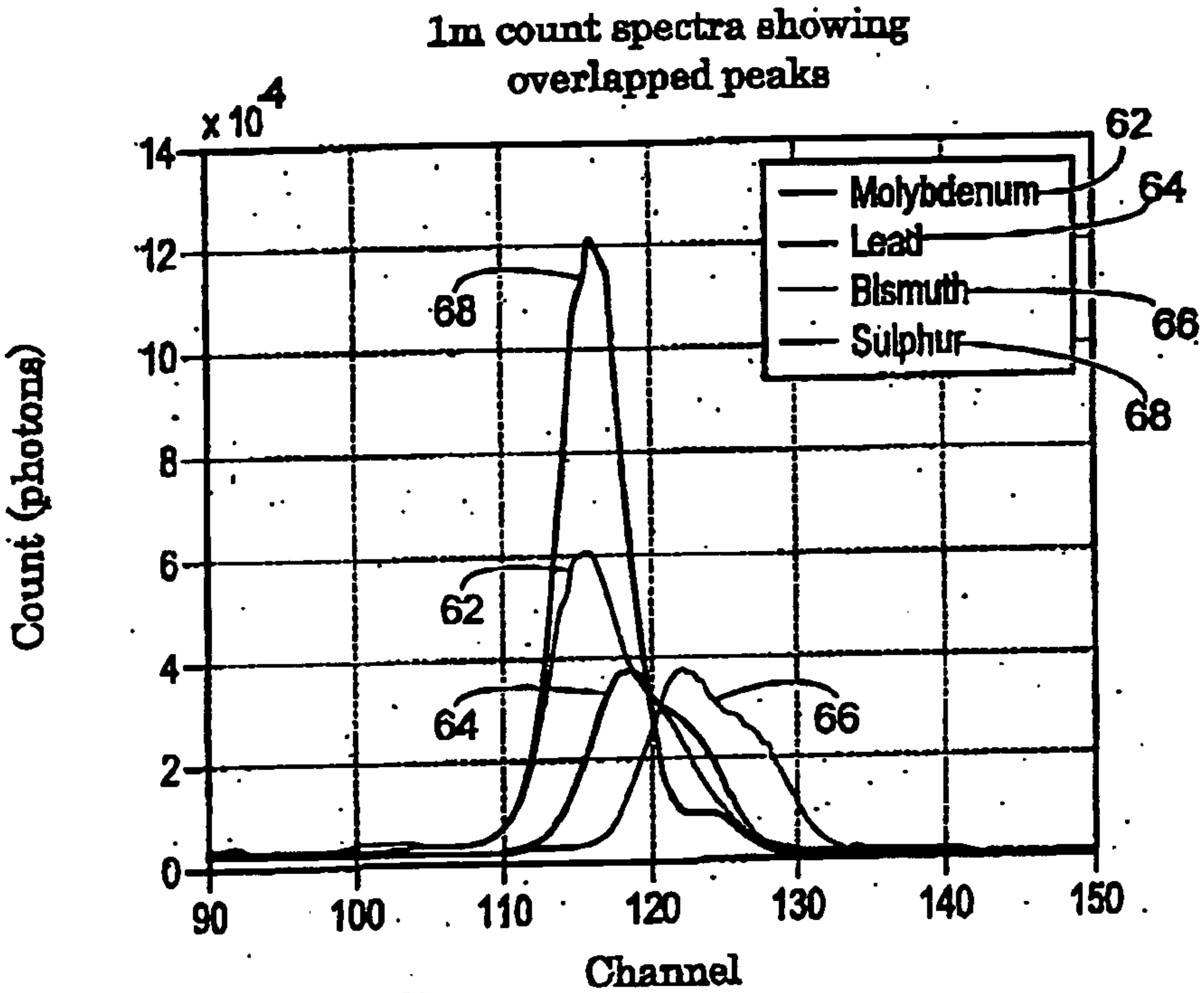

1m count spectra showing overlapped peaks
x 10^4
Count (photons)
14
12
10
8
6
4
2
0
90
100
110
120
130
140
150
Channel
Molybdenum
Lead
Bismuth
Sulphur
62
64
66
68
68
62
64
66

