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A very simple method for true elemental mapping using the scanning proton microprobe

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Abstract

An elemental map by means of SPM is traditionally obtained by total counts entering an energy window (TCEW) corresponding to a characteristic X-ray of that element. Besides the characteristic X-ray signals of the element, the total counts contain the contribution of continuum background and overlapping peaks of the interfering elements as well. A method called NCEW (net counts entering an energy window) has been developed for off-line true elemental mapping. The continuum background is calculated with a trapezoid area determined by the counts within border gates and is subtracted from the total counts of the peak. The branch ratios of the characteristic X-rays of the interfering elements are used to correct their overlapping peaks. Because the net counts eliminate the contribution of the background and the overlapping peaks from the total counts, the map obtained by the NCEW is free of artifacts due to the continuum background and the peak overlapping. This method was tested by scanning a microbeam over a multi-foil target. Applications of the NCEW method to some environmental and geological samples are described. © 1997 Elsevier Science B.V.

1. Introduction

The element distribution maps play an important role in the scanning proton microprobe analysis. In geological applications, the maps may give a direct and clear observation of element occurrences in different mineral phases within micron scale regions of the rock samples. Some small mineral grains and inclusions which are characterized by their geochemical elements, particularly their trace elements, may be discovered from the maps.

The traditional element maps are obtained by means of the total counts entering energy windows (TCEW) which are corresponding to the characteristic X-rays of the elements. Besides the characteristic X-ray signals of the elements, the TCEW also contain the contributions of the continuum background under the X-ray peaks and the overlapping peaks of the interfering elements. Sometimes one can avoid the element interference by selection of the correct X-ray branch lines. However, it is not always succeeded. Because of that, the TCEW method may introduce artifacts into the element maps, particularly for the trace element maps.

In order to get rid of the artifacts from the maps, the techniques for true element distribution maps are developed in many microprobe laboratories. Instead

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of the energy window setting, Ryan and Jamieson suggested to use a spectral decomposition method to produce the element maps that can effectively reject the influences of the background and overlapping peaks [1]. A transform matrix that closely approximated the time-consuming nonlinear least-square method was used for the spectral decomposition. The transform could be performed in live time to obtain continuously updated true element maps while the data accumulated. Because the transform matrix was based on the principle that each pixel on the map has equal PIXE yields and the same background shapes, the spectral decomposition method might introduce systematic errors when mapping samples with nonuniform composition.

Based on the TCEW method, some modifications were developed to overcome the problems of the artifacts on the maps and to keep the data processing method simple and direct. Pallon and Knox reported a simple method to resolve the interferential peak overlaps for element maps of biological samples [2]. The calcium map was produced by the counts within the calcium K_α energy window and the potassium K_β peak overlap within the calcium window was removed by an ordinary peak overlap resolving technique. Because the geological thick samples usually produce high continuum background under the X-ray peaks, it may also introduce obvious artifacts in the element maps. In order to remove the artifacts caused by the continuum background, Wu et al. proposed a background subtraction method based on the assumption that the X-ray background in a pixel was proportional to the total X-ray counts from the pixel [3]. This assumption was only correct if the matrix of the sample had a uniform composition and the X-ray background at each pixel had the same energy distribution.

We have developed a method called NCEW (net counts entering an energy window) for off-line true elemental mapping. The contribution of continuum background and overlapping peaks of the interfering elements were estimated and subtracted from the TCEW at each pixel separately on the element map. Because the background and the overlaps were calculated according to the X-ray spectra accumulated at each pixel individually, there was no necessity to assume that each pixel should have similar matrix composition and spectral shapes. The NCEW method was suitable to get true element distribution maps for samples with a widely inhomogeneous matrix, such as geological samples which contained different mineral grains, mineral phases and inclusions. The calculation of the data was based on the energy window setting. It kept the method simple, direct and other advantages of the traditional technique for element mapping. The program will run on a small computer.