FIG. 6

Zirconium / Platinum overlapping peak

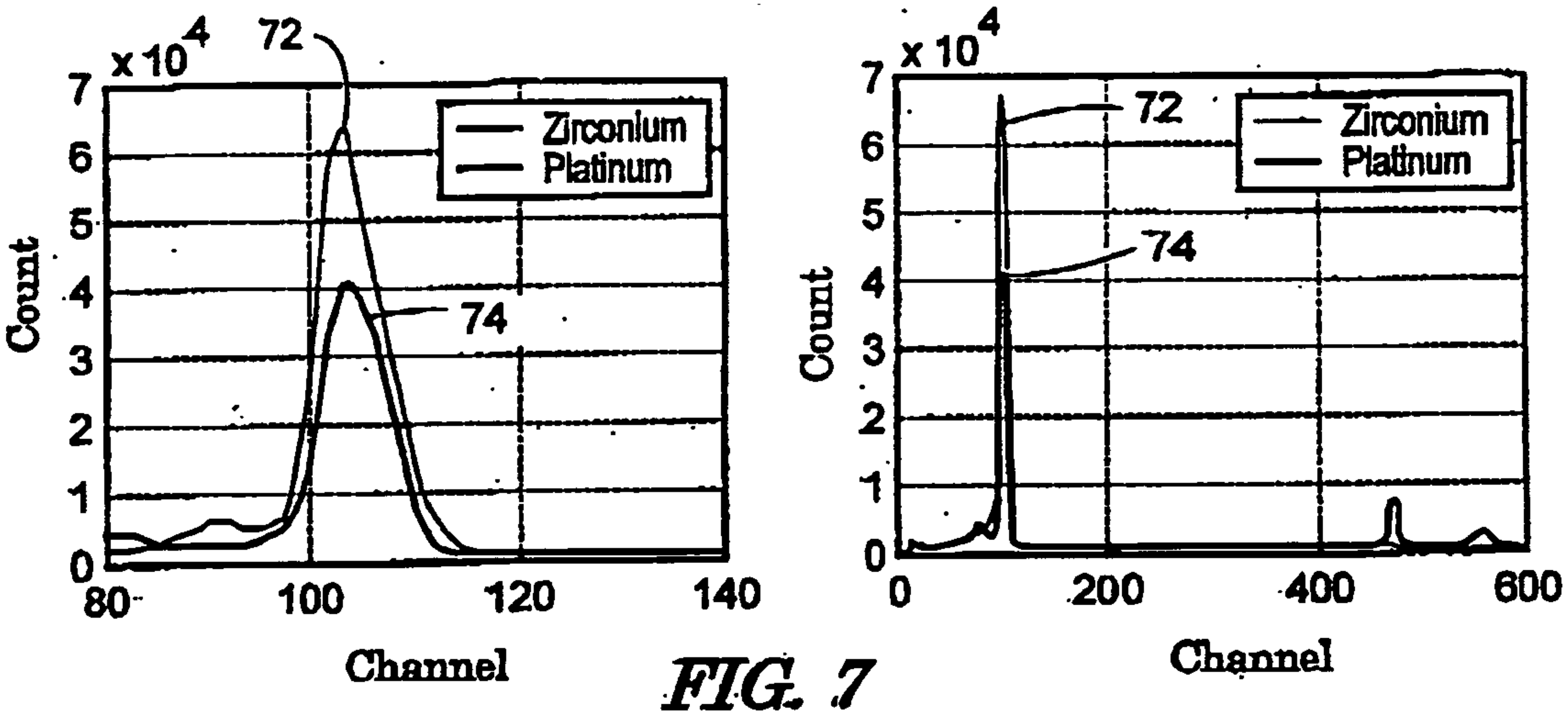


FIG. 7

Sodium / Zinc overlapping peak

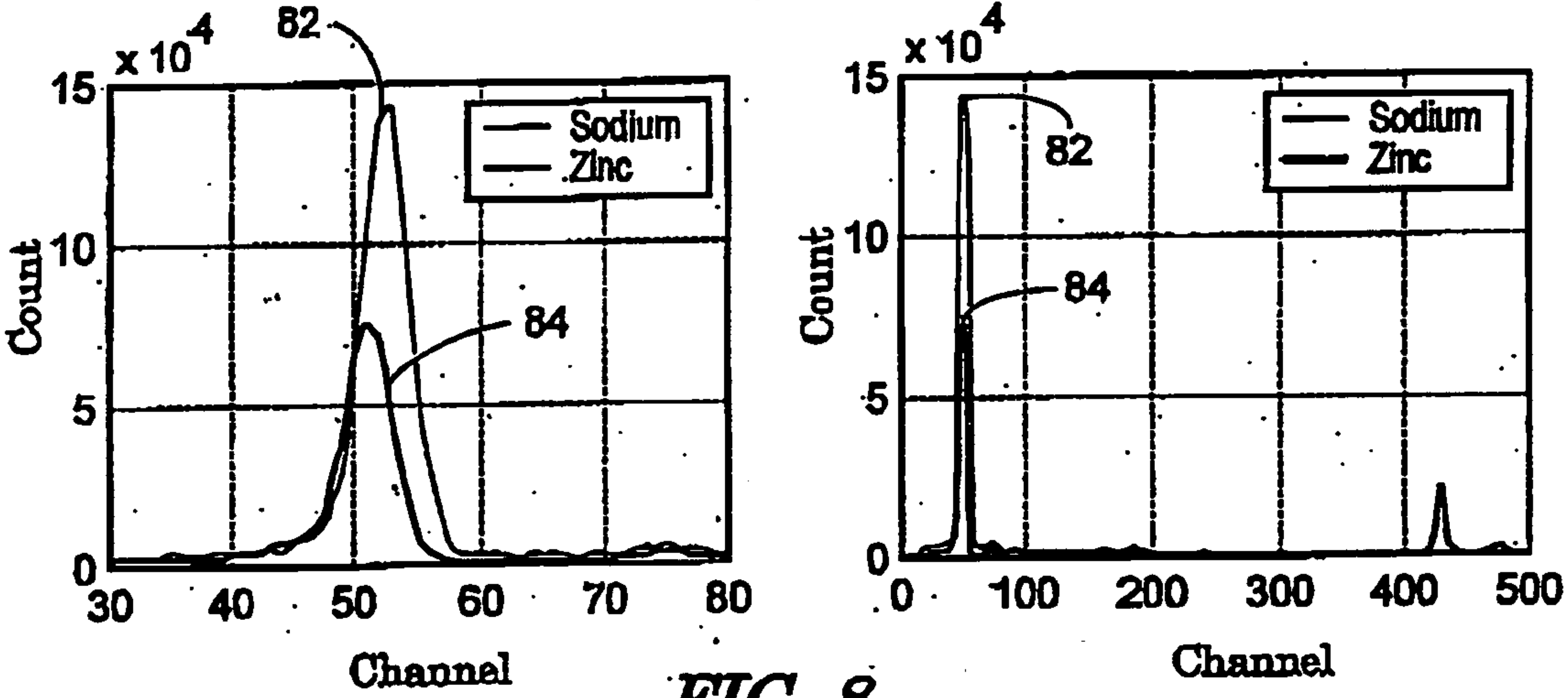


FIG. 8

Aluminium / Bromine overlapping peak

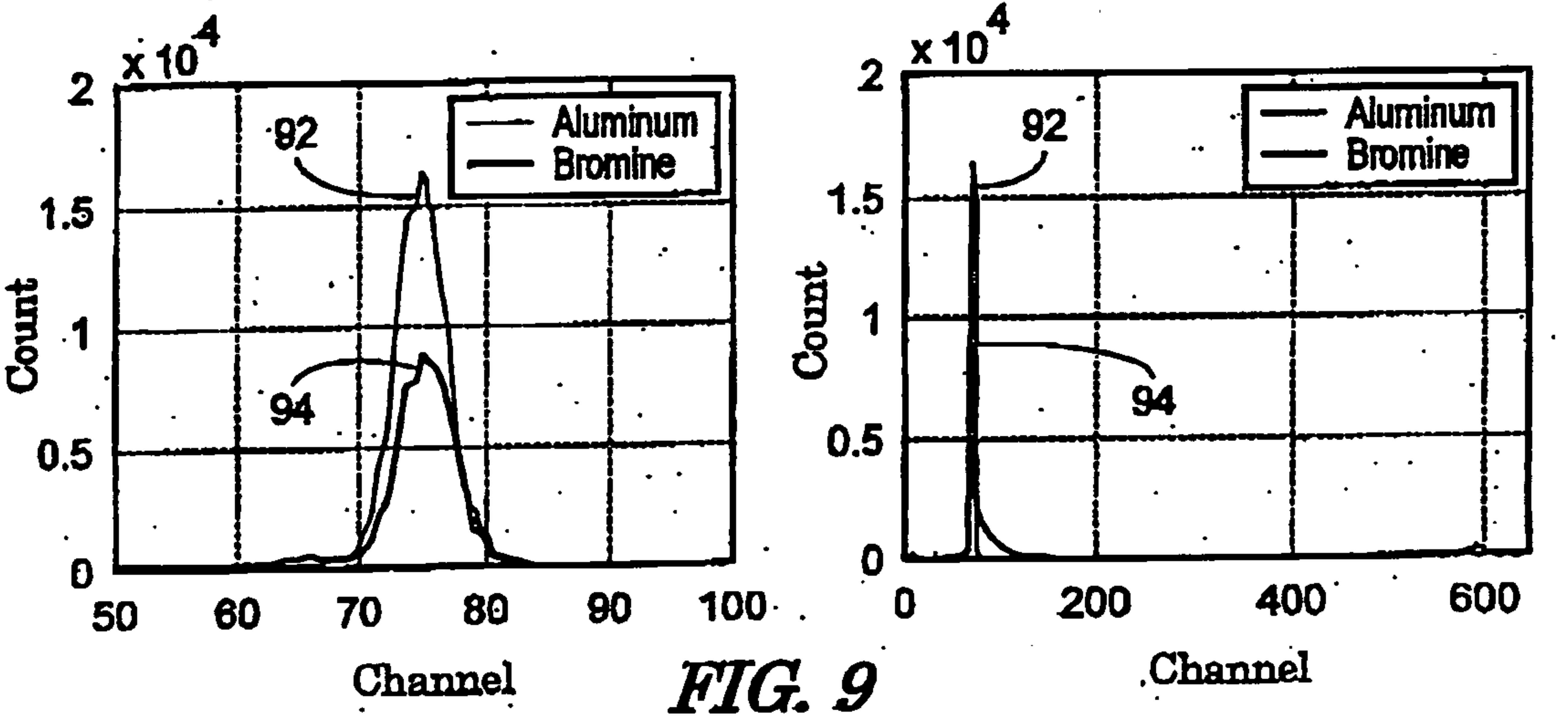


FIG. 9

Cadmium / Uranium overlapping peak

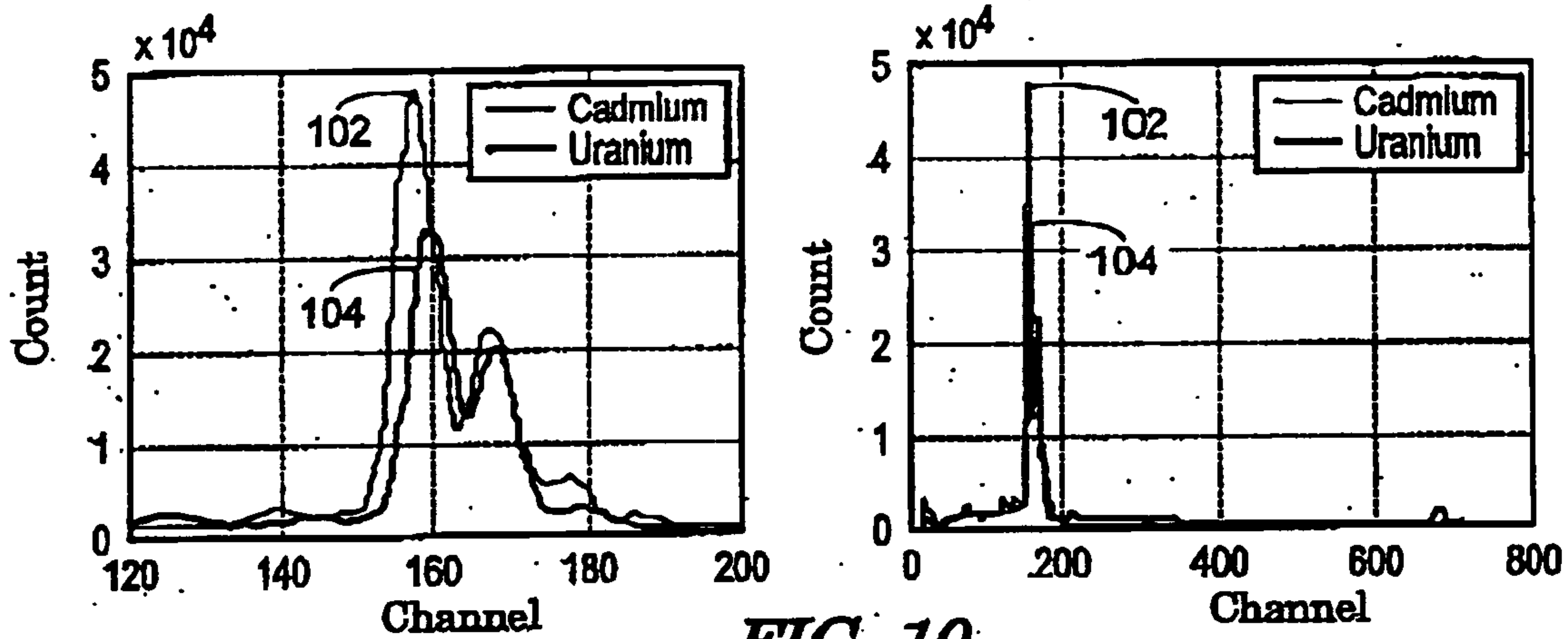


FIG. 10

Silver / Thorium overlapping peak

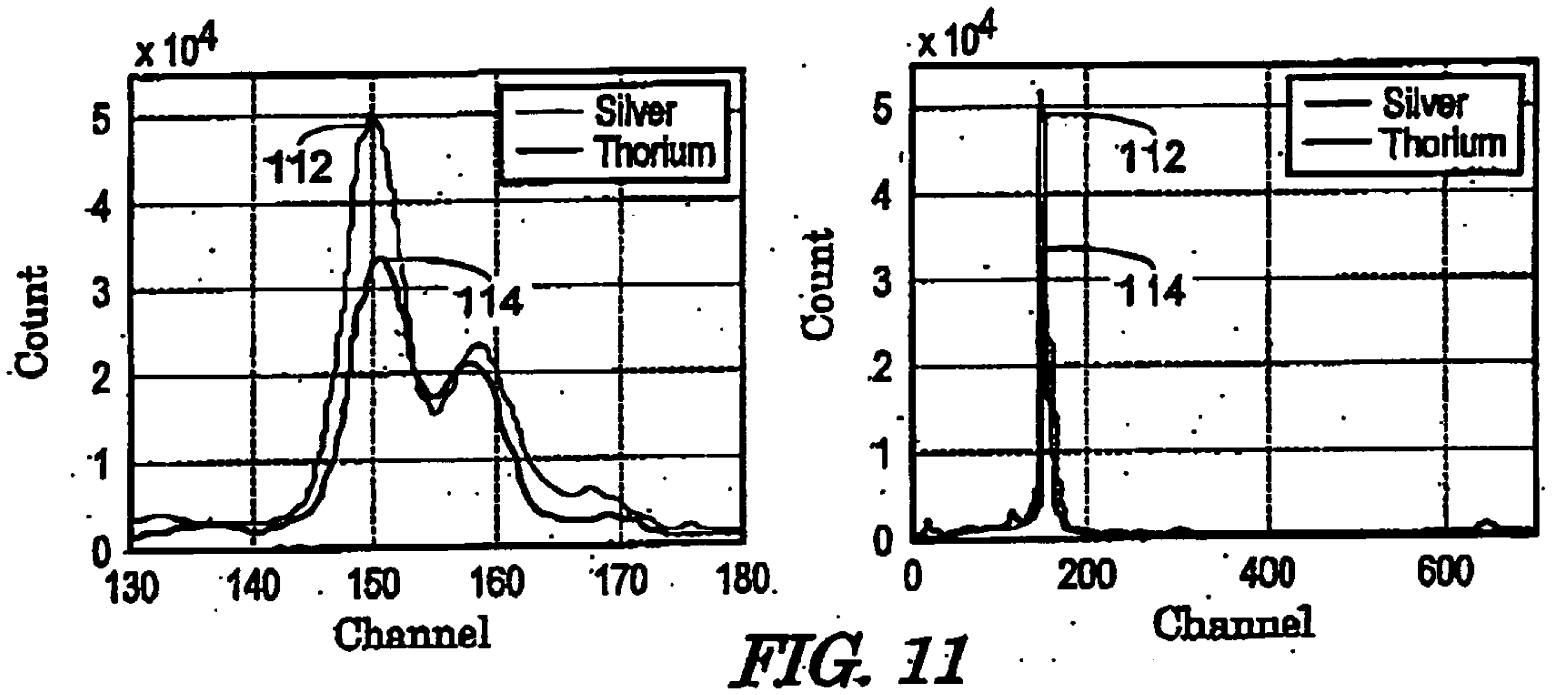


FIG. 11

Yttrium / Iridium overlapping peak

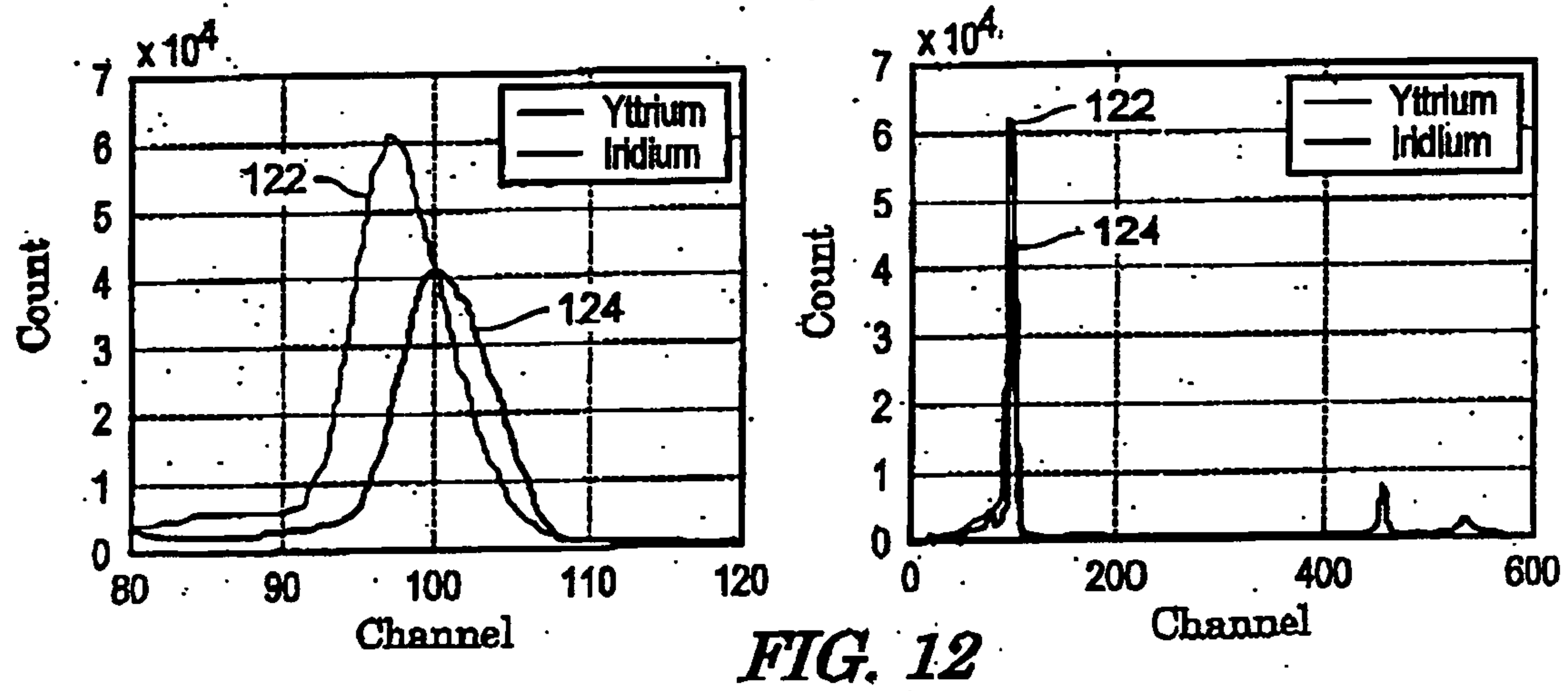


FIG. 12

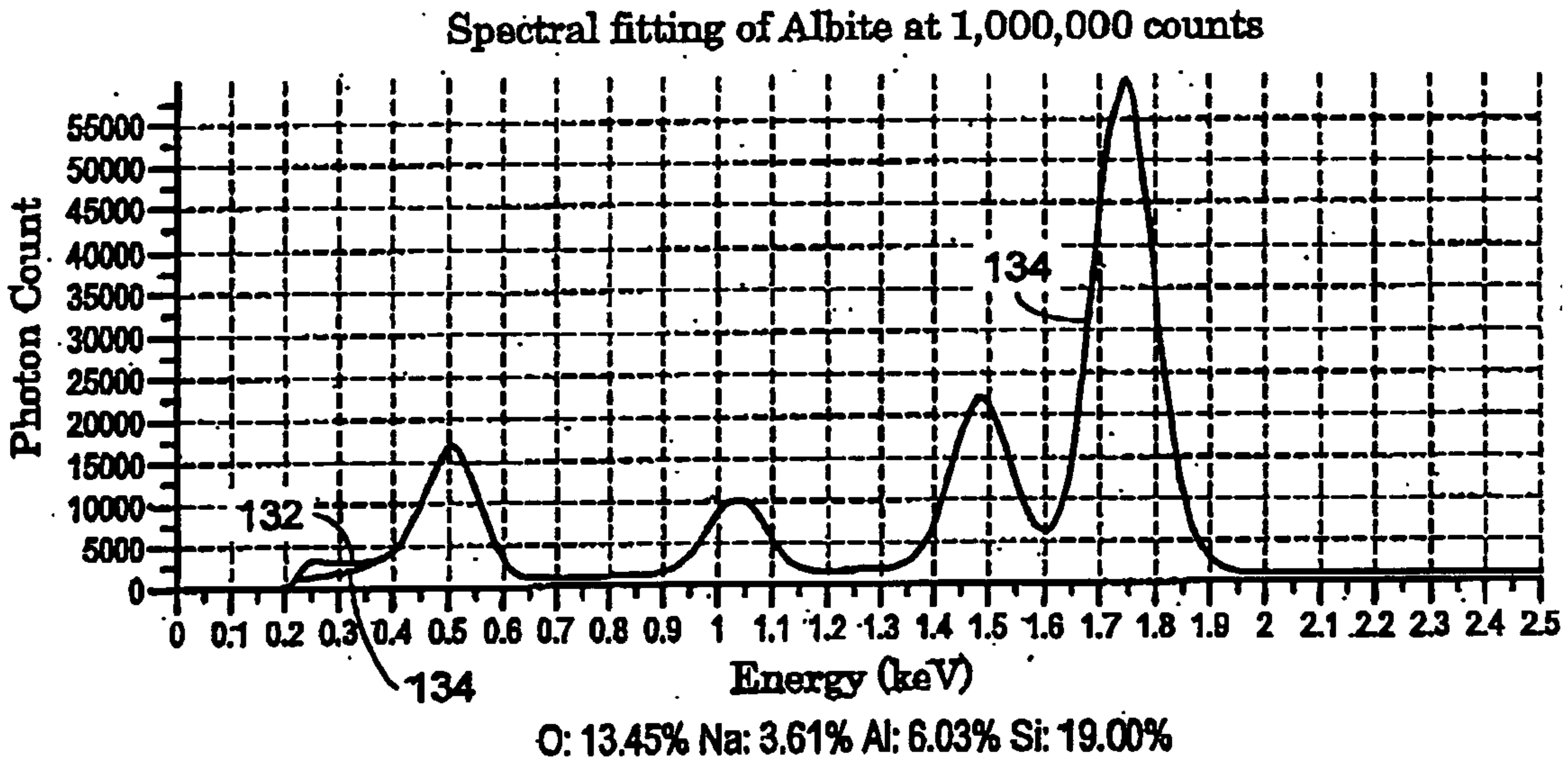

Spectral fitting of Albite at 1,000,000 counts
Photon Count
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2 2.1 2.2 2.3 2.4 2.5
Energy (keV)
132
134
134
O: 13.45% Na: 3.61% Al: 6.03% Si: 19.00%

FIG. 13

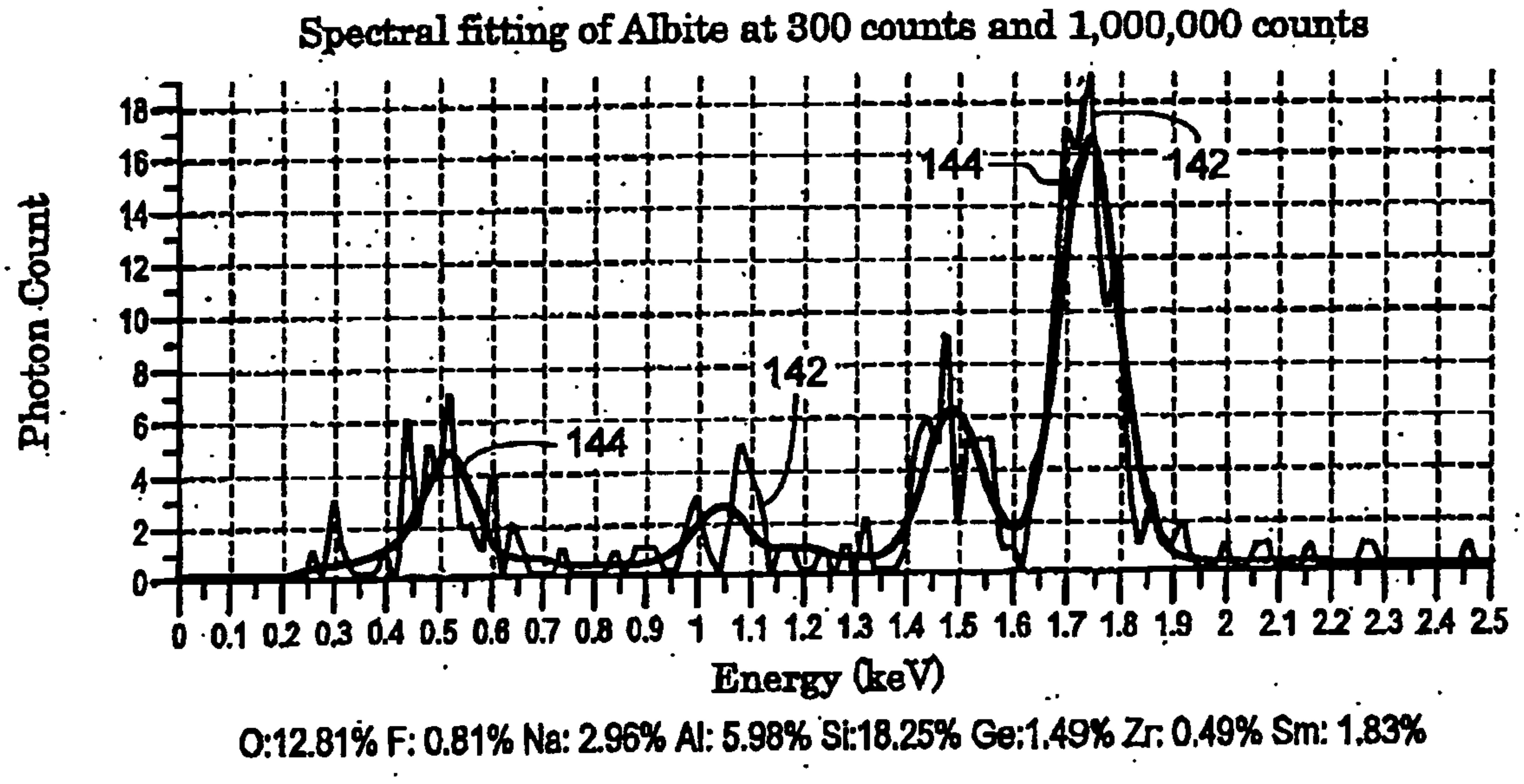

Spectral fitting of Albite at 300 counts and 1,000,000 counts
Photon Count
18
16
14
12
10
8
6
4
2
0
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2 2.1 2.2 2.3 2.4 2.5
Energy (keV)
144
142
142
144
O:12.81% F: 0.81% Na: 2.96% Al: 5.98% Si:18.25% Ge:1.49% Zr: 0.49% Sm: 1.83%

FIG. 14

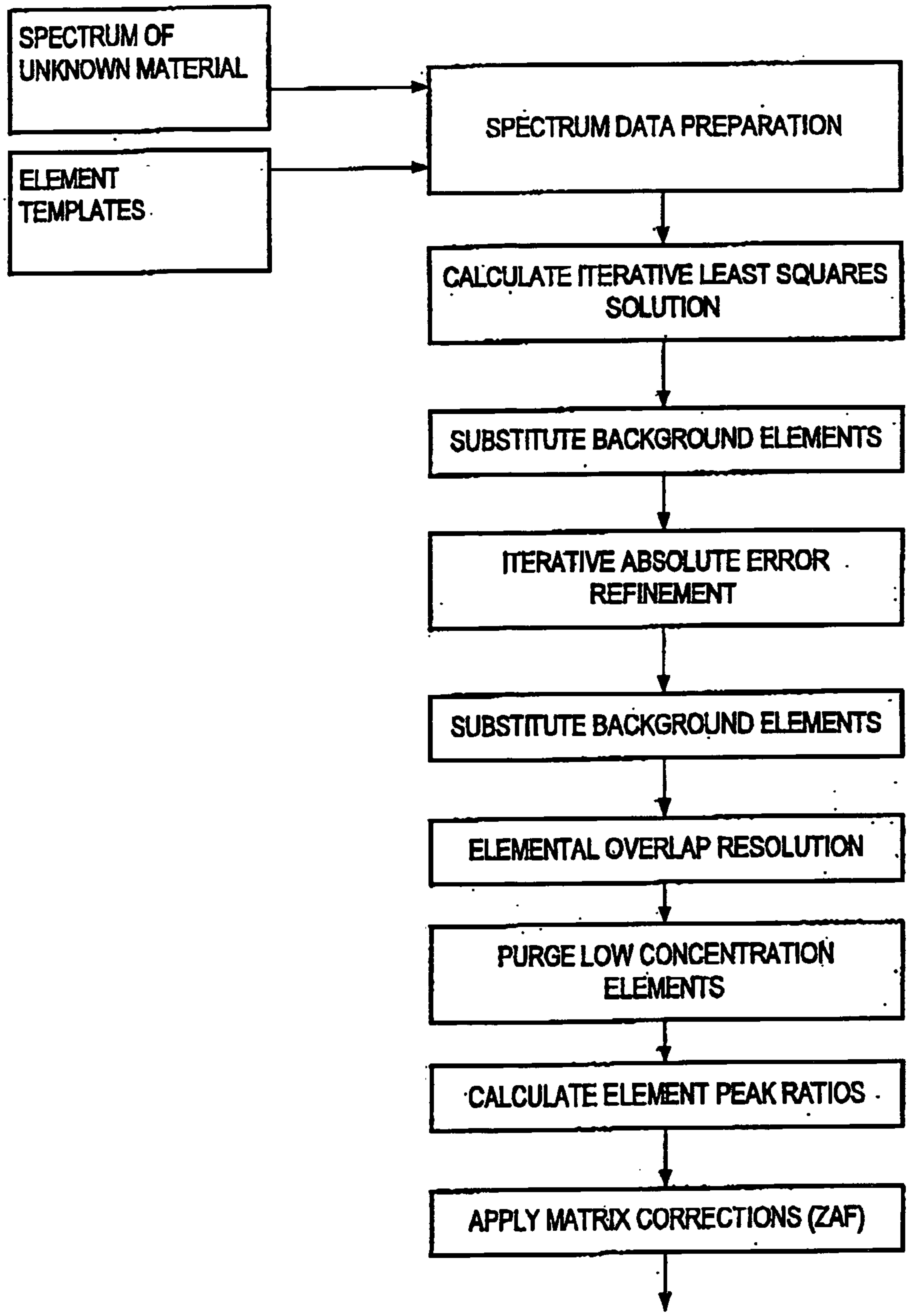


FIG. 15

High Level Iterative Least Squares Algorithm

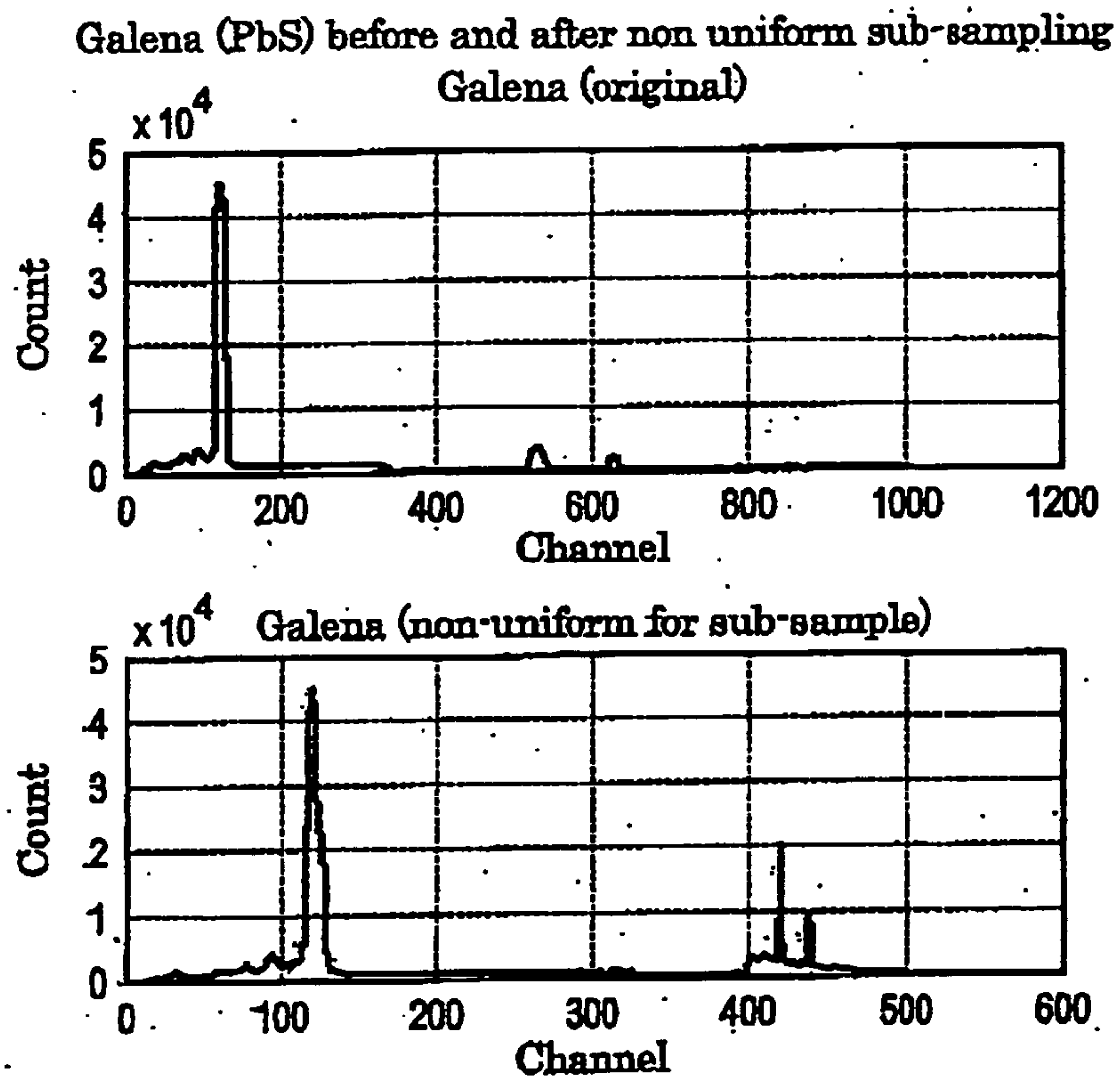

Galena (PbS) before and after non uniform sub-sampling
Galena (original)
x 10^4
5
4
3
2
1
0
Count
0
200
400
600
800
1000
1200
Channel
x 10^4 Galena (non-uniform for sub-sample)
5
4
3
2
1
0
Count
0
100
200
300
400
500
600
Channel

FIG. 16

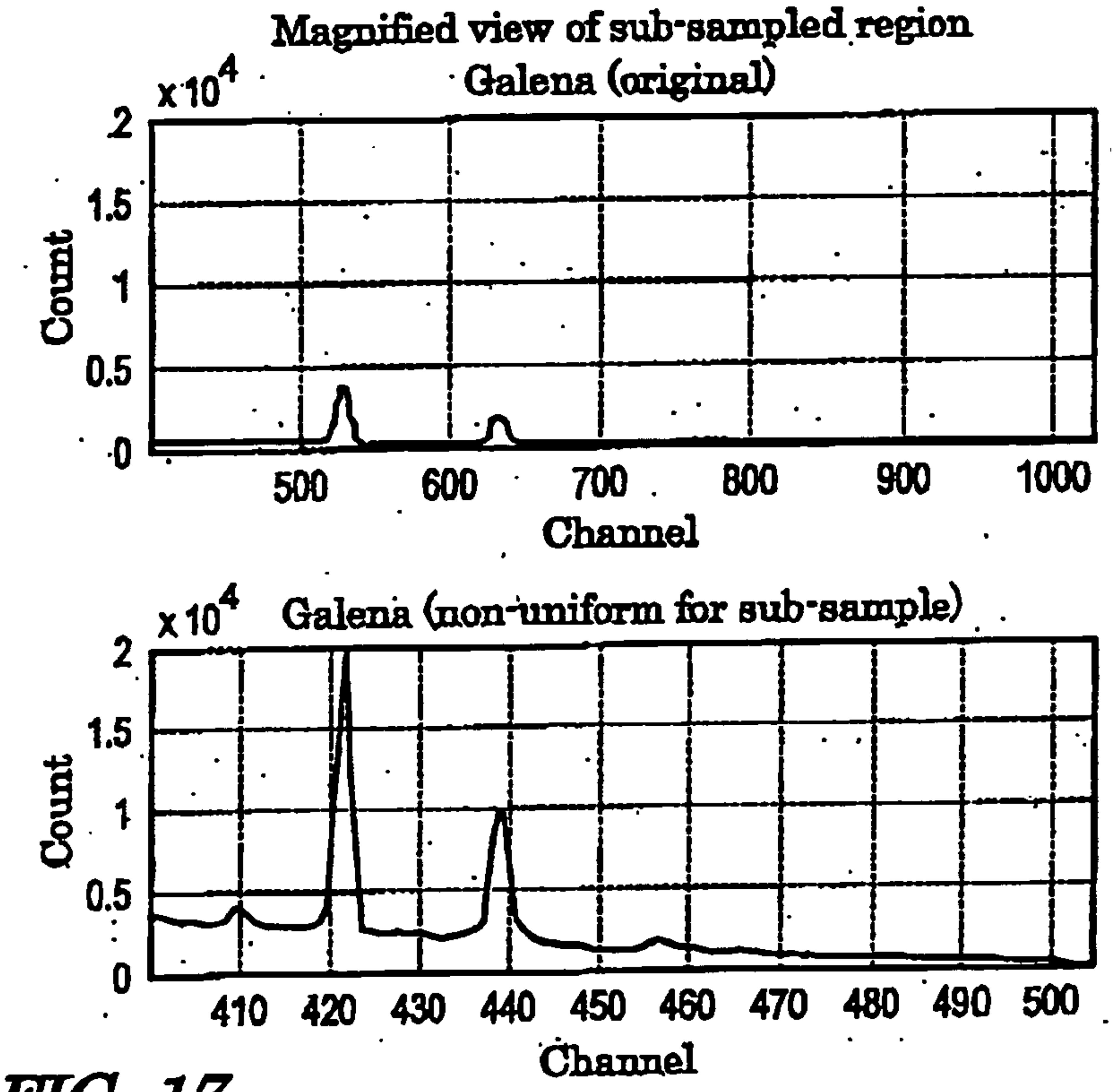

Magnified view of sub-sampled region
Galena (original)
x 10^4
2
1.5
1
0.5
0
Count
500
600
700
800
900
1000
Channel
x 10^4 Galena (non-uniform for sub-sample)
2
1.5
1
0.5
0
Count
410
420
430
440
450
460
470
480
490
500
Channel

FIG. 17

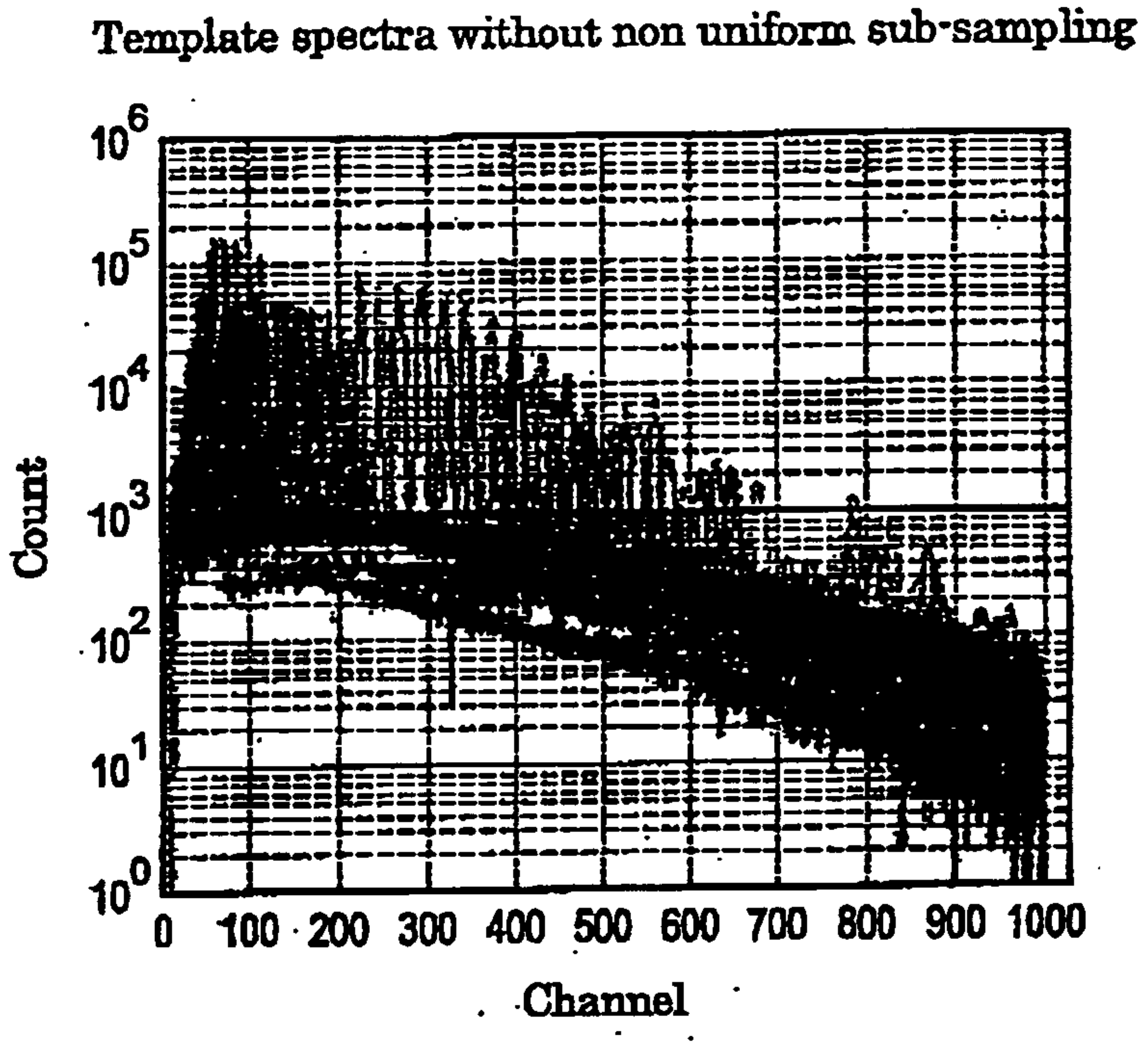

Template spectra without non uniform sub-sampling
Count
10^6
10^5
10^4
10^3
10^2
10^1
10^0
0
100
200
300
400
500
600
700
800
900
1000
Channel

FIG. 18

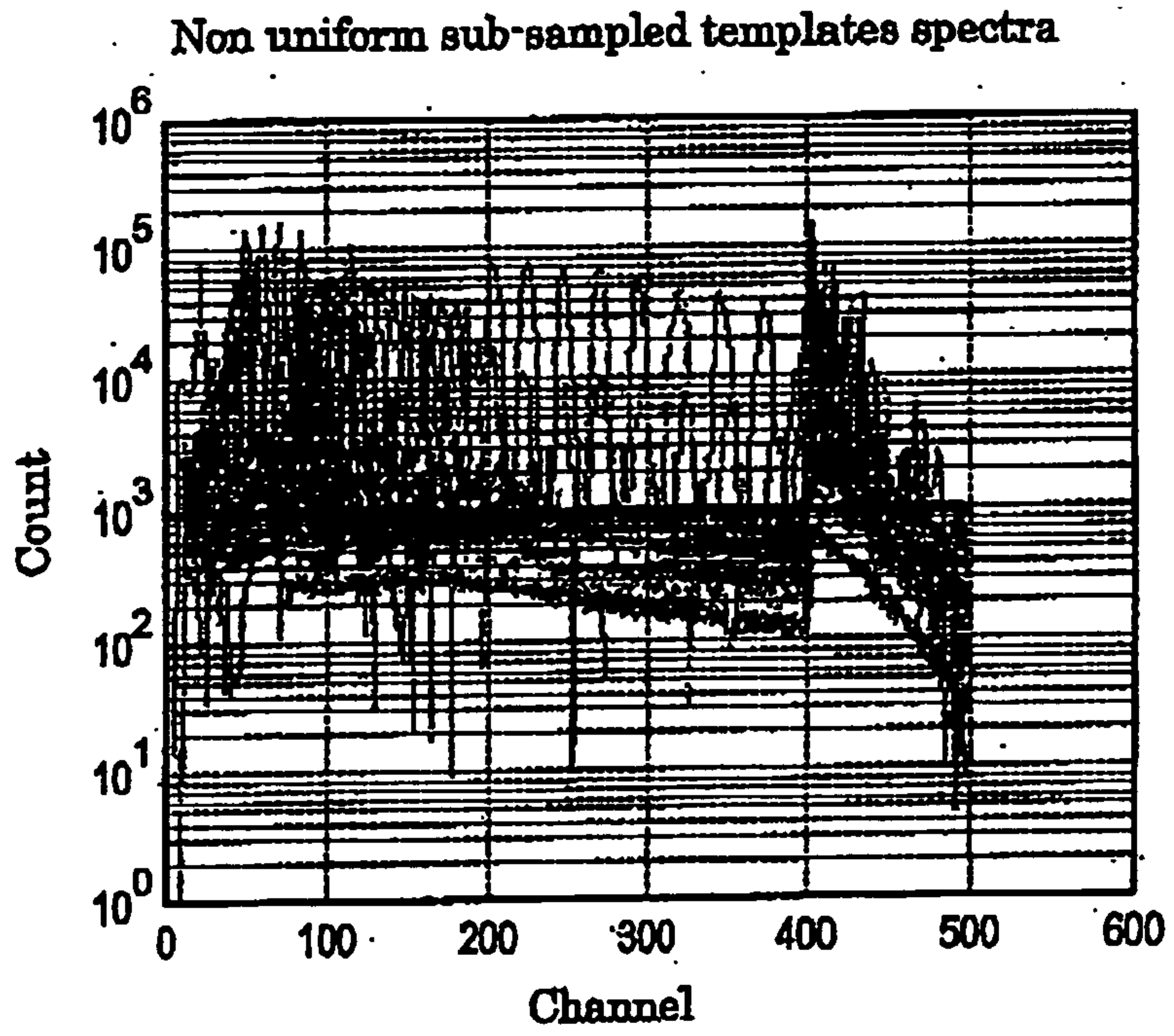
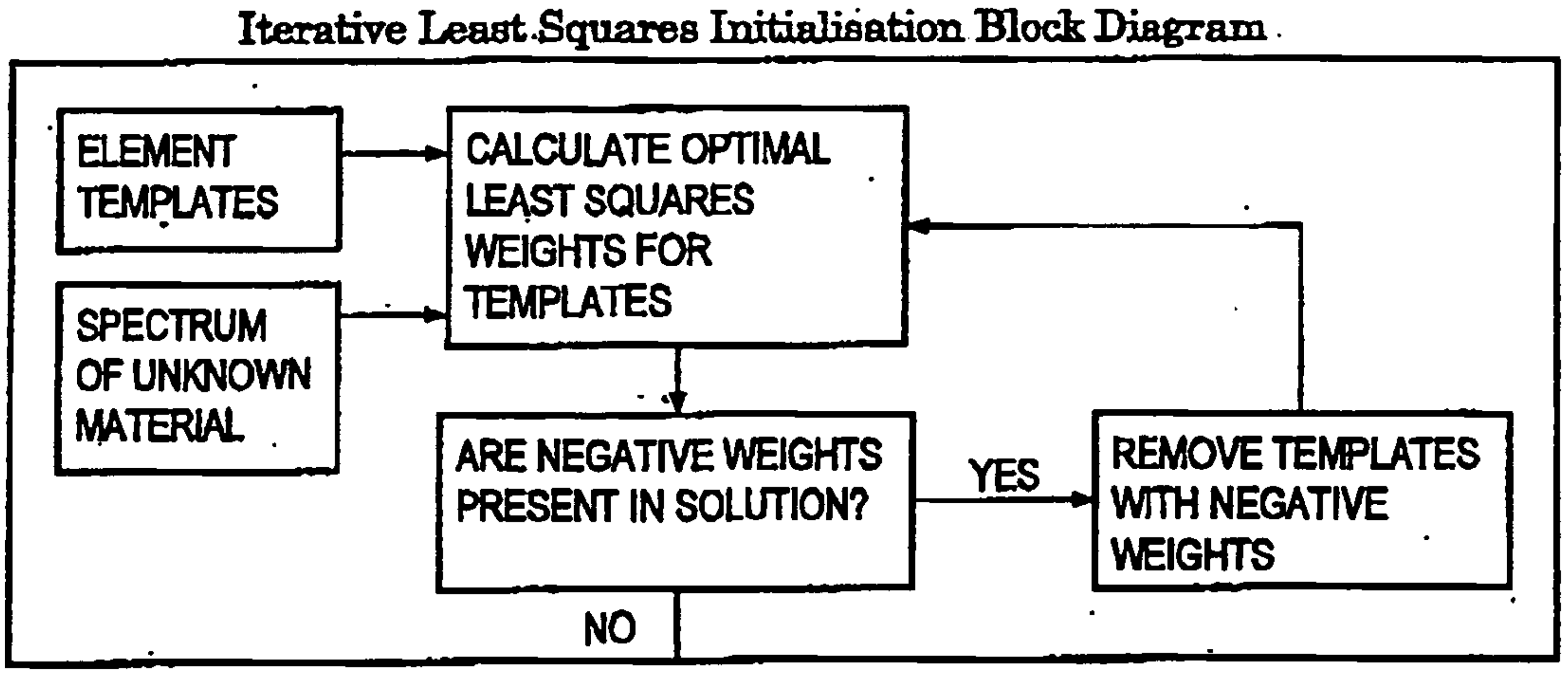
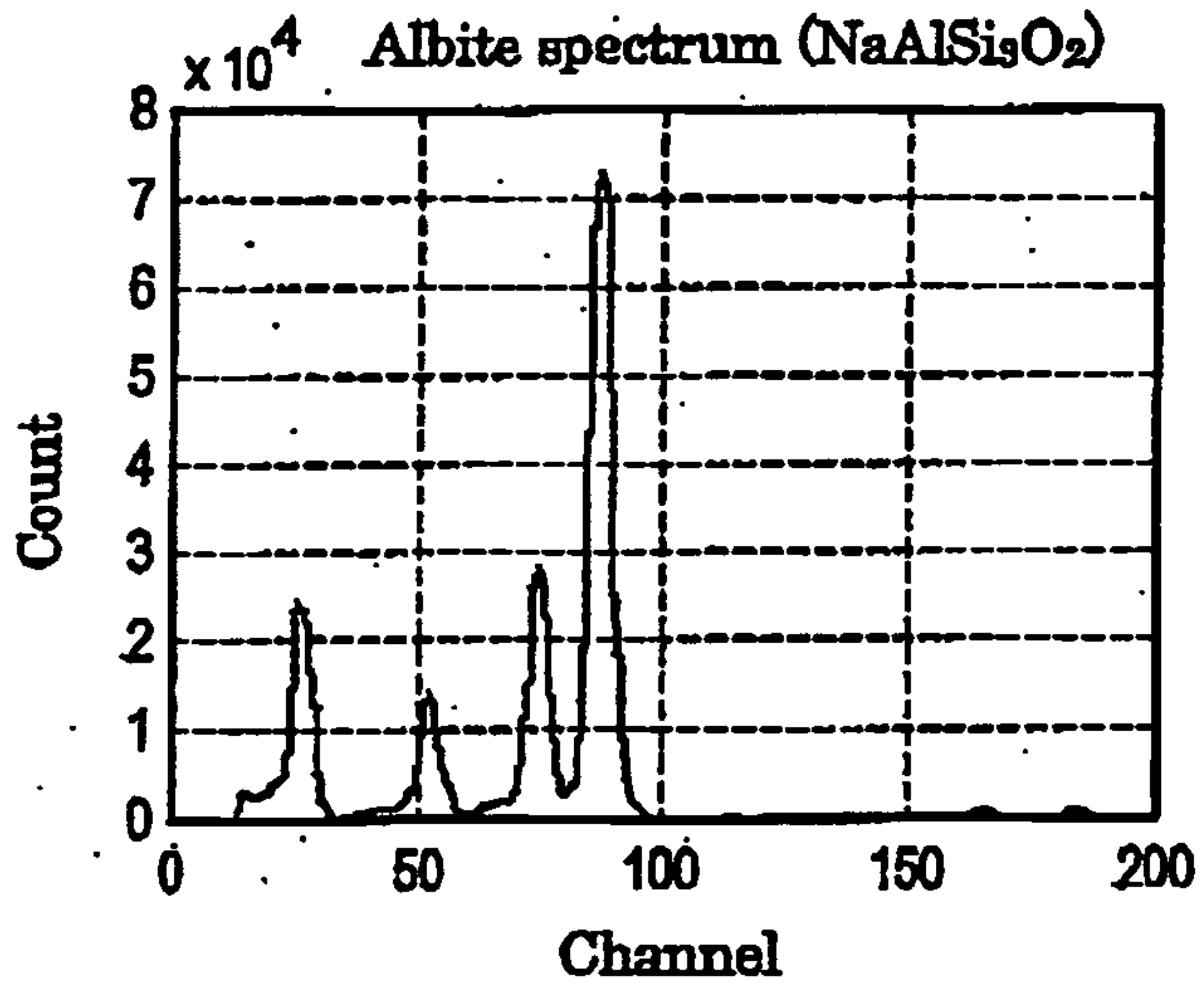

Non uniform sub-sampled templates spectra
Count
10^6
10^5
10^4
10^3
10^2
10^1
10^0
0
100
200
300
400
500
600
Channel

FIG. 19



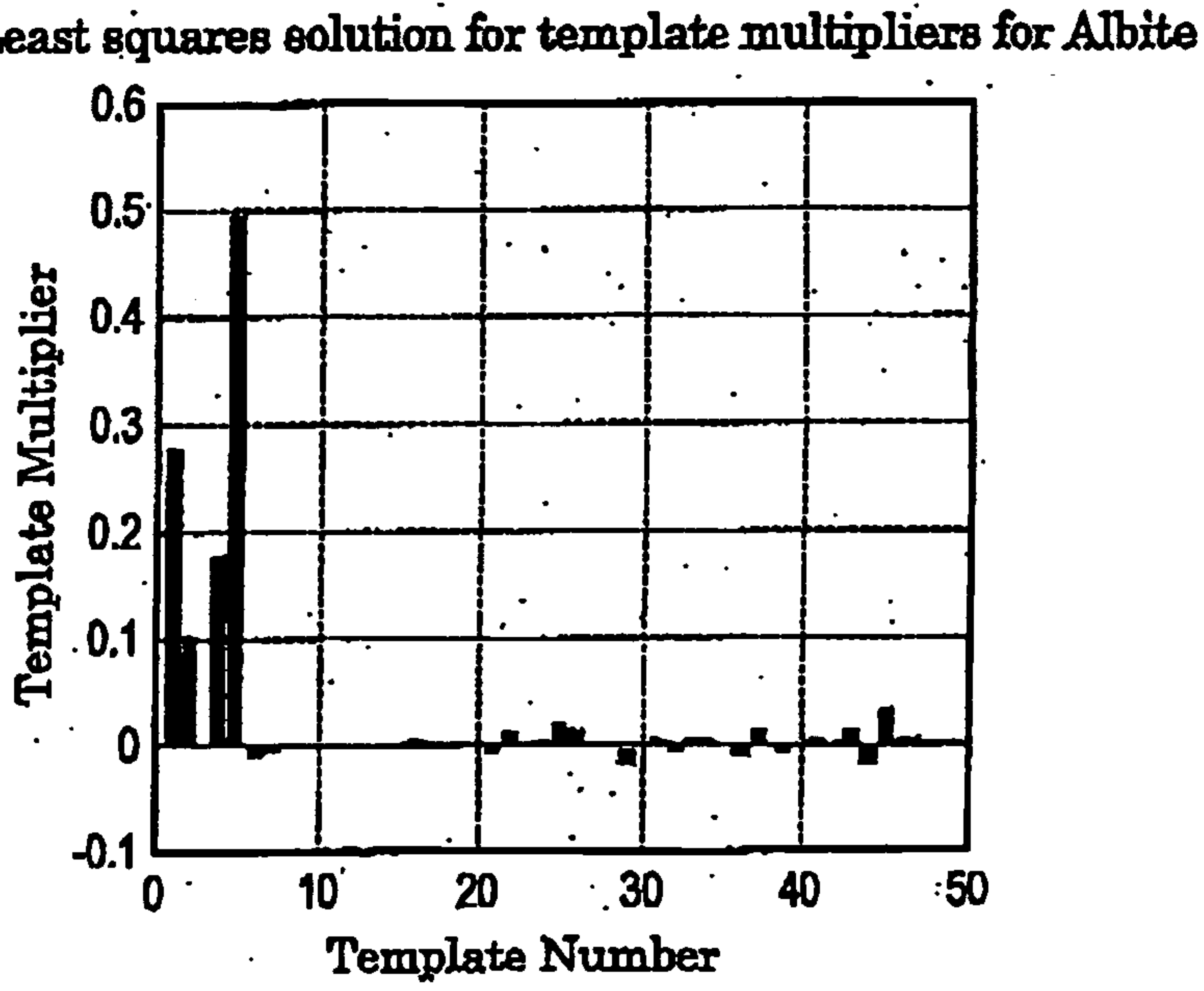
Iterative Least Squares Initialisation Block Diagram

FIG. 20



Albite spectrum ($NaAlSi_3O_2$)