2. Methodology of NCEW

The event by event data collection was used for total quantitative scanning analysis [4]. All information concerning the X-ray energy and the x–y coordinates of the scanning beam points should be recorded as events without any loss due to the energy window or the coordinate border setting. An off-line sorting program could produce distribution maps of X-ray yields in the scanned area with the collected event data. By the ordinary TCEW method, only one energy window under the peak of element i was set to produce a distribution map of the total X-ray counts entering the energy window $T_i(x, y)$. In order to evaluate the background counts under the peak, the Wasson method was used. Besides the element energy window, the right and the left border energy windows were also set to calculate the distribution maps of the background counts at the two borders of the peak $R_i(x, y)$ and $L_i(x, y)$. The background counts were $W_i(x, y) = n[R_i(x, y) + L_i(x, y)]/2$, where n was the channel number of the peak width. The distribution map of the net counts of element i exclusive of the background was calculated by the equation:

$$N_i'(x, y) = T_i(x, y) - W_i(x, y). \tag{1}$$

The branch ratio of the characteristic X-rays of the interfering element j was used to evaluate its interference on the analytical element i. The net counts of element i exclusive of both the background and the overlap were calculated by the following equation:

$$N_i(x, y) = N_i'(x, y) - B_{ij} N_j(x, y), \tag{2}$$

where B_{ij} was the branch ratio of the yield of the X-ray line which interfered the analytical element i to the yield of another X-ray line of the interfering element j, which could be measured without other interference. $N_j(x, y)$ was the measured net count of the interfering element j. The branch ratio B_{ij} might not be equal for different matrix composition. In order to estimate the changes of the branch ratio B_{ij}, we measured it for many materials with widely different composition. The results showed that the maximum fluctuation of B_{ij} was less than 10%.

The subtraction of the background and overlap would introduce more statistical errors into the net X-ray counts. According to Eqs. (1) and (2), the statistical division of the net counts $N_i(x, y)$ would be:

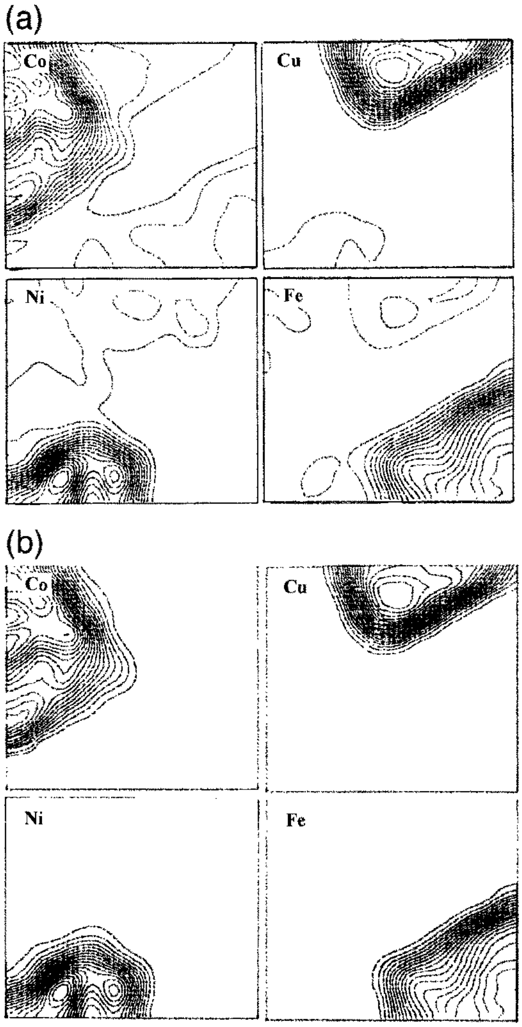

Fig. 1. Element maps of a 500×500 μm^2 scan area at a joint point of a multi-element foil sample. (a) Element maps of multi-element foils produced by ordinary TCEW method. (b) Element maps of multi-element foils produced by new NCEW method.

$$\sigma_i(x, y) = \left\{N_i(x, y) + (1 + n/2)W_i(x, y) + B_{ij}^2\left[N_j(x, y) + (1 + m/2)W_j(x, y)\right]\right\}^{1/2}. \quad (3)$$

The statistical division would make a trace element distribution map ambiguous. In order to clean up any of the ambiguities in the map, a threshold of counts for each pixel $H_i(x, y)$ was set to discriminate the trace element existence at pixels where the net X-ray counts were below the threshold. To obtain a 95% confidence level, the threshold level was set by $H_i(x, y) = 2\sigma_i(x, y)$.