FIG. 21



Least squares solution for template multipliers for Albite

FIG. 22

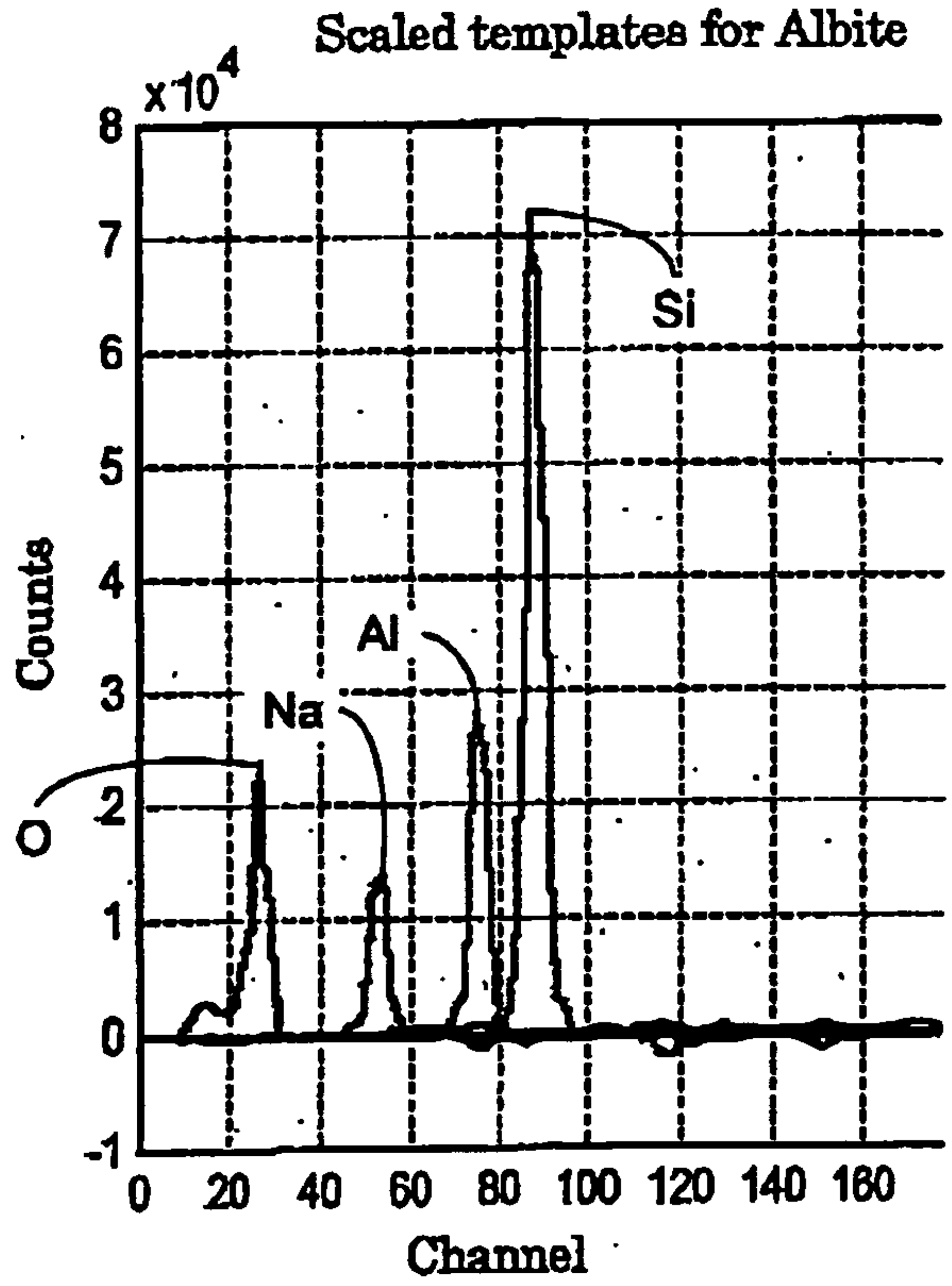

Scaled templates for Albite
x10^4
8
7
6
5
4
3
2
1
0
-1
Counts
0 20 40 60 80 100 120 140 160
Channel
Si
Al
Na
O

FIG. 23

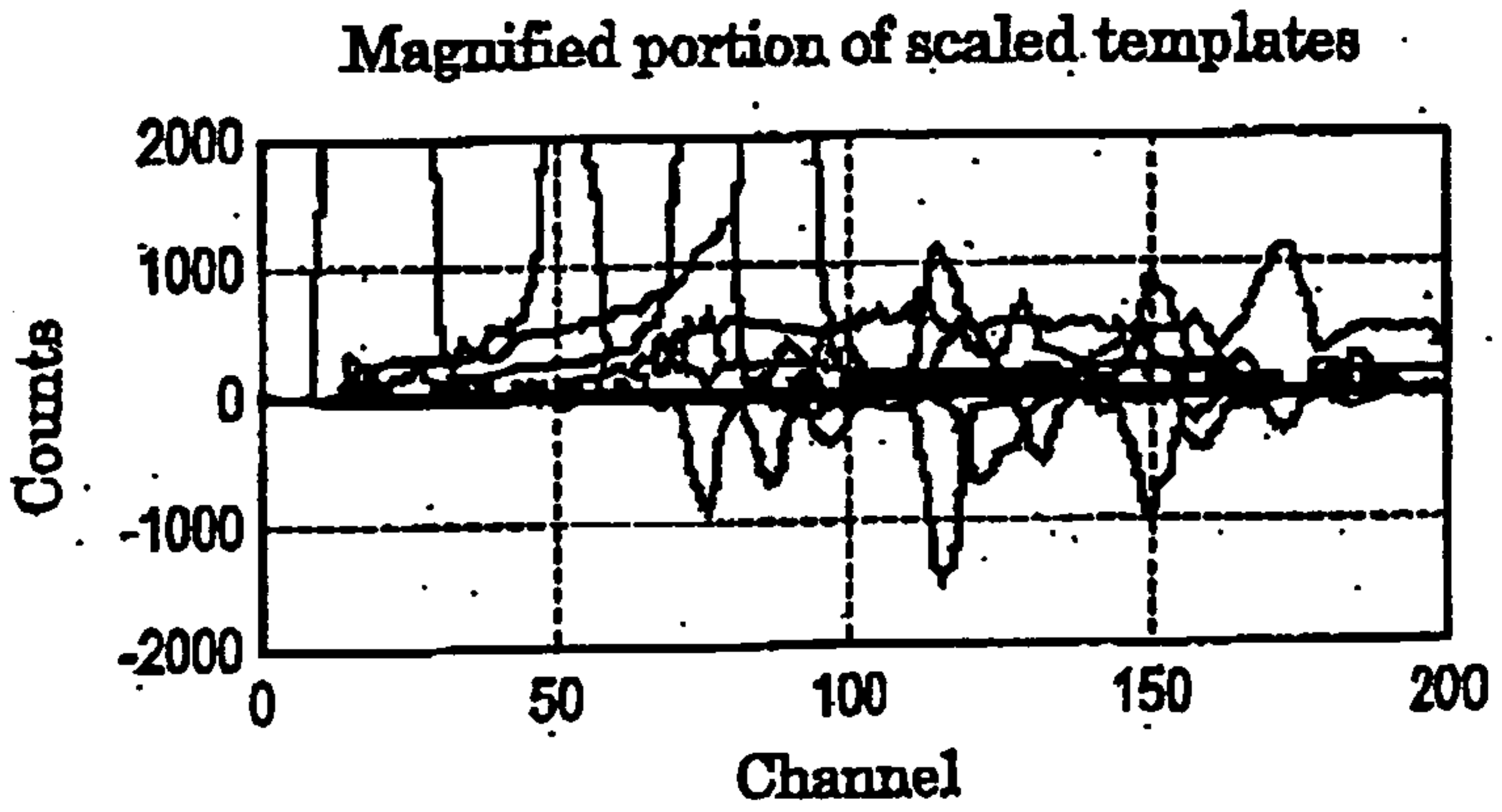
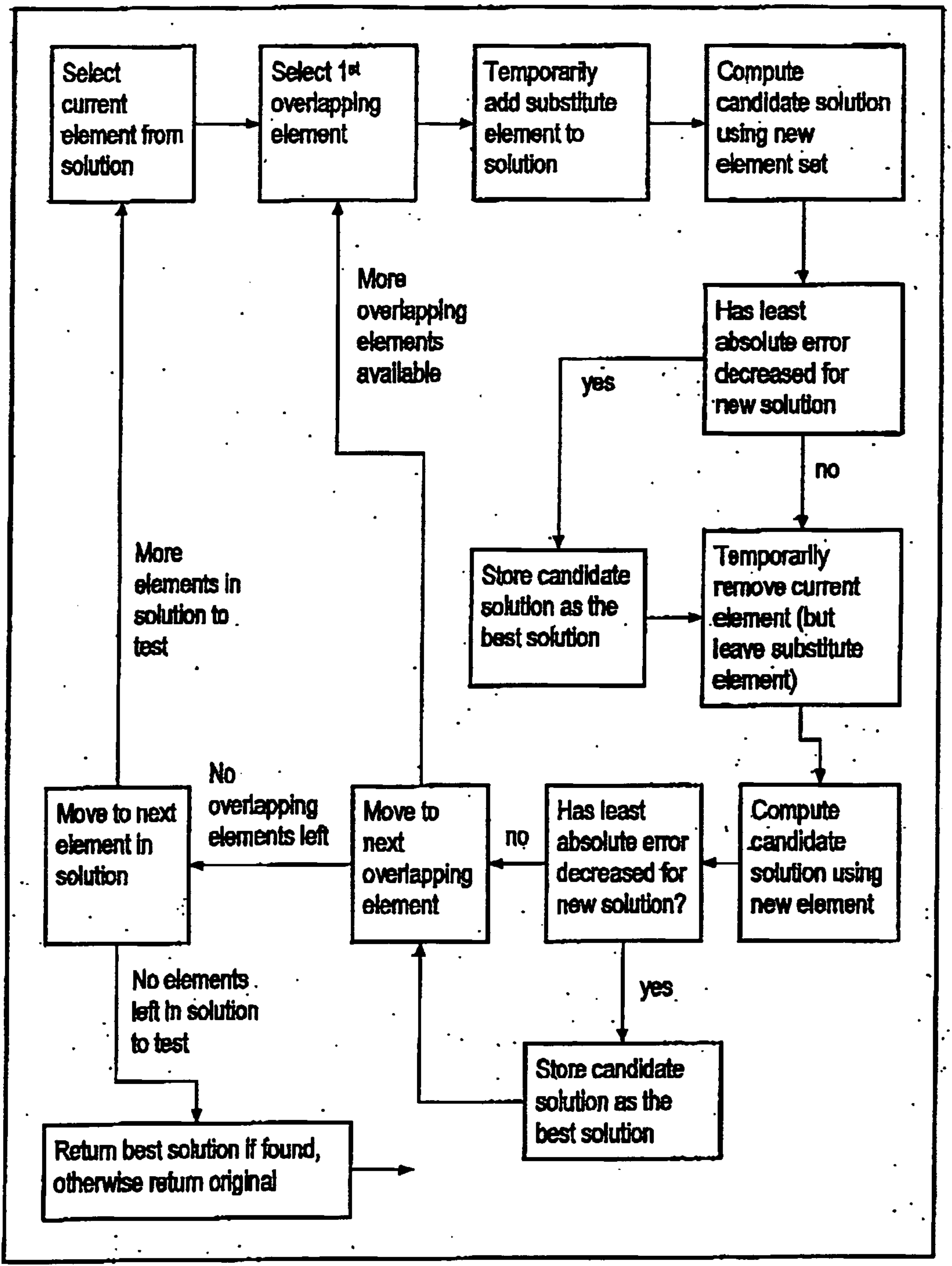
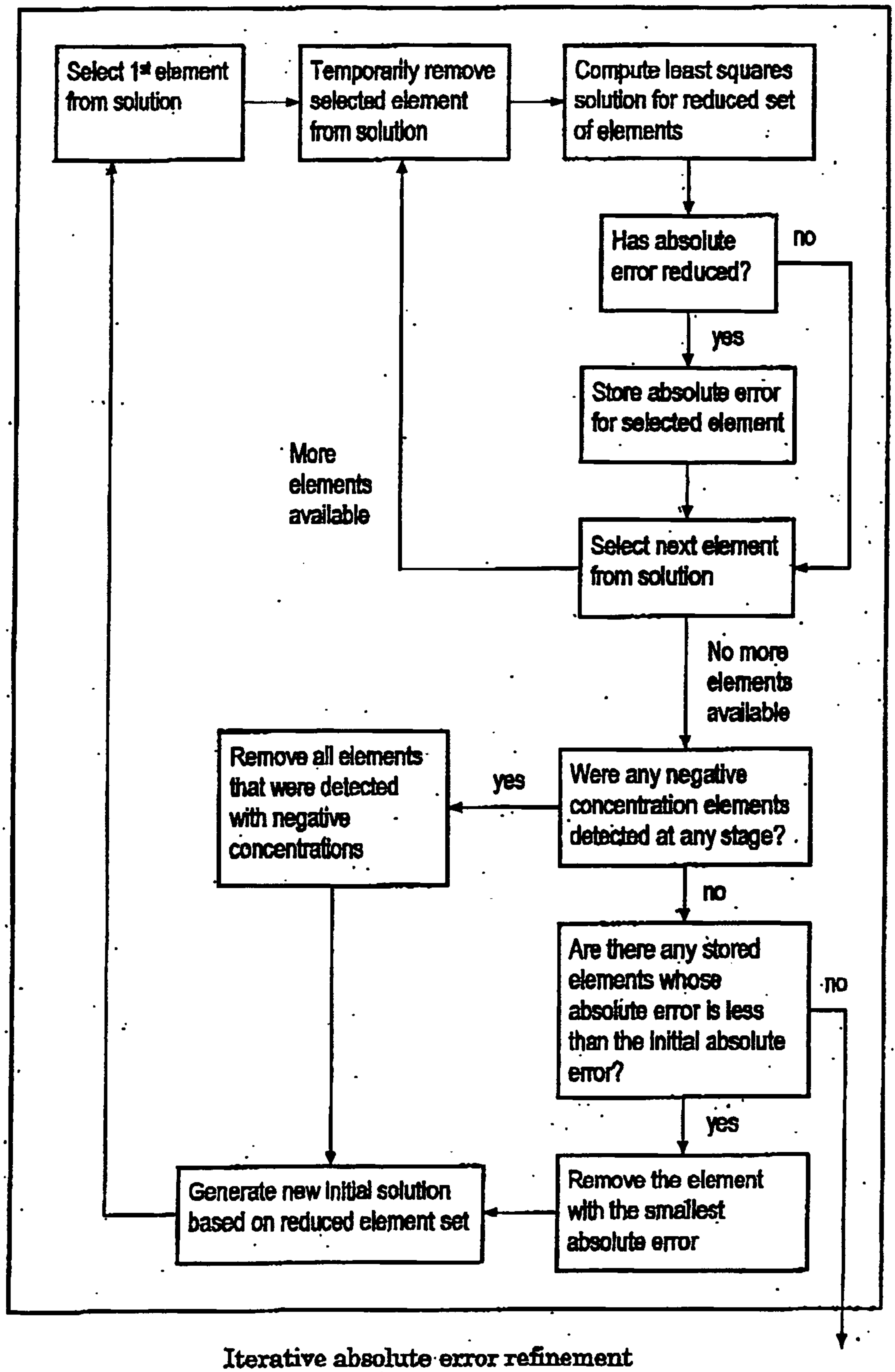

Magnified portion of scaled templates
2000
1000
0
-1000
-2000
Counts
0 50 100 150 200
Channel

FIG. 24



Background element substitution algorithm

FIG. 25



Iterative absolute error refinement

FIG. 26

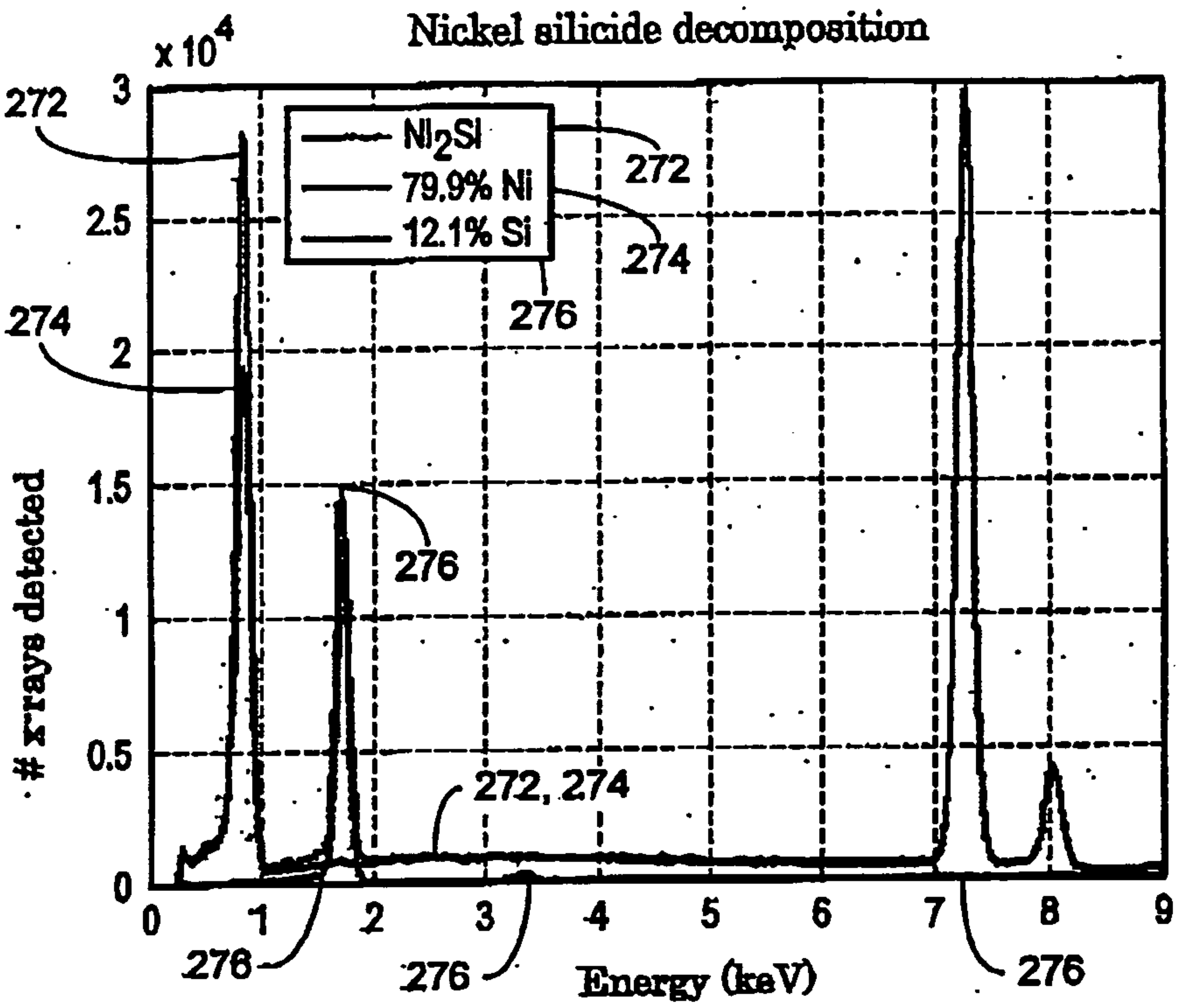

Nickel silicide decomposition
x 10^4
272
274
276
272, 274
Ni2Si
79.9% Ni
12.1% Si
x-rays detected
Energy (keV)
0
0.5
1
1.5
2
2.5
3
0
1
2
3
4
5
6
7
8
9

FIG. 27

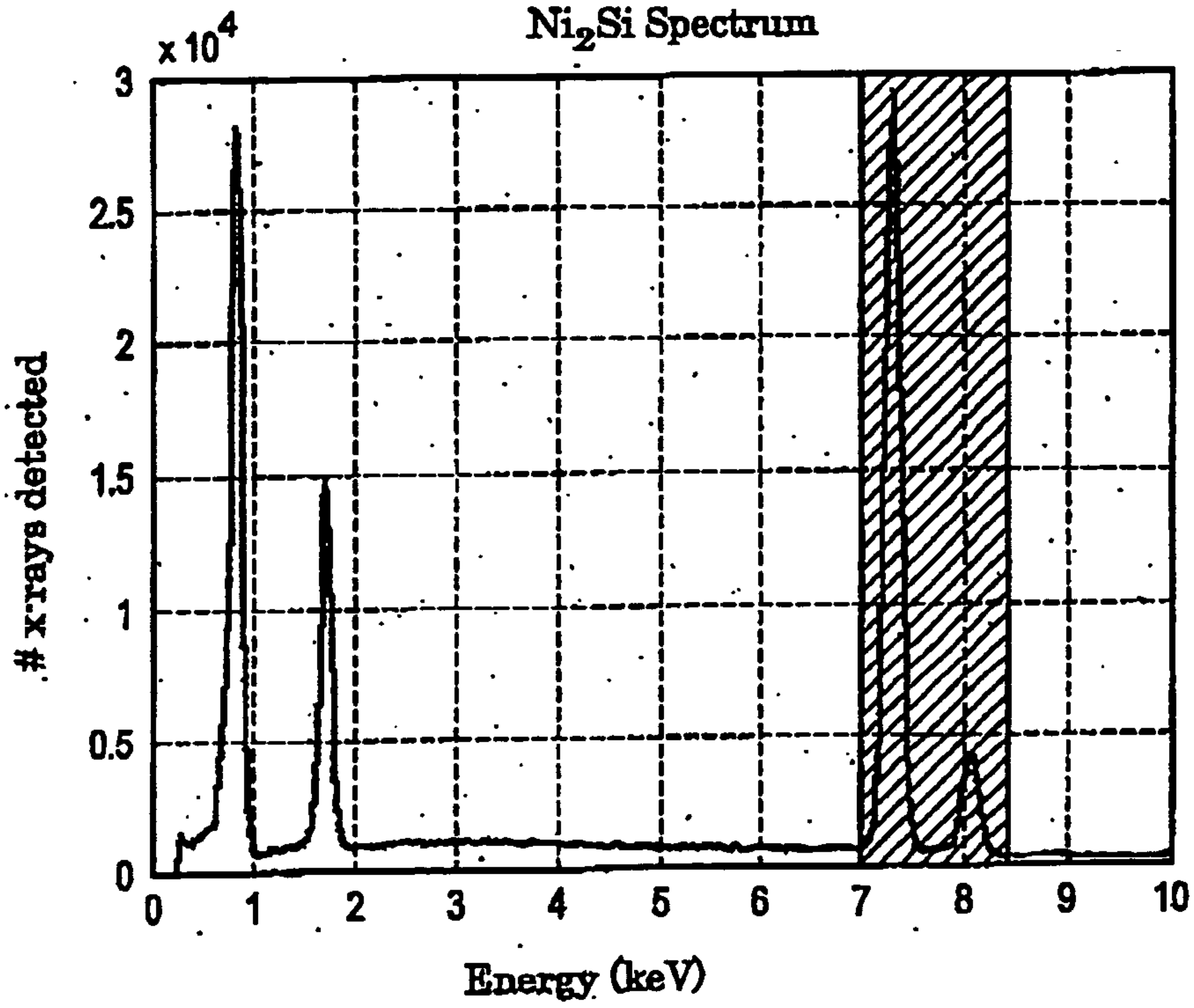

Ni2Si Spectrum
x 10^4
x-rays detected
Energy (keV)
0
0.5
1
1.5
2
2.5
3
0
1
2
3
4
5
6
7
8
9
10

FIG. 28

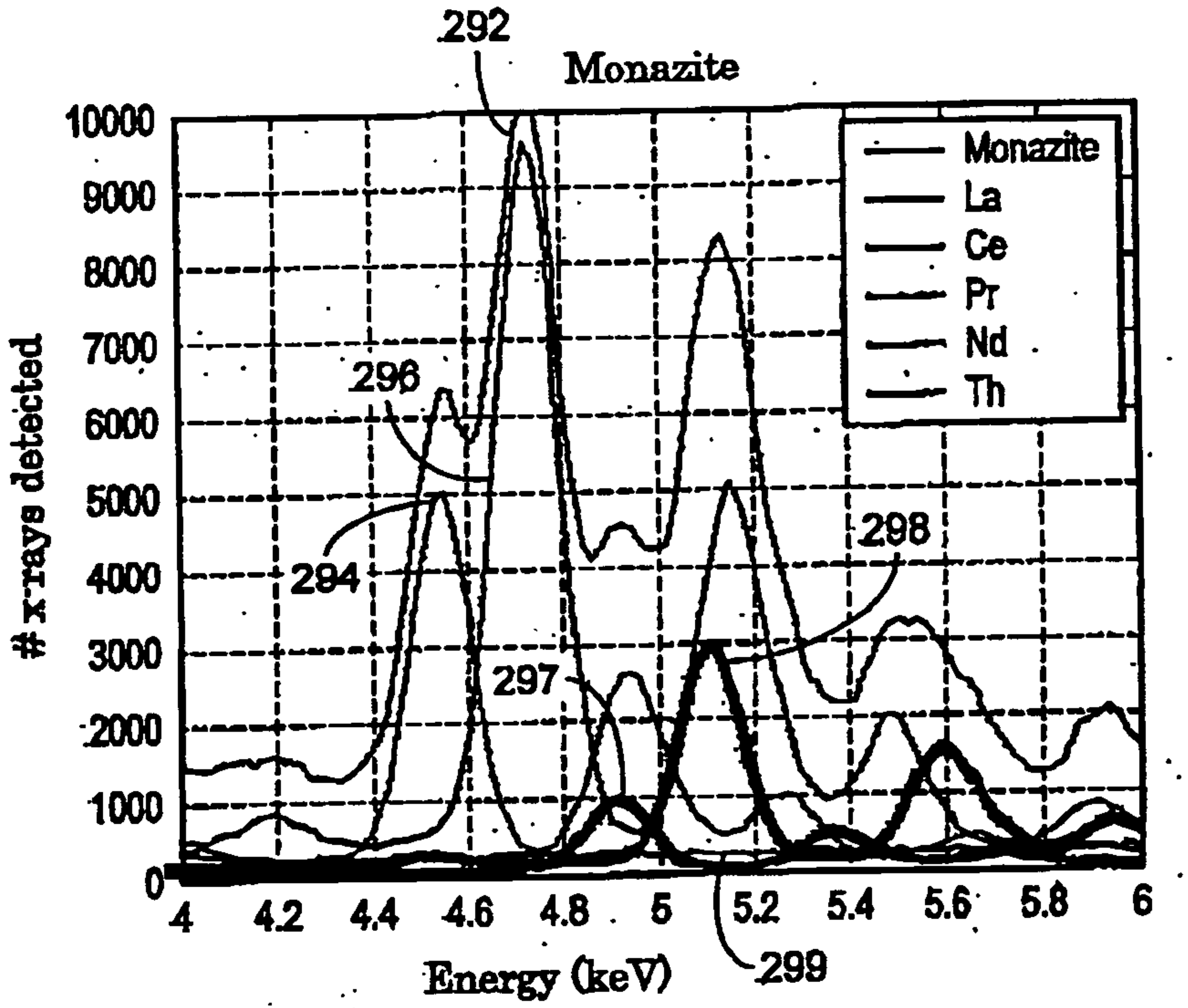


FIG. 29: Monazite

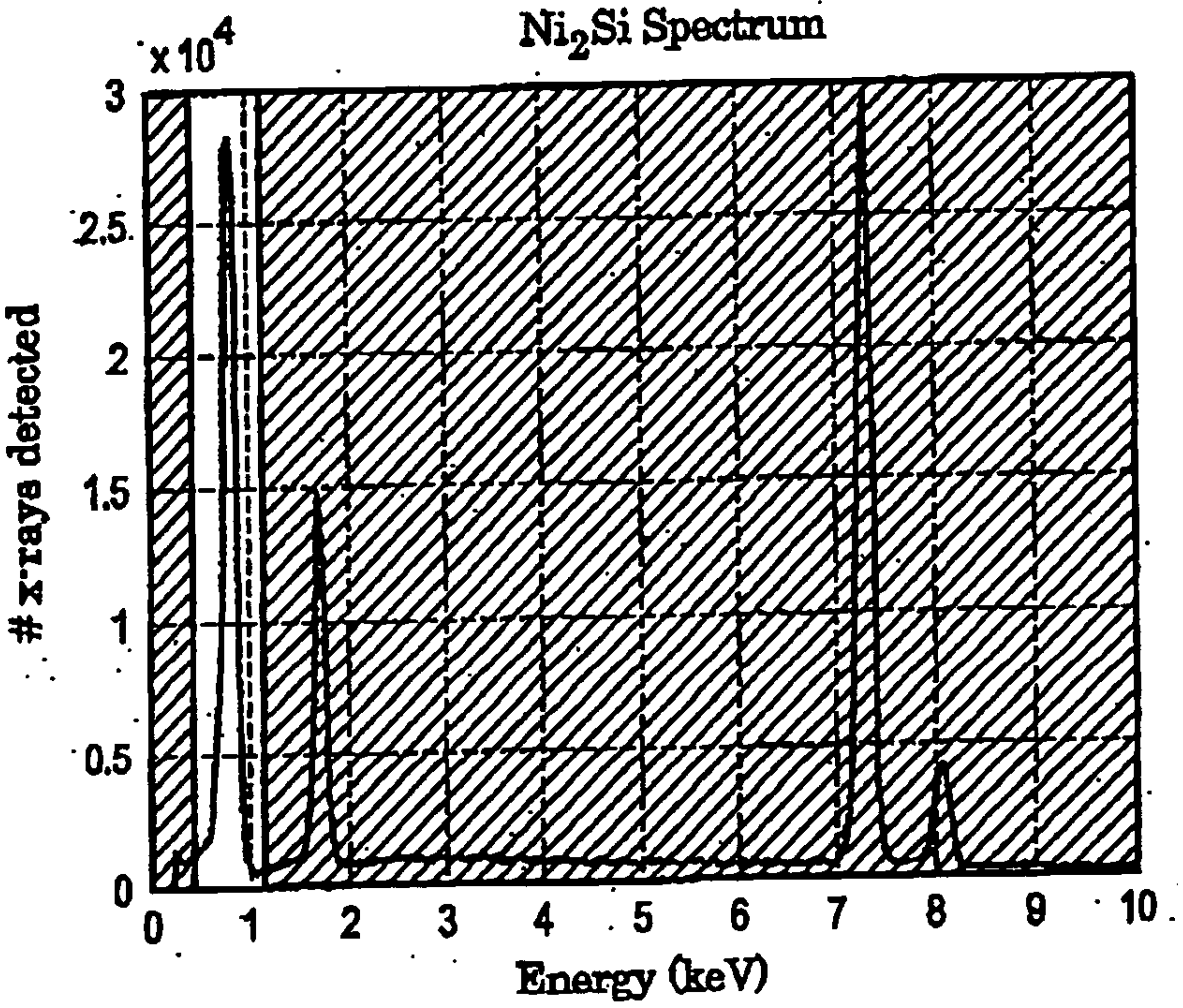


FIG. 30

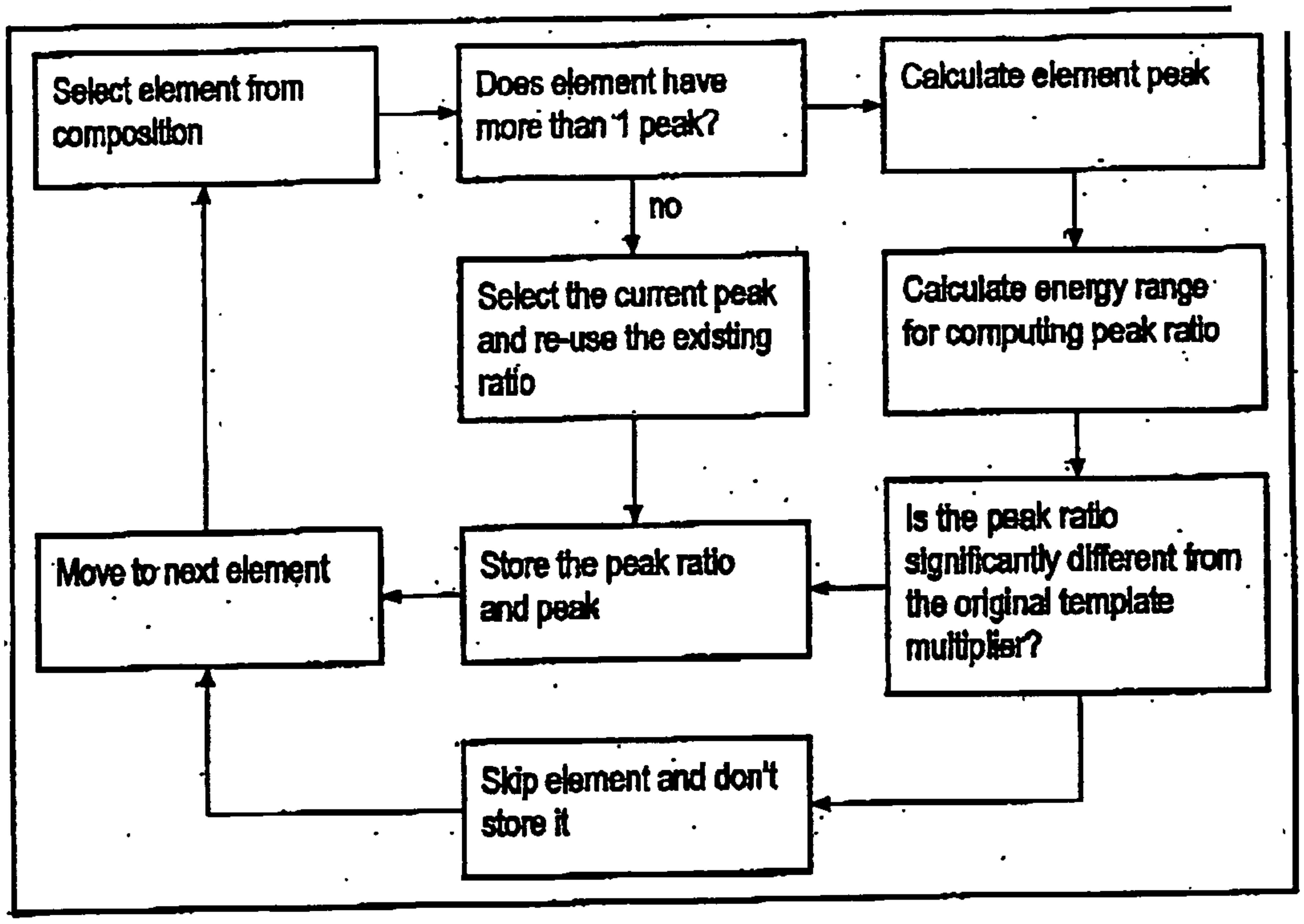

Select element from composition
Does element have more than 1 peak?
no
Calculate element peak
Select the current peak and re-use the existing ratio
Calculate energy range for computing peak ratio
Is the peak ratio significantly different from the original template multiplier?
Move to next element
Store the peak ratio and peak
Skip element and don't store it

FIG. 31

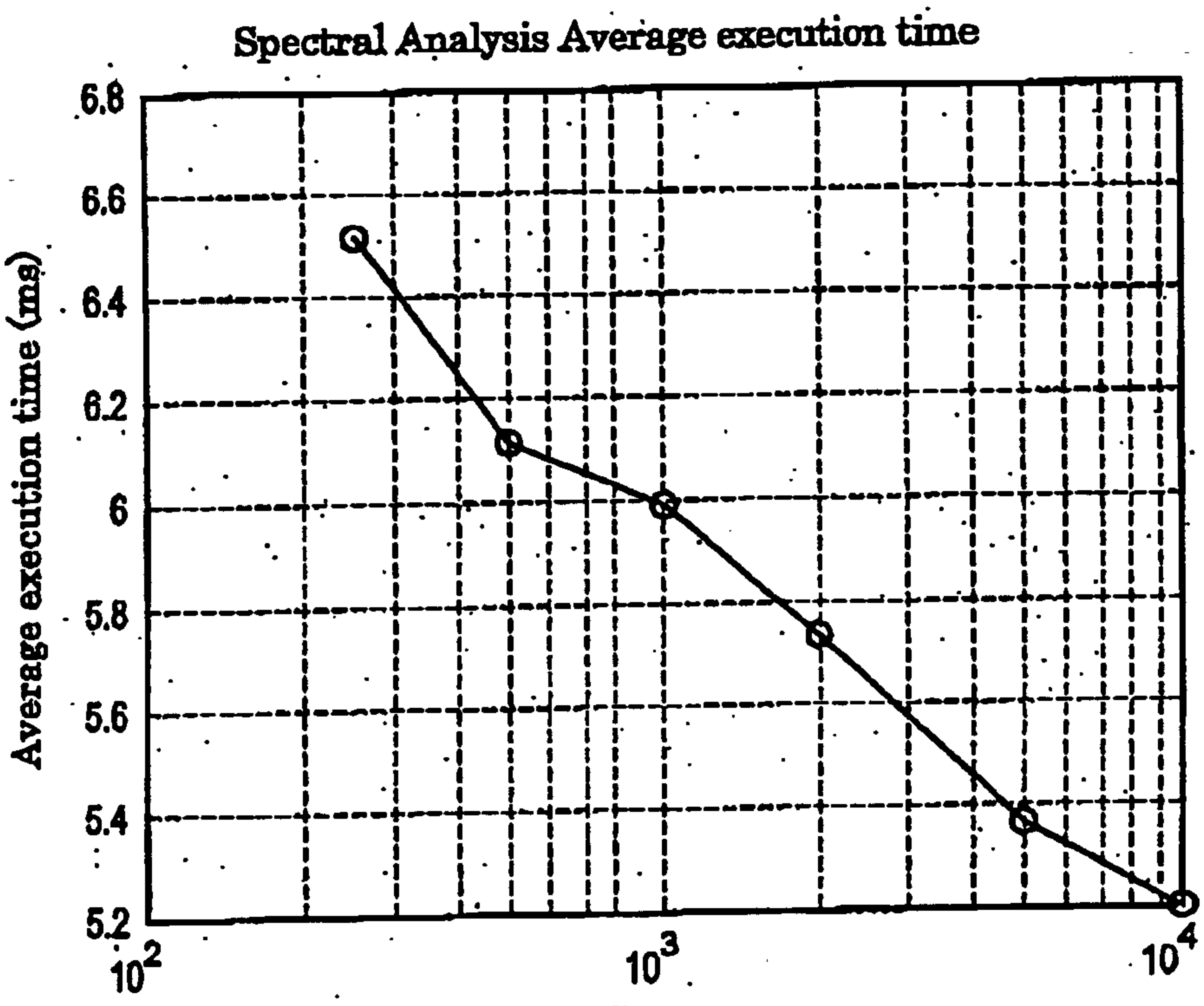
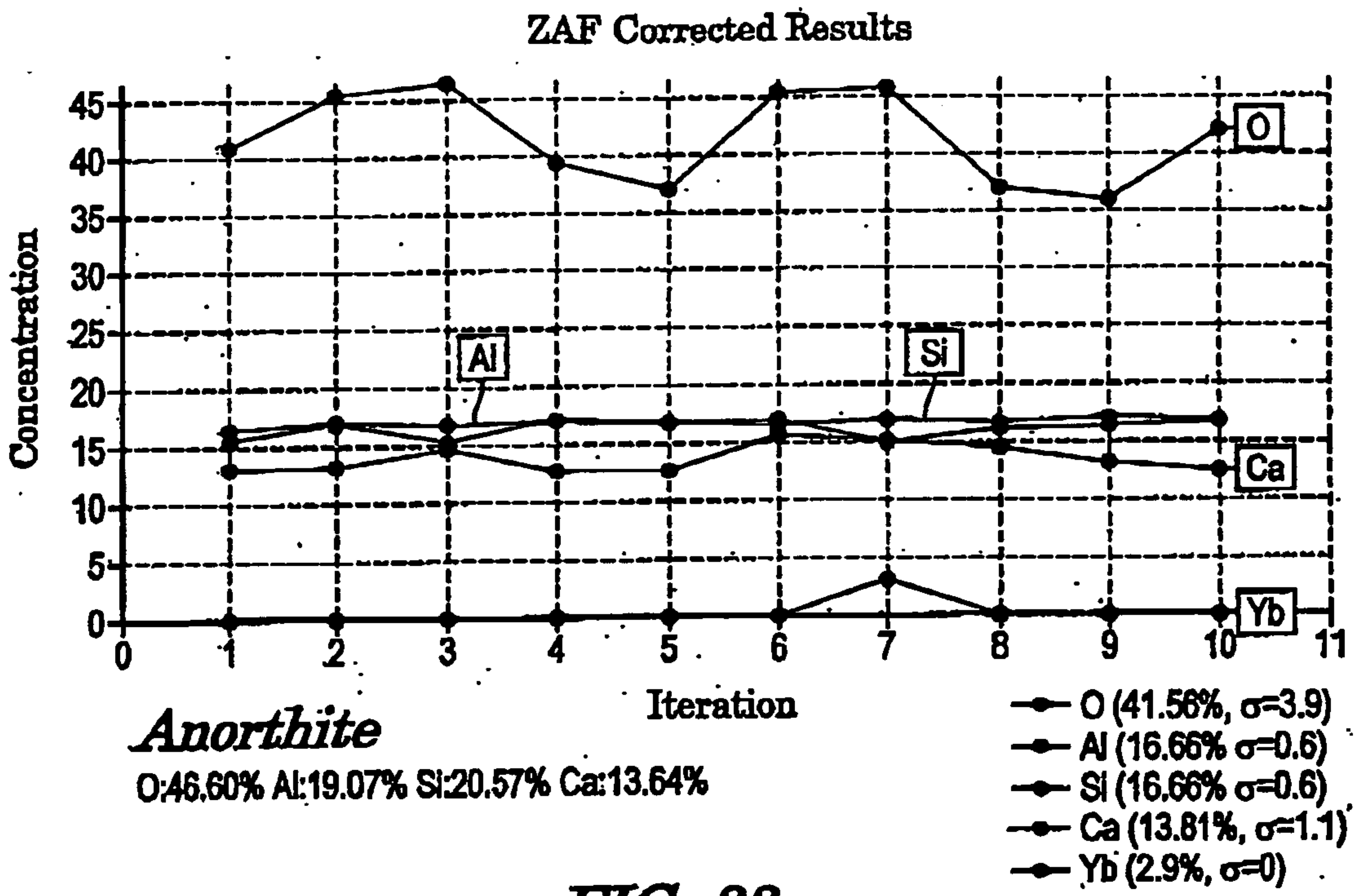
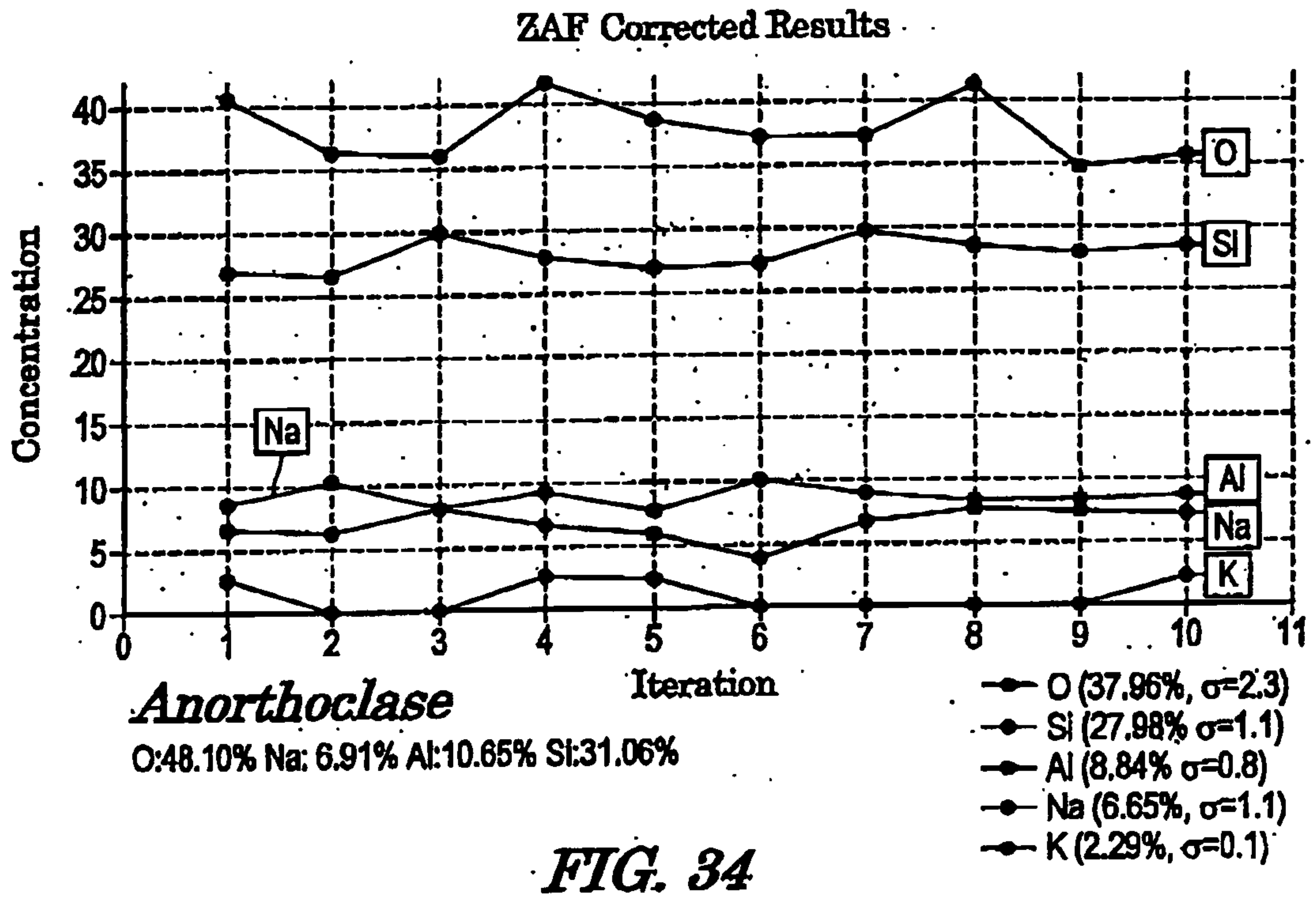