3. Test experiments of the NCEW method

3.1. Measurement of multi-element foil sample

The sample was made by gluing Fe, Co, Ni and Cu metal foils side by side on a plastic plate. A 500 × 500 μm^2 scan area was covered across four corners of the metal foils. The element maps produced by the ordinary TCEW method (in Fig. 1a) showed obvious artifacts caused by the overlaps and continuum background in the spectrum. If the same data were treated by means of the NCEW method, one could produce high-quality element maps like Fig. 1b without artifacts. Each element map in Fig. 1b picked out only those regions where the corresponding metal foils resided.

3.2. Measurement of sulfide ore samples

In a section of sulfide ore samples the distribution of some different mineral phases has been observed by an optical microscope. In a 500 × 500 μm^2 scan area, the identified mineral phases are chalcopyrite ($CuFeS_2$), chalcomiclite (Cu_5FeS_4), pentlandite ($[Fe,Ni]_9S_3$) and sperrylite ($PtAs_2$). The PIXE spectrum in the area is dominated by the X-rays of matrix elements Si, S, Ca, Fe and Cu. The element maps produced by the traditional TCEW method are shown in Fig. 2a. As a comparison, the element maps produced by the new NCEW method are shown

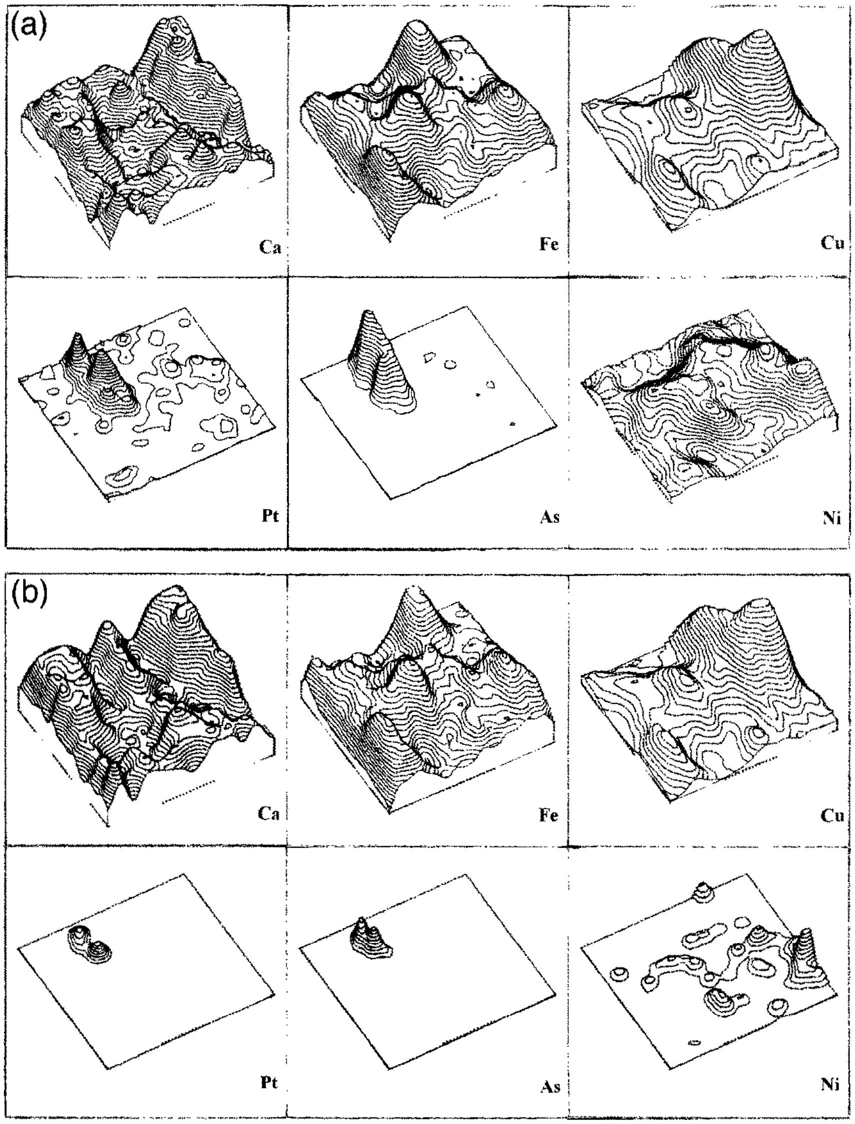

Fig. 2. Element maps of a 500 × 500 μm^2 scan area in a sulfide ore sample which contains mineral grains of chalcopyrite, chalcomiclite, Pentlandite and sperrylite. (a) Element maps produced by ordinary TCEW method. (b) Element maps produced by new NCEW method.

in Fig. 2b. The maps obtained from both methods for the major elements Ca, Fe, and Cu are essentially identical. However, the Pt, As and Ni maps obtained from the two methods showed remarkable differences. The energy window of the PtL_α peak is used for Pt mapping. In Fig. 2a, high statistical fluctuation of the background counts broaden the area where only the mineral phase of sperrylite ($PtAs_2$) exists. In contrast, the artifacts in the Pt map of Fig. 2b are removed by subtraction of the background from the total counts. A clear and small area in the Pt and As maps of Fig. 2b indicates the exact location of the sperrylite mineral phase. In the Ni map of Fig. 2a, element Ni seems to disperse over a very large region. In fact, Ni is only enriched in the mineral phase of pentlandite. The small grains of mineral pentlandite can be seen clearly in the Ni map of Fig. 2b which is produced by the NCEW method. The