Spectral Analysis Average execution time
Average execution time (ms)
6.8
6.6
6.4
6.2
6
5.8
5.6
5.4
5.2
10^2
10^3
10^4
Counts

FIG. 32



ZAF Corrected Results

FIG. 33



ZAF Corrected Results

FIG. 34

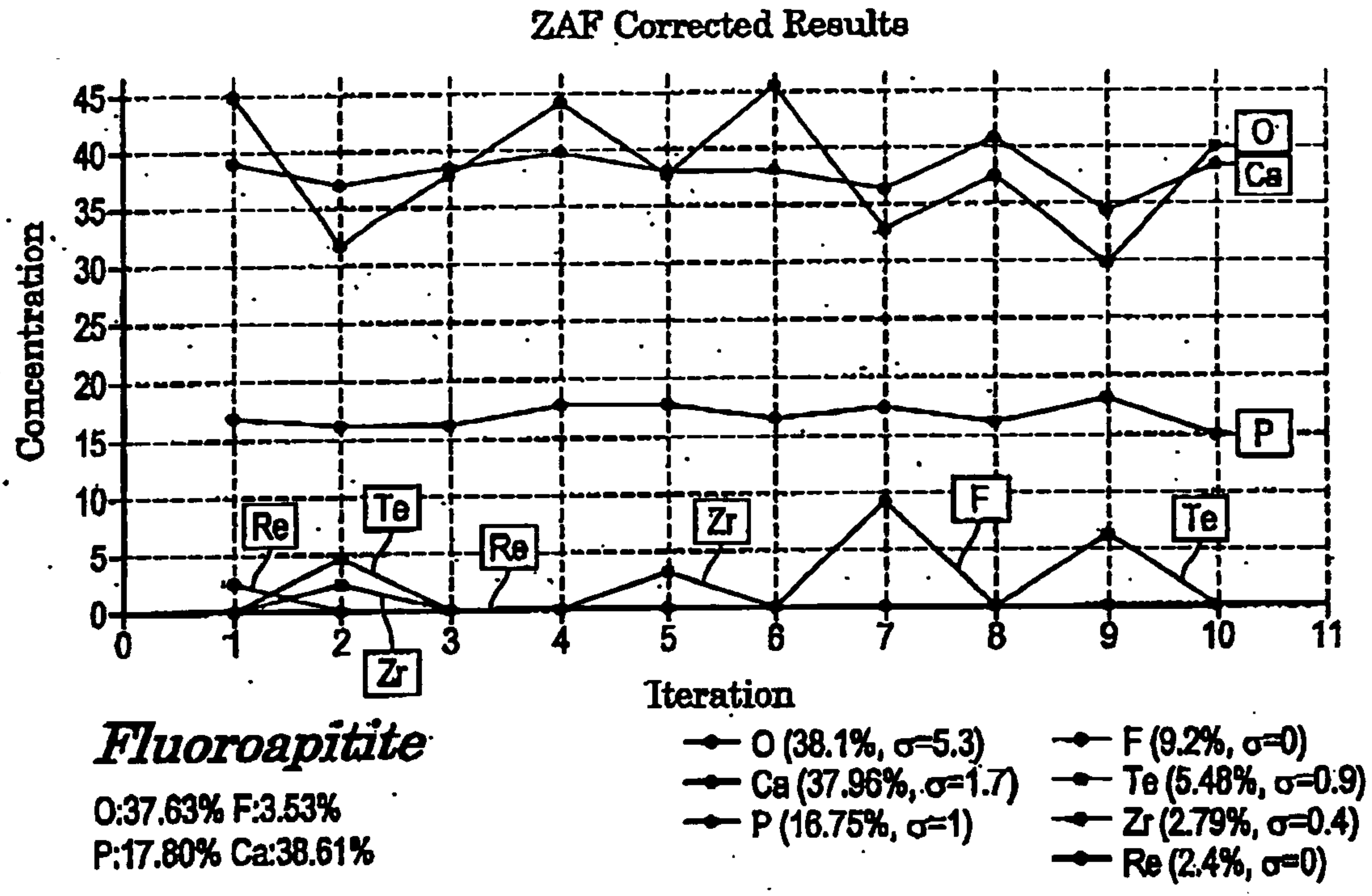

ZAF Corrected Results
Concentration
Iteration
0
5
10
15
20
25
30
35
40
45
0
1
2
3
4
5
6
7
8
9
10
11
O
Ca
P
Re
Te
Re
Zr
F
Te
Zr
Fluoroapitite
O:37.63% F:3.53%
P:17.80% Ca:38.61%
O (38.1%, σ=5.3)
Ca (37.96%, σ=1.7)
P (16.75%, σ=1)
F (9.2%, σ=0)
Te (5.48%, σ=0.9)
Zr (2.79%, σ=0.4)
Re (2.4%, σ=0)

FIG. 35

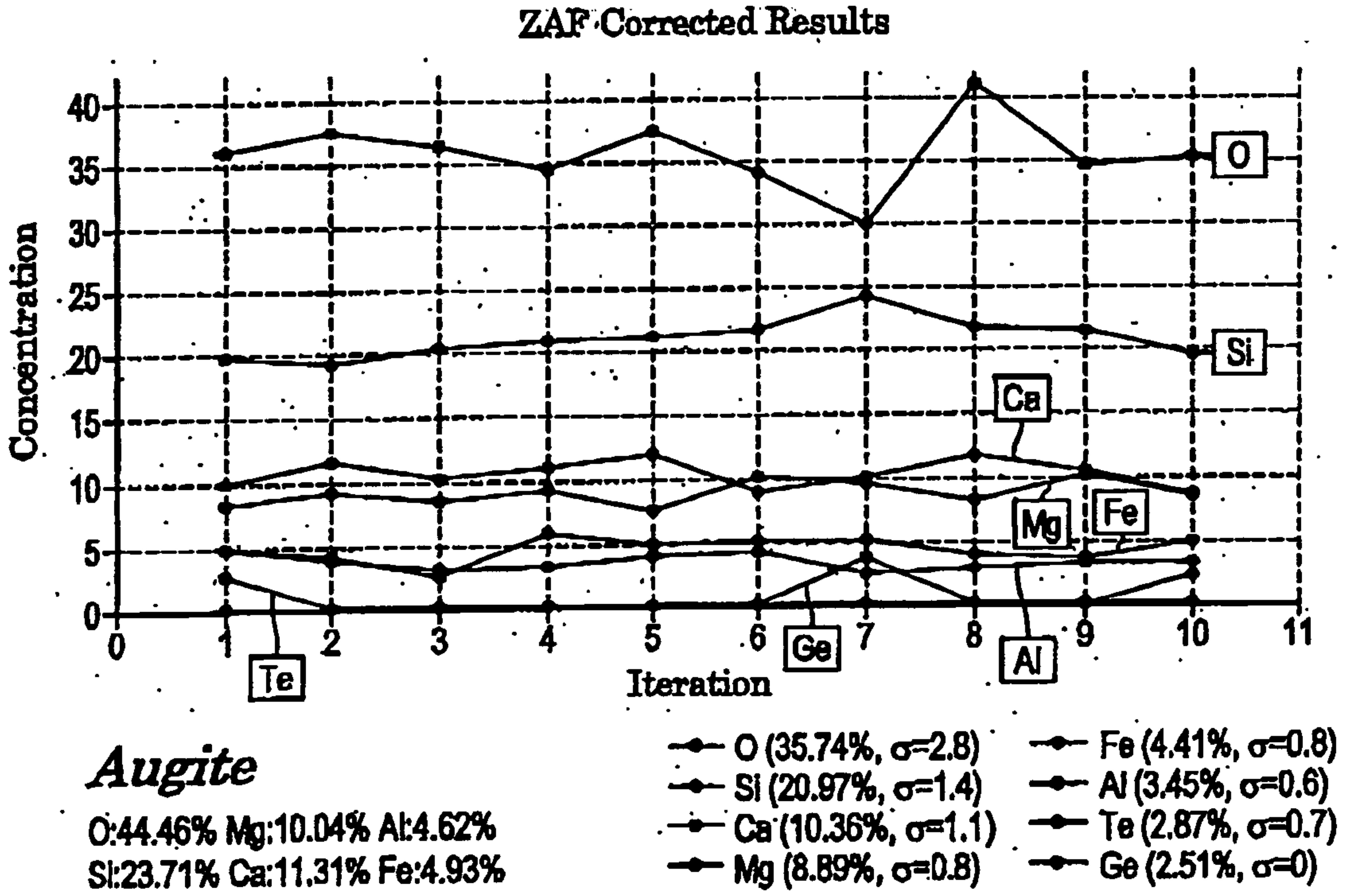

ZAF Corrected Results
Concentration
Iteration
0
5
10
15
20
25
30
35
40
0
1
2
3
4
5
6
7
8
9
10
11
O
Si
Ca
Mg
Fe
Te
Ge
Al
Augite
O:44.46% Mg:10.04% Al:4.62%
Si:23.71% Ca:11.31% Fe:4.93%
O (35.74%, σ=2.8)
Si (20.97%, σ=1.4)
Ca (10.36%, σ=1.1)
Mg (8.89%, σ=0.8)
Fe (4.41%, σ=0.8)
Al (3.45%, σ=0.6)
Te (2.87%, σ=0.7)
Ge (2.51%, σ=0)

FIG. 36

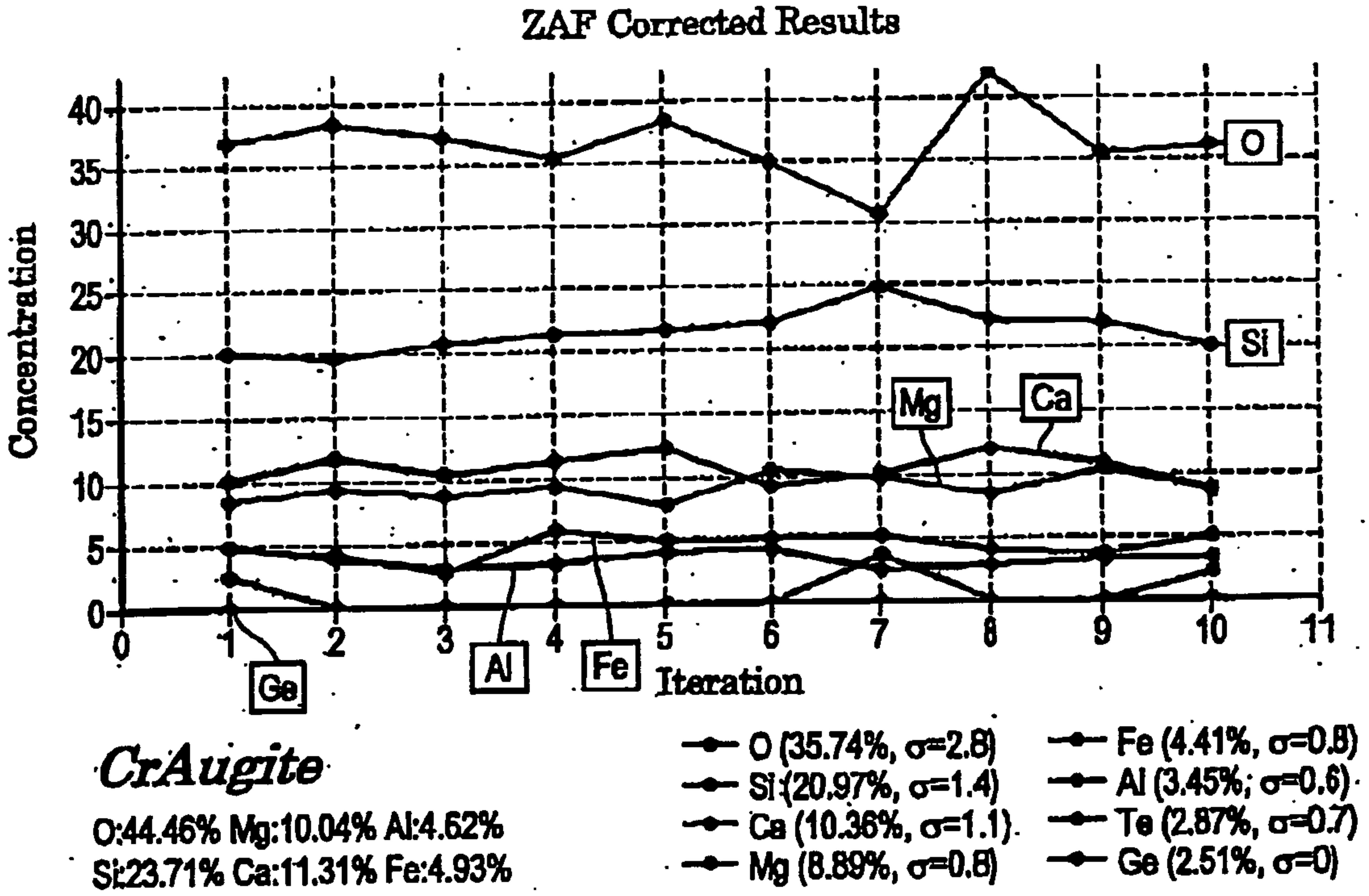

ZAF Corrected Results
Concentration
Iteration
40
35
30
25
20
15
10
5
0
0 1 2 3 4 5 6 7 8 9 10 11
O
Si
Mg
Ca
Ge
Al
Fe
CrAugite
O:44.46% Mg:10.04% Al:4.62%
Si:23.71% Ca:11.31% Fe:4.93%
O (35.74%, σ=2.8)
Si (20.97%, σ=1.4)
Ca (10.36%, σ=1.1)
Mg (8.89%, σ=0.8)
Fe (4.41%, σ=0.8)
Al (3.45%, σ=0.6)
Te (2.87%, σ=0.7)
Ge (2.51%, σ=0)

FIG. 37

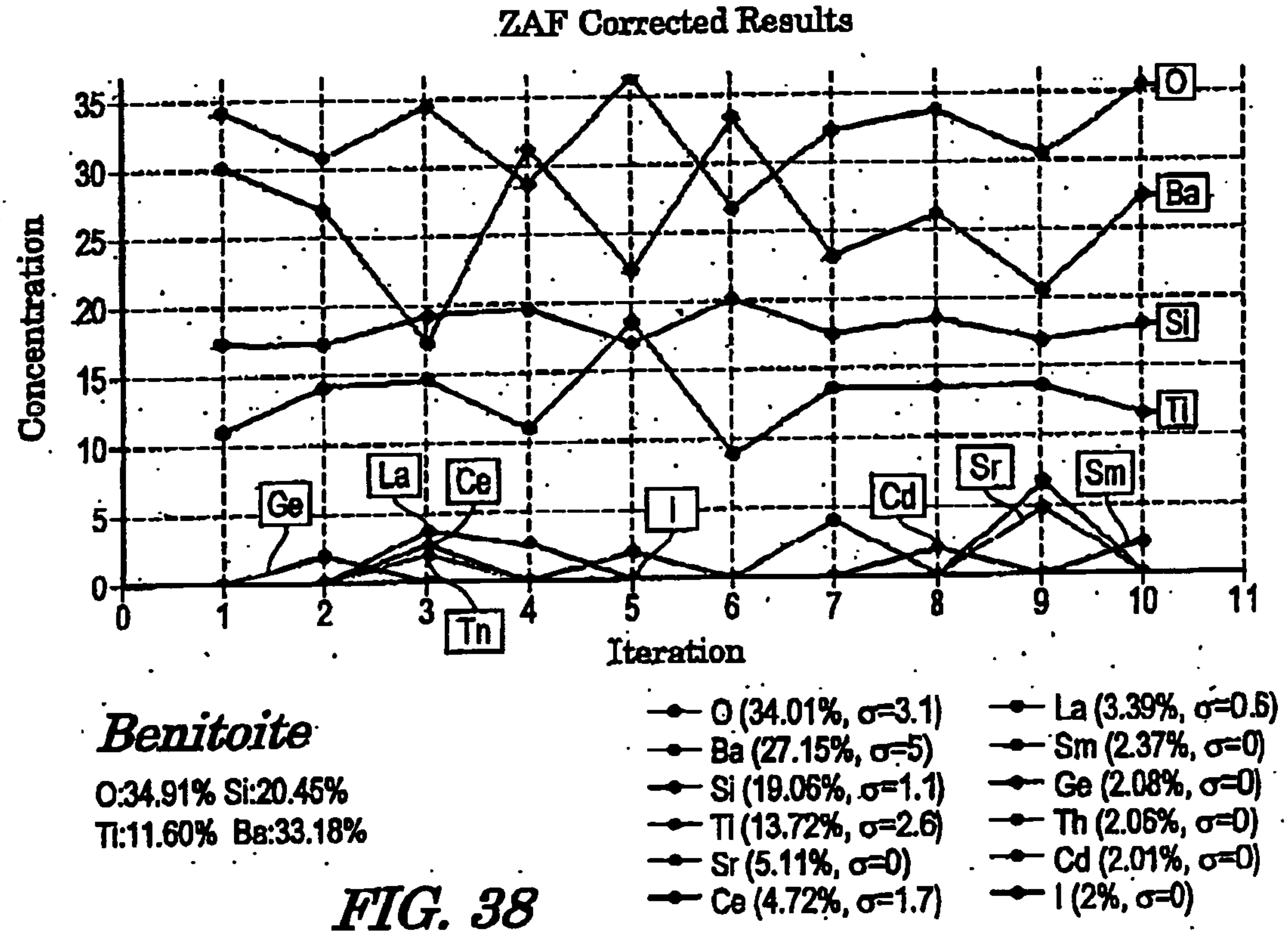

ZAF Corrected Results
Concentration
Iteration
35
30
25
20
15
10
5
0
0 1 2 3 4 5 6 7 8 9 10 11
O
Ba
Si
Ti
Ge
La
Ce
I
Cd
Sr
Sm
Tn
Benitoite
O:34.91% Si:20.45%
Ti:11.60% Ba:33.18%
O (34.01%, σ=3.1)
Ba (27.15%, σ=5)
Si (19.06%, σ=1.1)
Ti (13.72%, σ=2.6)
Sr (5.11%, σ=0)
Ce (4.72%, σ=1.7)
La (3.39%, σ=0.6)
Sm (2.37%, σ=0)
Ge (2.08%, σ=0)
Th (2.06%, σ=0)
Cd (2.01%, σ=0)
I (2%, σ=0)

FIG. 38

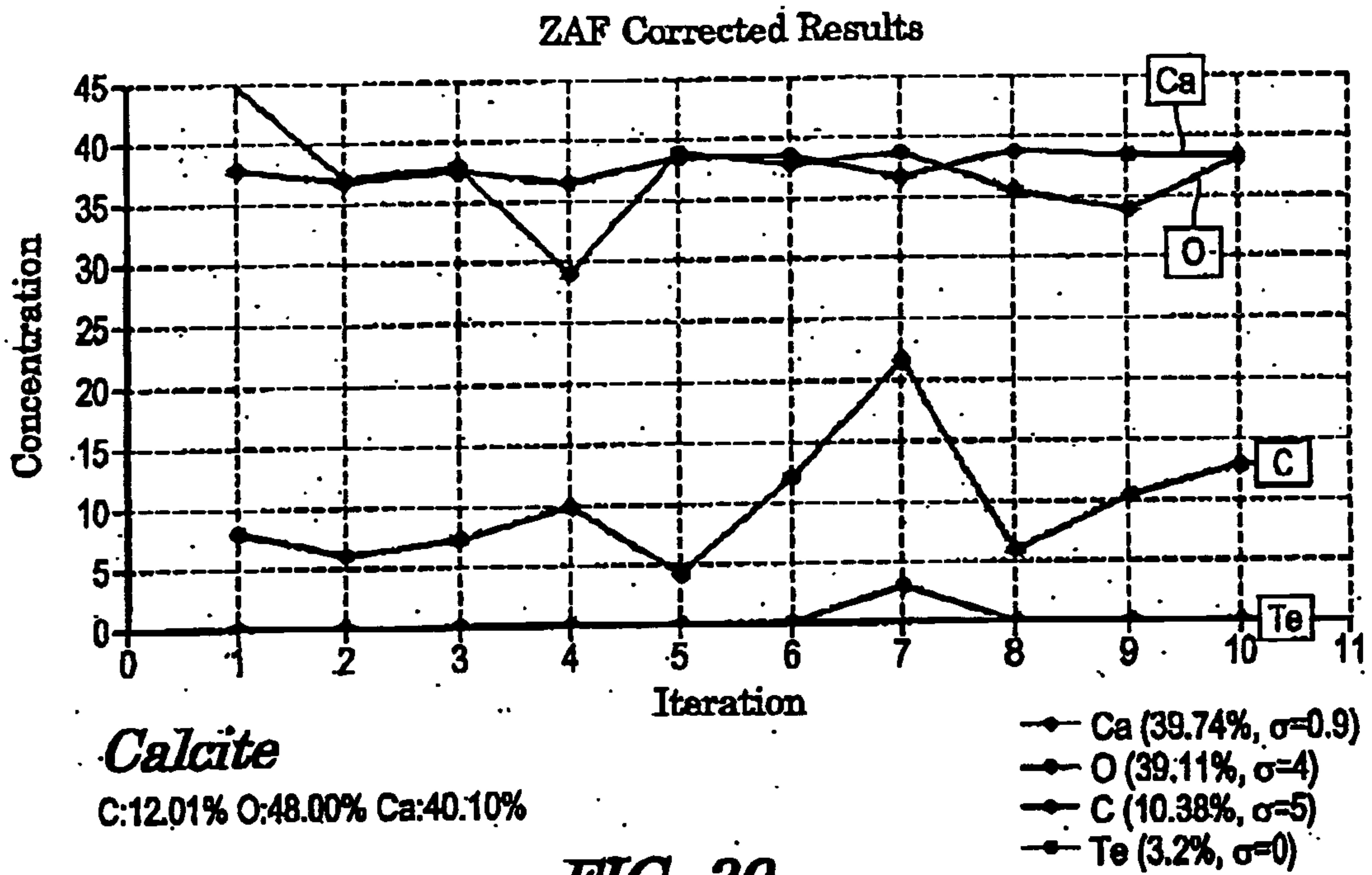

ZAF Corrected Results
Concentration
45
40
35
30
25
20
15
10
5
0
Iteration
0
1
2
3
4
5
6
7
8
9
10
11
Ca
O
C
Te
Calcite
C:12.01% O:48.00% Ca:40.10%
Ca (39.74%, σ=0.9)
O (39.11%, σ=4)
C (10.38%, σ=5)
Te (3.2%, σ=0)

FIG. 39

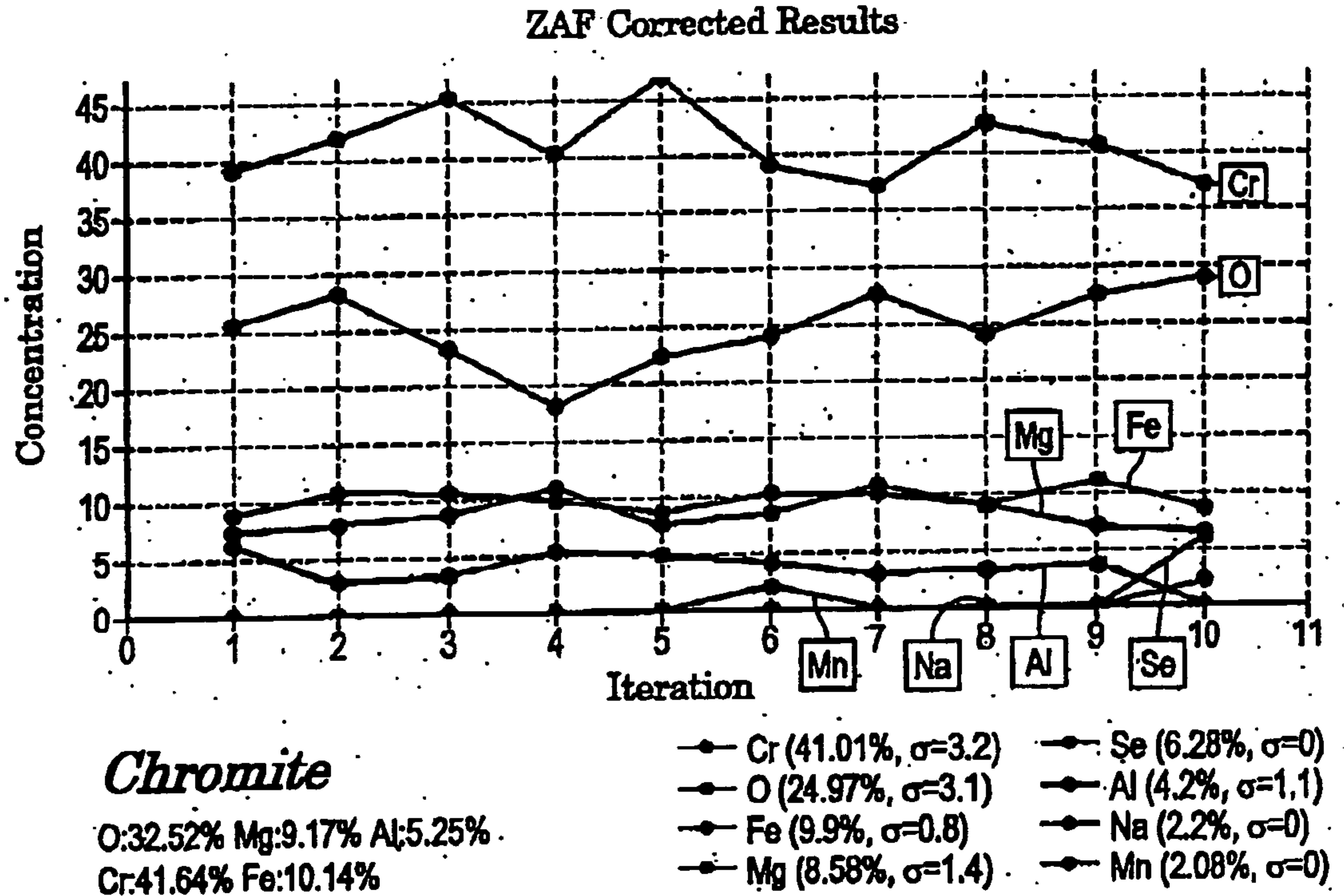

ZAF Corrected Results
Concentration
45
40
35
30
25
20
15
10
5
0
Iteration
0
1
2
3
4
5
6
7
8
9
10
11
Cr
O
Mg
Fe
Mn
Na
Al
Se
Chromite
O:32.52% Mg:9.17% Al:5.25%
Cr:41.64% Fe:10.14%
Cr (41.01%, σ=3.2)
O (24.97%, σ=3.1)
Fe (9.9%, σ=0.8)
Mg (8.58%, σ=1.4)
Se (6.28%, σ=0)
Al (4.2%, σ=1.1)
Na (2.2%, σ=0)
Mn (2.08%, σ=0)

FIG. 40

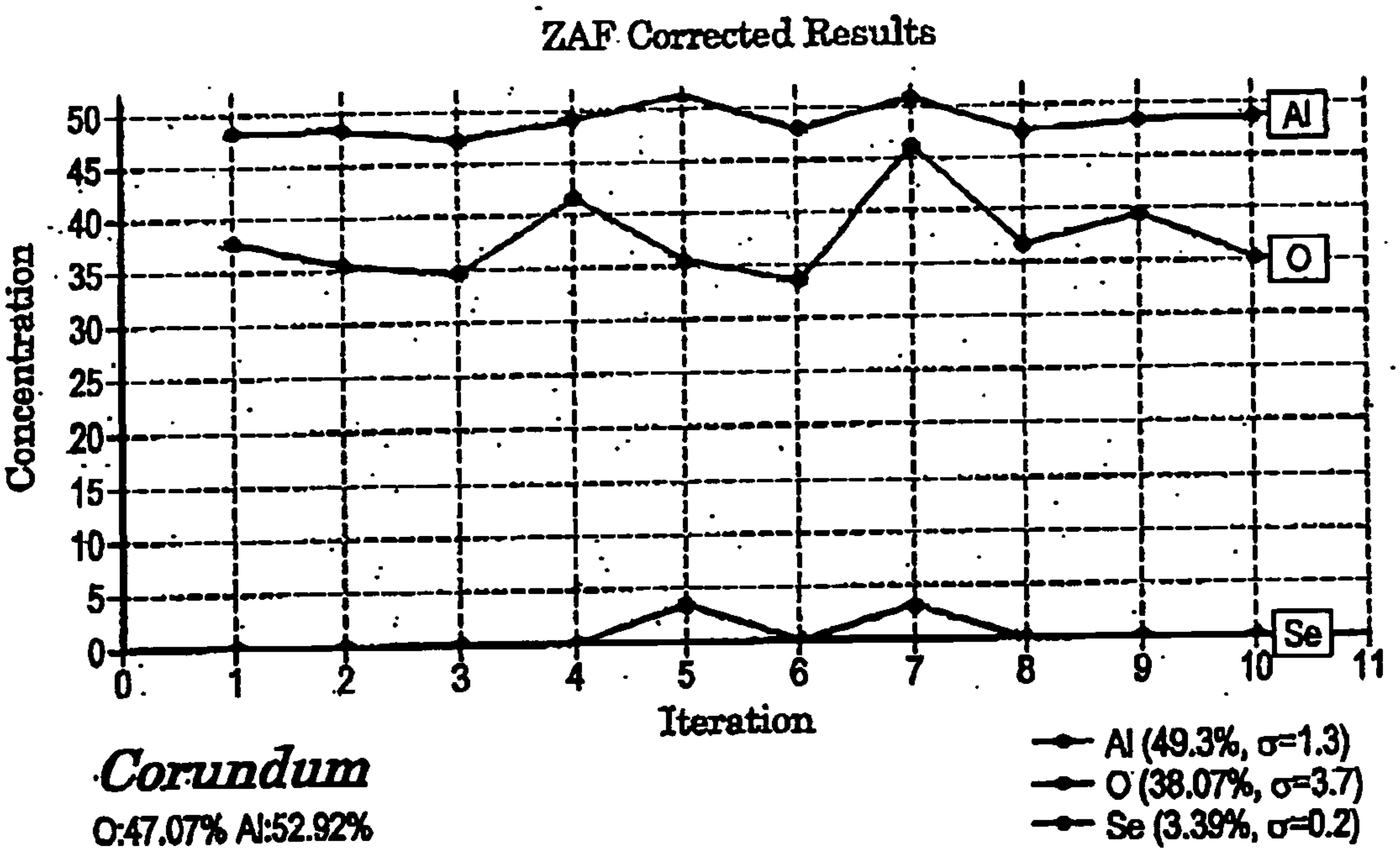

ZAF Corrected Results
Concentration
50
45
40
35
30
25
20
15
10
5
0
0
1
2
3
4
5
6
7
8
9
10
11
Iteration
Al
O
Se
Corundum
O:47.07% Al:52.92%
Al (49.3%, σ=1.3)
O (38.07%, σ=3.7)
Se (3.39%, σ=0.2)

FIG. 41

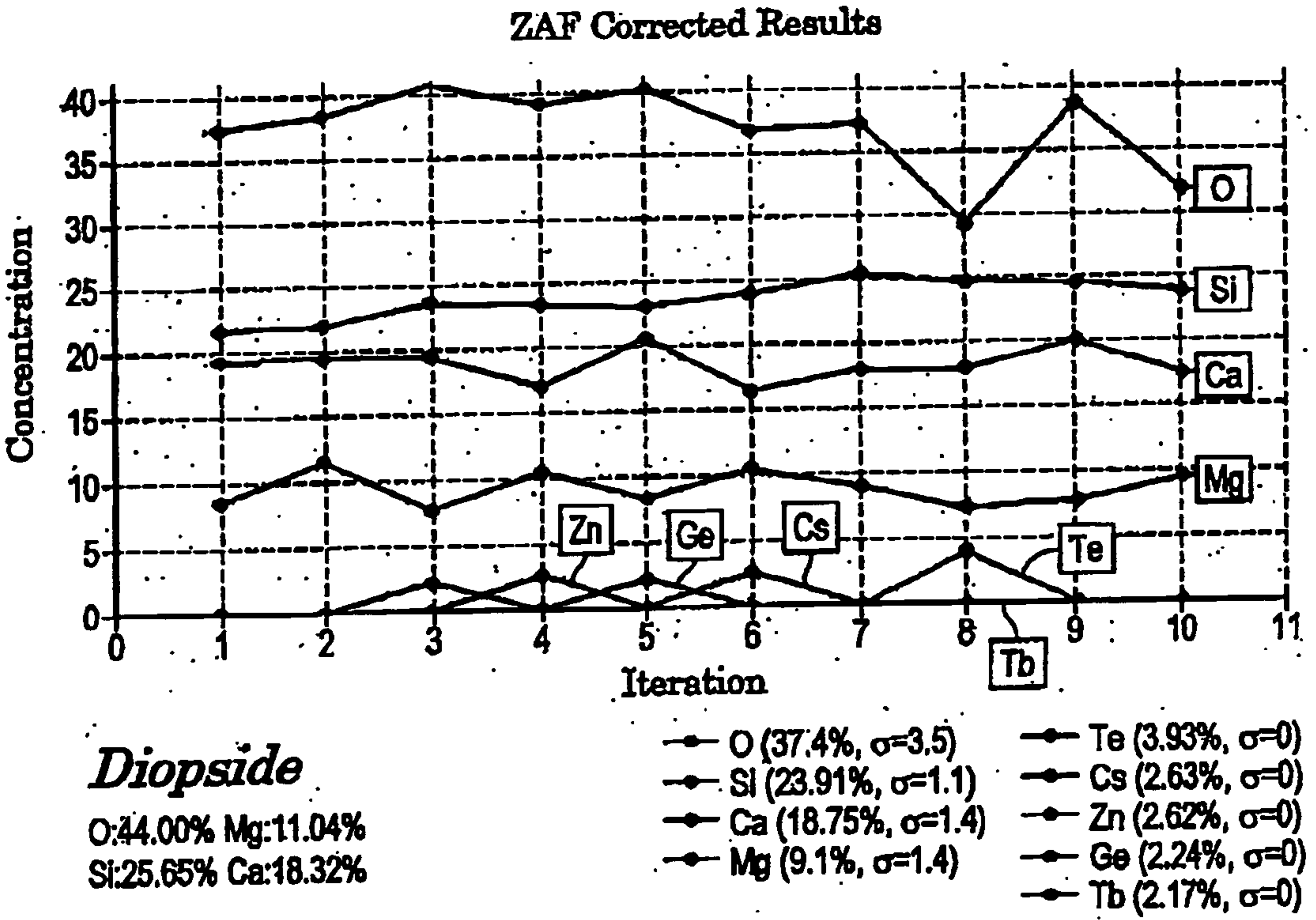

ZAF Corrected Results
Concentration
40
35
30
25
20
15
10
5
0
0
1
2
3
4
5
6
7
8
9
10
11
Iteration
O
Si
Ca
Mg
Zn
Ge
Cs
Te
Tb
Diopside
O:44.00% Mg:11.04%
Si:25.65% Ca:18.32%
O (37.4%, σ=3.5)
Si (23.91%, σ=1.1)
Ca (18.75%, σ=1.4)
Mg (9.1%, σ=1.4)
Te (3.93%, σ=0)
Cs (2.63%, σ=0)
Zn (2.62%, σ=0)
Ge (2.24%, σ=0)
Tb (2.17%, σ=0)

FIG. 42

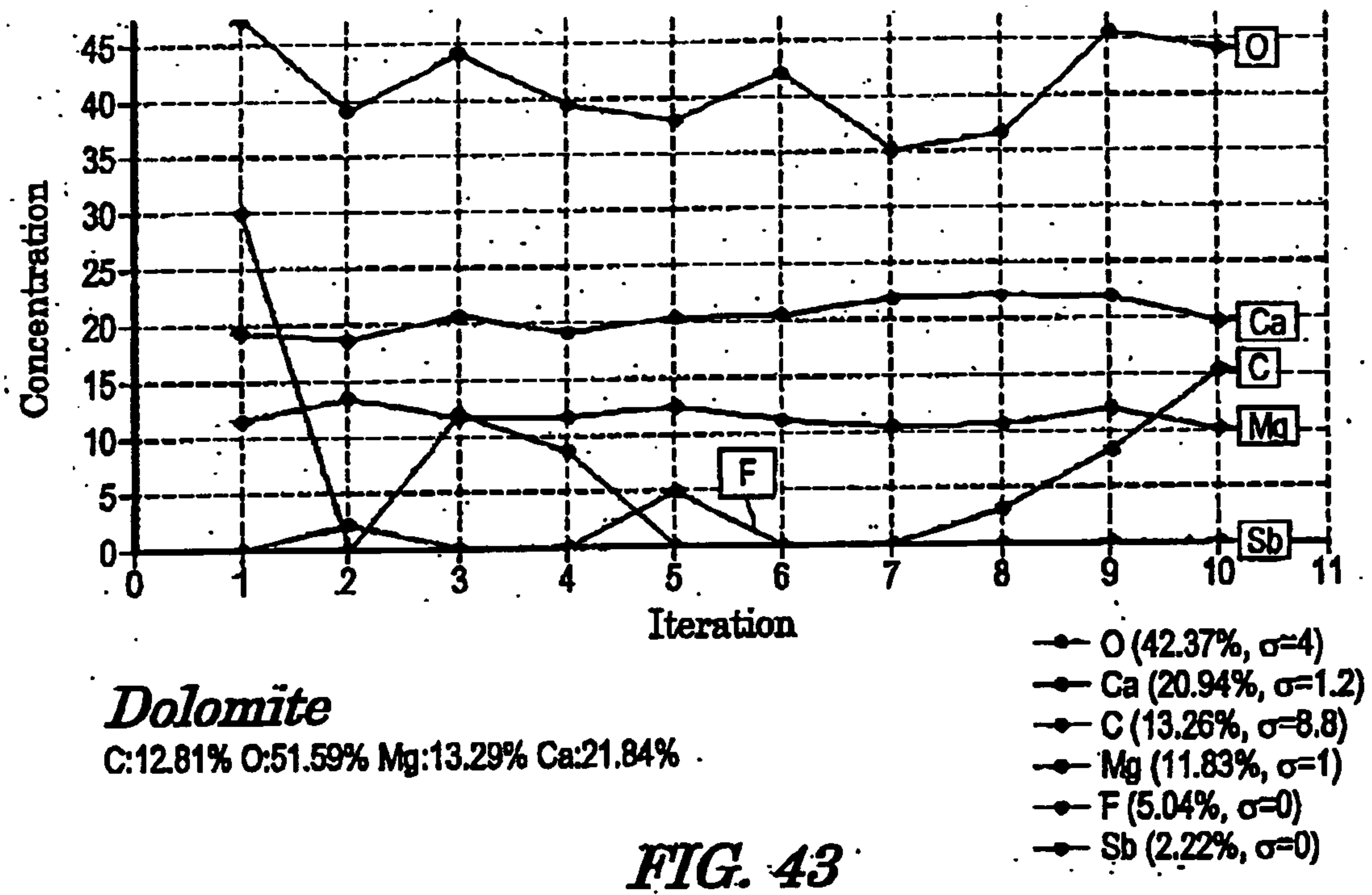

Concentration
0
5
10
15
20
25
30
35
40
45
Iteration
0
1
2
3
4
5
6
7
8
9
10
11
O
Ca
C
Mg
F
Sb
O (42.37%, σ=4)
Ca (20.94%, σ=1.2)
C (13.26%, σ=8.8)
Mg (11.83%, σ=1)
F (5.04%, σ=0)
Sb (2.22%, σ=0)
Dolomite
C:12.81% O:51.59% Mg:13.29% Ca:21.84%

FIG. 43

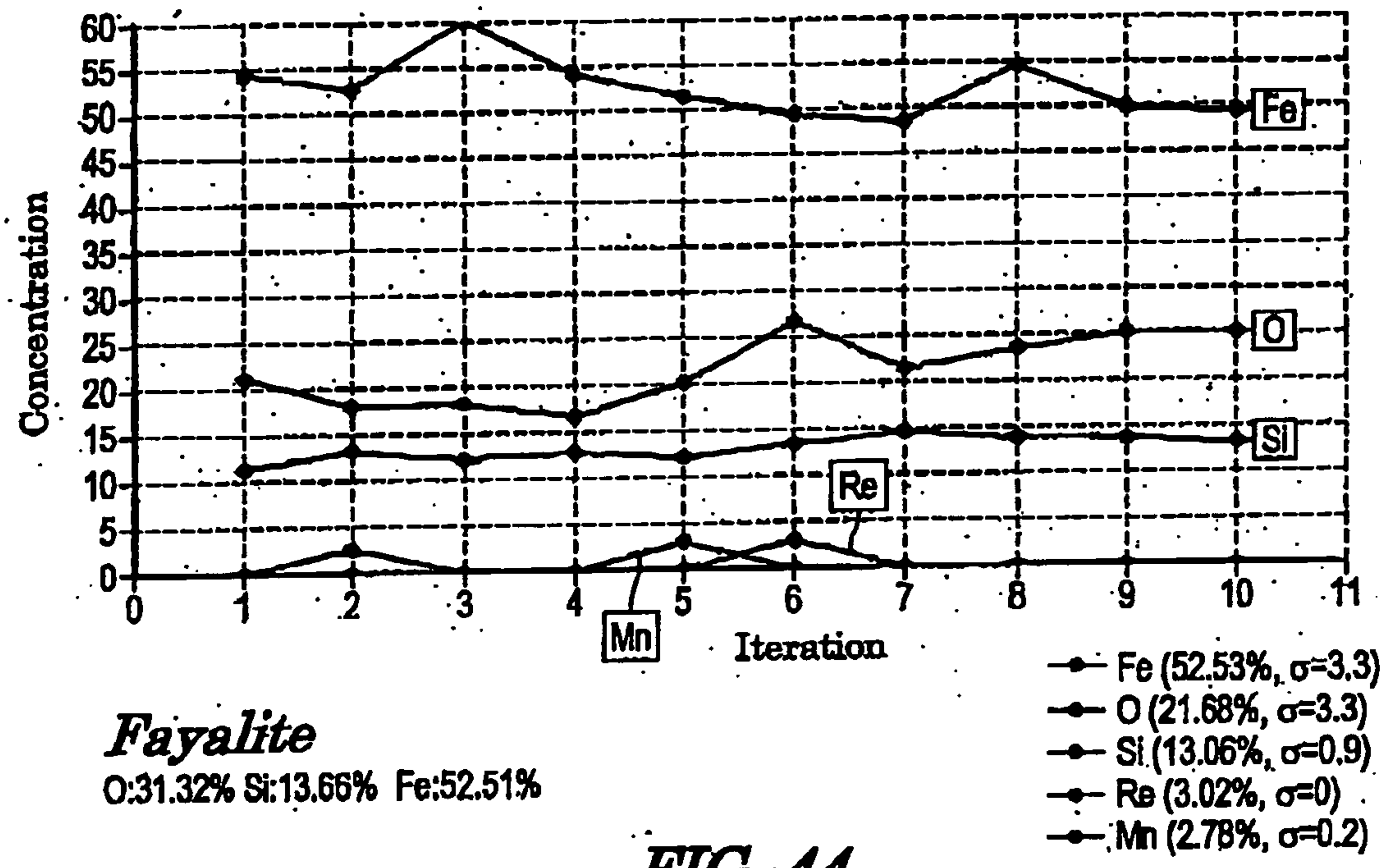

Concentration
0
5
10
15
20
25
30
35
40
45
50
55
60
Iteration
0
1
2
3
4
5
6
7
8
9
10
11
Fe
O
Si
Re
Mn
Fe (52.53%, σ=3.3)
O (21.68%, σ=3.3)
Si (13.06%, σ=0.9)
Re (3.02%, σ=0)
Mn (2.78%, σ=0.2)
Fayalite
O:31.32% Si:13.66% Fe:52.51%