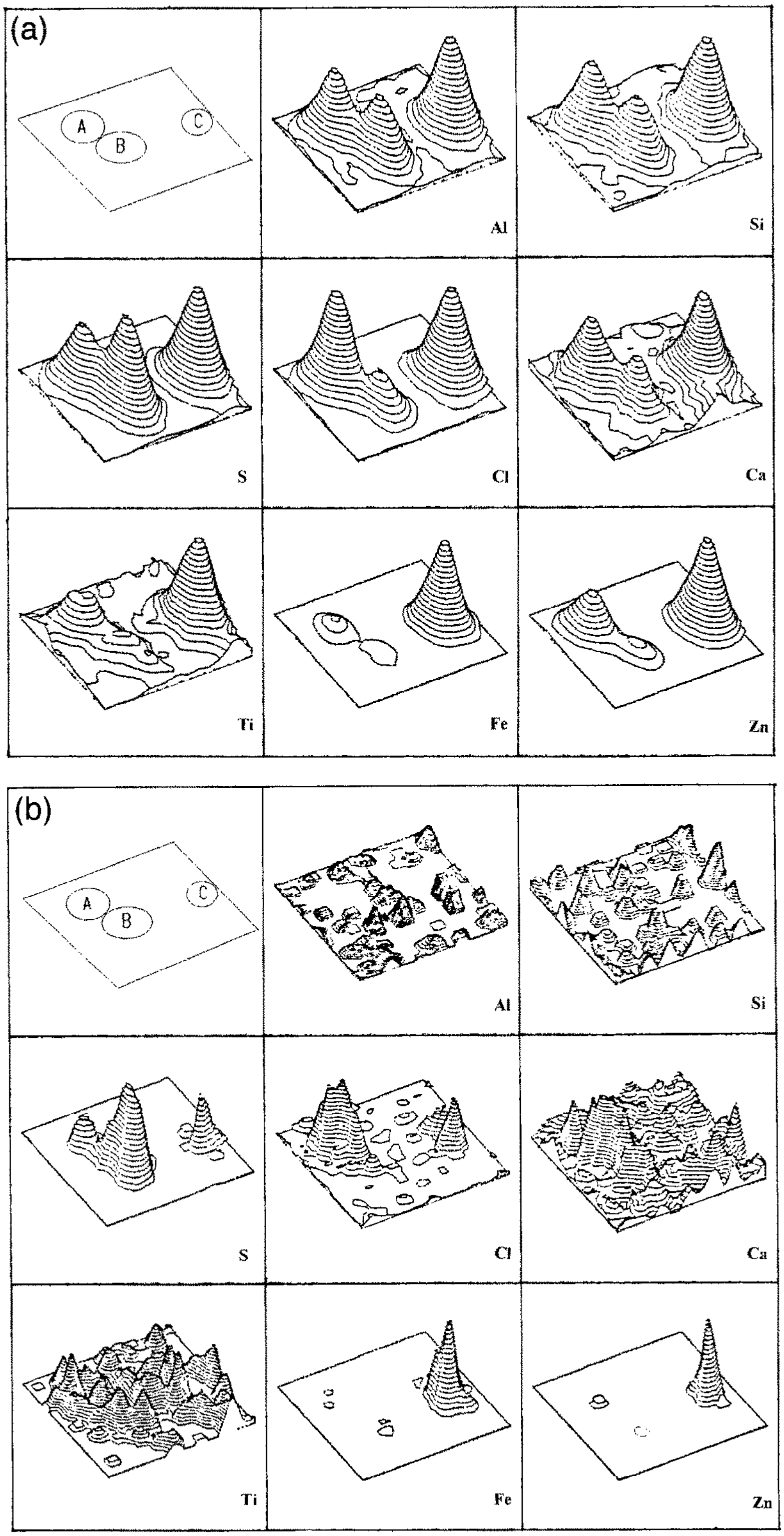

Fig. 3. Element maps of a 50 × 50 μm^2 scan area which contains three single atmospheric aerosol particles. (a) Element maps produced by ordinary TCEW method. (b) Element maps produced by new NCEW method.

results of the element maps by NCEW method are well consistent with the observation by optical microscopes.

3.3. Measurement of single atmospheric aerosol particles

Air pollution comes from various sources. Microscopic analysis of single atmospheric aerosol particles by nuclear microprobe is a useful means for identifying the sources of pollution [5]. Fig. 3 shows an example of three particles in a $50 \times 50\ \mu m^2$ scan area. The element distribution maps in the scan area produced by means of TCEW and NCEW are displayed separately in panels a and b of Fig. 3. A comparison of the two methods reveals that the TCEW method produces some false information on the element distribution, particularly for the elements with low X-ray yields and a high background, such as the maps of Na, Al, Si, and Ti. From the element maps in Fig. 3b, we find that particle B is enriched in S and it is identified as air pollution from a coal burning power station. Particle A mainly consists of Cl and S. It comes from the exhaust of vehicle engines. Elements Fe and Zn are concentrated in particle C. It is a particle coming from the metallurgic industry.

4. Conclusions

A very simple method to reduce an X-ray spectrum from overlaps of continuum background and interfering peaks can be used to calculate the net counts entering an energy window (NCEW) of a characteristic X-ray peak of an element. The method can effectively produce true element distribution maps with litter-specific information caused by the X-ray background and interference of other X-ray peaks. The statistical performance of the true element maps can be improved by setting a threshold for each pixel on the map to filter the data with poor statistics. The feasibility of the NCEW method for SPM element mapping has been demonstrated by measurements of a multi-element foil sample, some geological samples and some single atmospheric aerosol particles.

Acknowledgements

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