FIG. 44

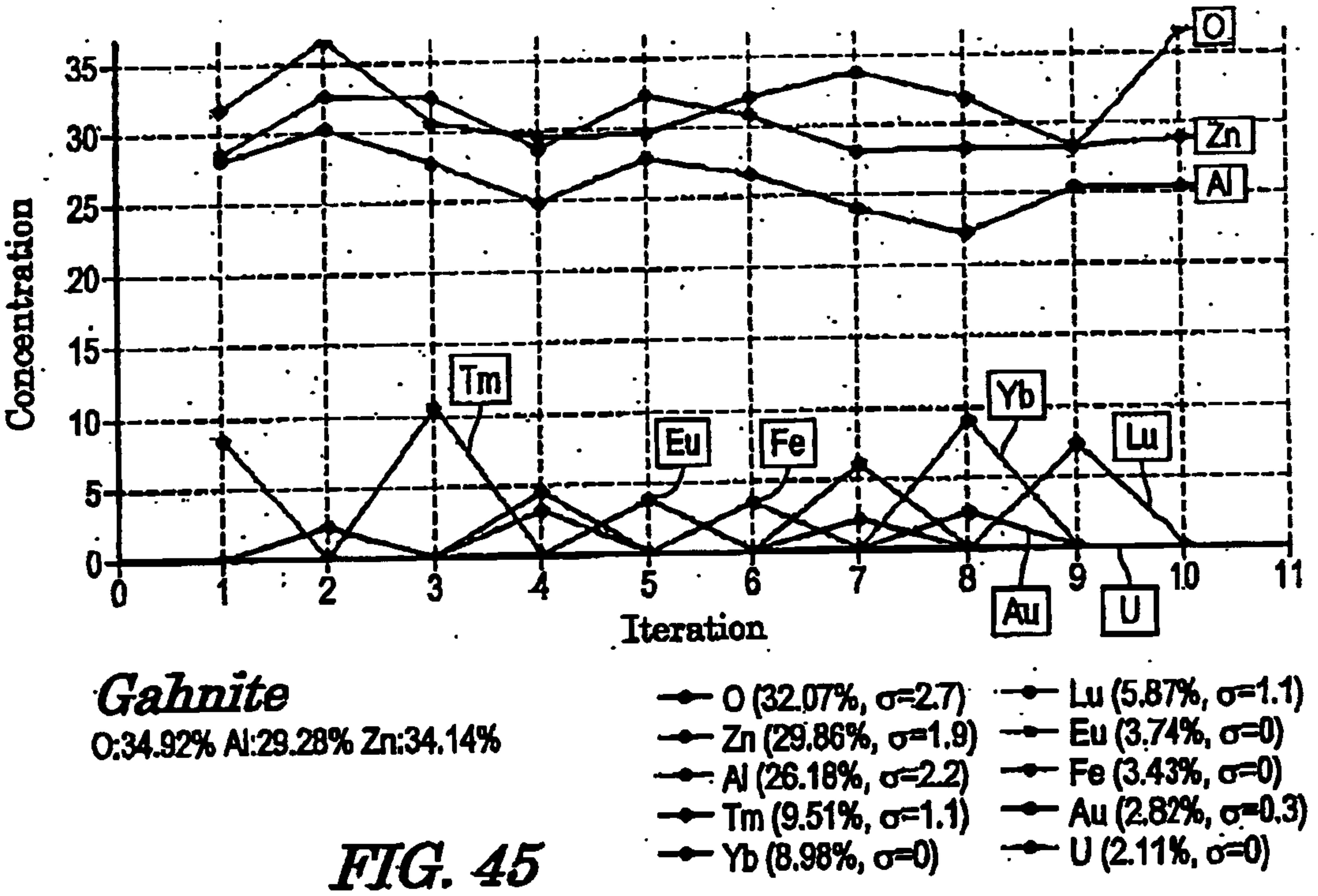

Concentration
35
30
25
20
15
10
5
0
Iteration
0
1
2
3
4
5
6
7
8
9
10
11
O
Zn
Al
Tm
Eu
Fe
Yb
Lu
Au
U
Gahnite
O:34.92% Al:29.28% Zn:34.14%
O (32.07%, σ=2.7)
Zn (29.86%, σ=1.9)
Al (26.18%, σ=2.2)
Tm (9.51%, σ=1.1)
Yb (8.98%, σ=0)
Lu (5.87%, σ=1.1)
Eu (3.74%, σ=0)
Fe (3.43%, σ=0)
Au (2.82%, σ=0.3)
U (2.11%, σ=0)

FIG. 45

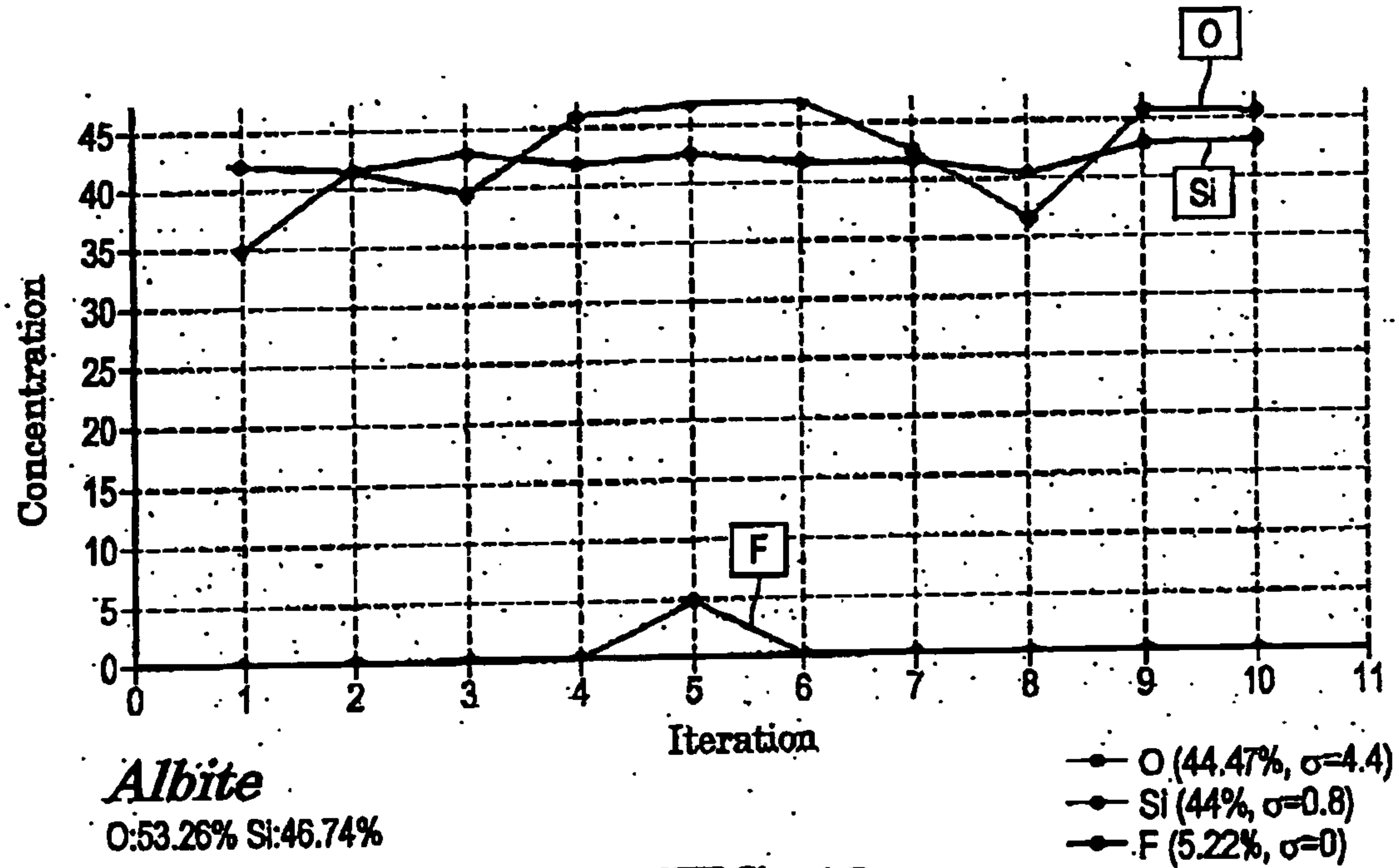

Concentration
45
40
35
30
25
20
15
10
5
0
Iteration
0
1
2
3
4
5
6
7
8
9
10
11
O
Si
F
Albite
O:53.26% Si:46.74%
O (44.47%, σ=4.4)
Si (44%, σ=0.8)
F (5.22%, σ=0)

FIG. 46

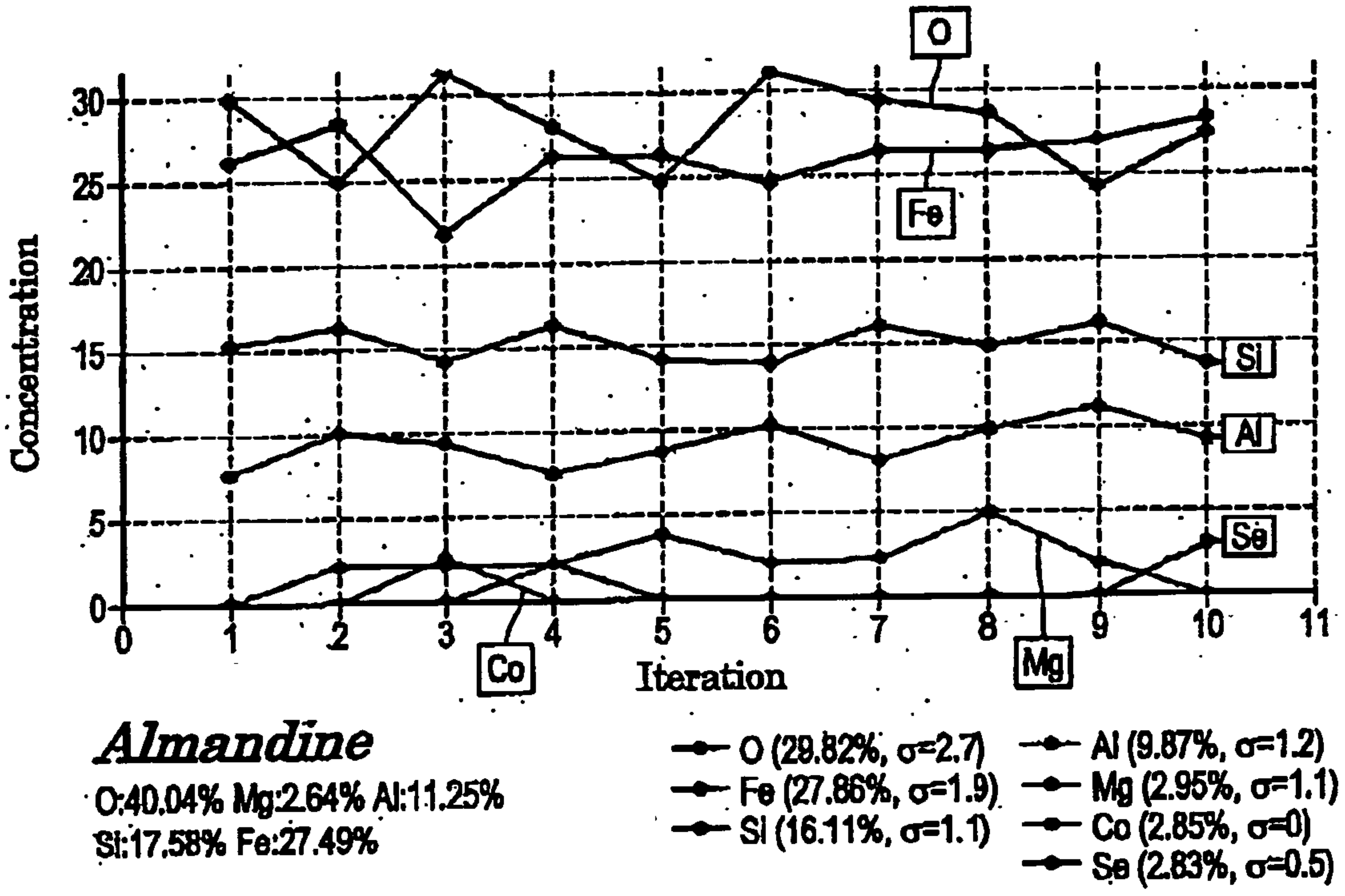

O
Fe
Si
Al
Se
Co
Mg
Concentration
0
5
10
15
20
25
30
Iteration
0
1
2
3
4
5
6
7
8
9
10
11
Almandine
O:40.04% Mg:2.64% Al:11.25%
Si:17.58% Fe:27.49%
O (29.82%, σ=2.7)
Fe (27.86%, σ=1.9)
Si (16.11%, σ=1.1)
Al (9.87%, σ=1.2)
Mg (2.95%, σ=1.1)
Co (2.85%, σ=0)
Se (2.83%, σ=0.5)

FIG. 47

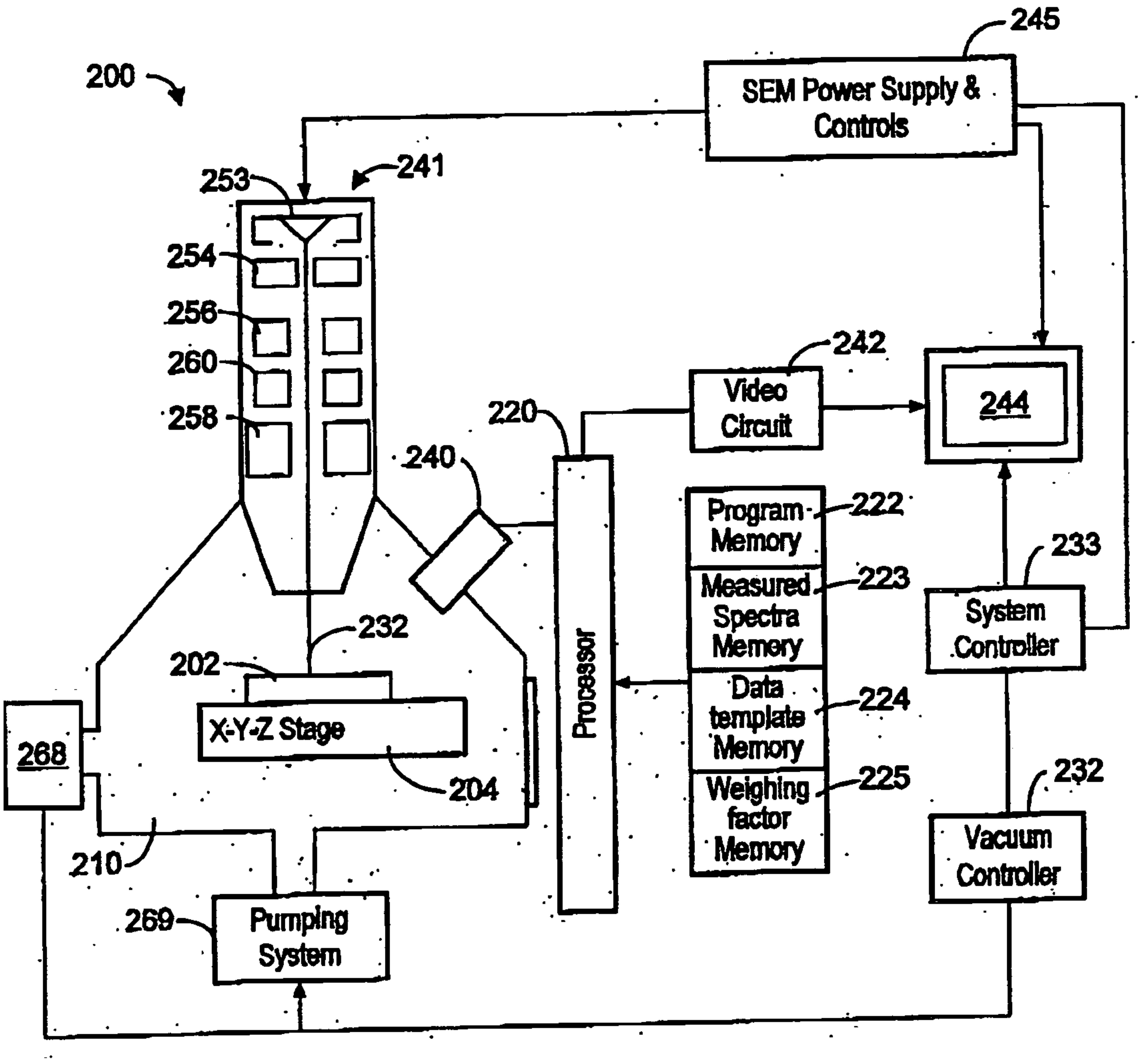
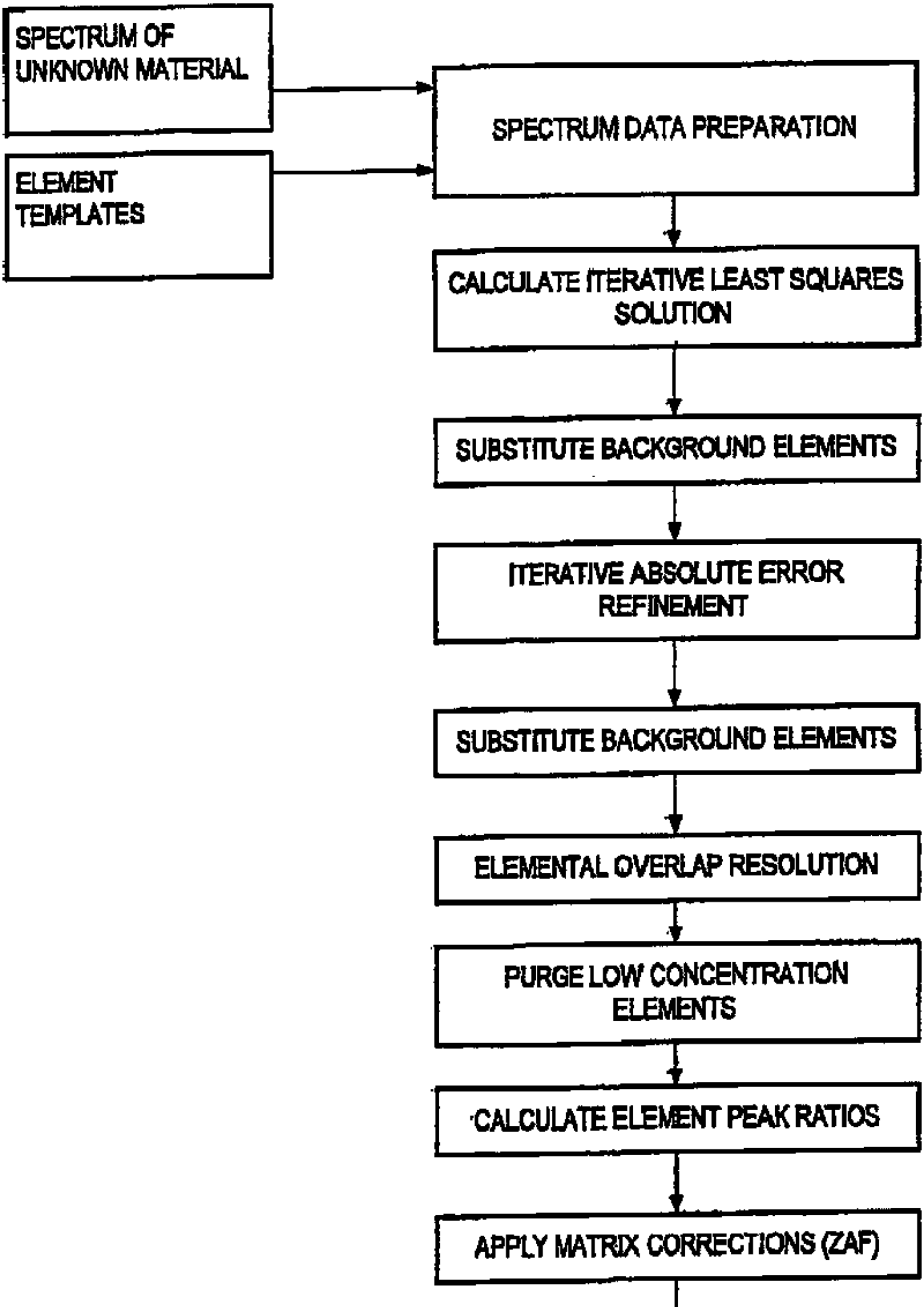

200
245
SEM Power Supply & Controls
253
241
254
256
260
258
242
Video Circuit
244
220
240
Program Memory
222
Measured Spectra Memory
223
Data template Memory
224
Weighing factor Memory
225
Processor
233
System Controller
232
202
X-Y-Z Stage
204
268
232
Vacuum Controller
210
269
Pumping System

FIG. 48



High Level Iterative Least Squares Algorithm