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Algorithm for fitting XRF, SEM and PIXE X-ray spectra backgrounds

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Abstract

Existing background fitting of energy dispersive X-ray spectra (X-ray, electron or proton excited) algorithms (e.g. parabolas or polynomials) are not universally applicable. Various limitations exist tying each algorithm to specific spectral shapes. This project aimed to find a generic algorithm which could reliably fit background independent of X-ray spectra source and form. A frequency differentiated non-linear digital filter "rolling ball" was chosen as a promising possibility. The algorithm is based on a square wave with an energy variable width as the structuring function, operated on by a gray scale morphological transformation. A wide range of spectra types have been successfully fitted. This algorithm behaves equivalently to traditional polynomial backgrounds in simple spectra e.g. PIXE aerosol spectra with funny filter, and is considerably more robust for multiple overlapping peaks, rapidly varying backgrounds, and is independent of X-ray energy filter or excitation mode.

1. Introduction

Application of Si(Li) detectors to collect X-ray spectra from samples of various types has become widespread, with various X-ray excitation mechanisms involved in both research and commercial machines. Our experience as a research group using multiple X-ray excitation mechanisms, is that the need to changing software packages to perform the same spectral reduction tasks for each excitation technique has been frustrating. As the available software packages do not all include the same range of features the inability to apply some useful option to spectra collected using different excitation mechanisms, different energies or different filters seriously affected accuracy of results produced. Attempts to transfer spectra between the software packages identified the background fitting algorithm as the more troublesome aspect of inter-technique spectra transfer. This led to the development of a fitting technique independent of the excitation mechanism. This is hopefully the first step towards a universal X-ray spectrum software package combining the most effective features of the practices of the different disciplines.

Investigations showed that characteristics of various spectra are identical except for the shape of the backgrounds. These backgrounds varied due to the X-ray filters applied, the excitation method, excitation energy and the sample backing or matrix. Also most of the fitting models were limited in the types of background they could handle. Traditional PIXE fitting algorithms rely on theory to define their polynomial fitted shape and thus do not transfer well. Other techniques are limited in their ability to handle some background shapes e.g. flat or concave areas are not well fitted using the parabola models. A survey of spectra fitting techniques was performed and a number of possibilities were identified. One of these was chosen for testing as the most promising, yet simple and mathematically elegant.

This paper gives the results of the initial tests and compares this technique with traditional methods.

2. Method

The mathematical technique selected for universal X-ray spectra background fitting is a modification of a digital image processing technique used to adjust image sharpness [1,3]. Technically, it is a frequency differentiated non-linear digital filter based on a square wave with an energy variable width as the structuring function, operated on by a gray scale morphological transformation [2]. It can be described as the mathematical equivalent to rolling a ball below the spectra and marking out the

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background as the locus of the ball at each moment. To account for the varying peak width of the Si(Li) detector energy spectra as energy increases this ball gradually increases in diameter, expanding proportional to the energy induced peak width broadening. The mathematical functions involved in the technique are maxima, minima and averages over a moving window of the channels. These are relatively simple arithmetic functions that are efficiently performed by a computer.

Distortion of the peaks does occur but as the Gaussian which is filtered for fitting can also be reconstructed this transformation of the peaks does not adversely affect display options or fit results.

One advantage of using this mathematically simple technique is that the actions of the filter on the spectra and the Gaussian peaks can be calculated in reverse and the spectra, with background and peaks plotted for the operator to inspect visually. This gives the operator a powerful tool for problem solving. If adequate fits are not being achieved visual inspection is often the quickest means to identify reasons preventing convergence of the fits.

The filter equations can be summarised as

$$Y_i = f_G(i) = \max\{f_{i-v}^{(1)}, \cdots, f_i^{(1)}, \cdots \leftarrow f_{i+v}^{(1)}\},$$

$$f_i^{(1)} = \min\{f_{i-v}, \cdots, f_i, \cdots, f_{i+v}\}.$$

f_i is an expanding square wave filter.

3. Algorithm

The algorithm used for the background fitting is easiest to present in the form of computer code. The following listing gives the algorithm in Pascal. Pascal was chosen as it is a common teaching language and is elementary to understand.

```
PROGRAM WHEXFIT;
  CONST {potential fit parameters to be varied with least squares fitting}
     pwhma  =0.4;  {peak width half max a}
     pwhmb  =0.2;  {peak width half max b}
     fitconst=5;  {constant to ensure ball is slightly wider than the peaks - fit adjusted}
     Cenergy=4.123;  {Energy calibration const}
     Menergy=0.0204;  {Energy calibration gradient}
  TYPE Spectras=ARRAY[1..1024] of Integer;
     Peaks=ARRAY[1..1024,1..5] of Real;
  VAR Peaklist : Peaks;
     Spec, Back, Peak, Espc : Spectras;
     Inputfile, Backfile, SpecFile, PeakFile, ErrrFile : Text;
     Error, FitisGood : Boolean;

  PROCEDURE FitBack;
    VAR i,j,width : Integer;
      T1,T2,T3,Count : Spectras; {Array[1..1024] of integer}
    PROCEDURE SetWidth(k:Integer);
      VAR Energy, WidthE : real;
      BEGIN
        Energy :=k*menergy+Cenergy;    {Convert channels to energy}
        WidthE :=Energy*pwhma+pwhmb;    {set width in energy scale}
        Width :=Round((((WidthE-Cenergy)/menergy)+fitconst)/2);    {convert to channels}
          (*****fitconst is a fitted parameter meaning that the ball is slightly wider than the peaks
             Two main options are possible - 1. it is constant or 2. it also expands with energy.
             The optimum of these two has not yet been identified.*****)
    END;
  BEGIN
    For i :=1 to 1024 do begin    {initialise}
      T1[i] :=32767; {max integer}
      T2[i] :=0;
      T3[i] :=0;
      Count[i] :=0;
```

```
    End;
    For i :=1 to 1024 do begin    {minimise}
      SetWidth(i);
      For j :=-width to width do begin
        If ((i+j)>0) AND ((i+j)<1025) then
          If T1[i]<Spec[i+j] then T1[i] :=Spec[i+j];
      End;
    End;
    For i :=1 to 1024 do begin    {maximise}
      SetWidth(i);
      For j :=-width to width do begin
        If ((i+j)>0) AND ((i+j)<1025) then
          If T2[i]>T1[i+j] then T2[i] :=T1[i+j];
      End;
    End;
    For i :=1 to 1024 do begin    {smooth}
      SetWidth(i);
      For j :=-width to width do begin
        If ((i+j)>0) AND ((i+j)<1025) then begin
          T3[i] :=T3[i]+T2[i+j]; {sum}
          Count[i] :=Count[i]+1;
        End;
      End;
      Back[i] :=Round(T3[i]/Count[i]);  {average}
    End;
  End; {Fitback}

BEGIN
  Openfiles;
  Initialise;
  Repeat
    Fitback;
    FitPeaks;
    MinimiseError;
  Until ERROR or FITISGOOD;
  WriteResults;
END.
```

4. Results

The background fit has been applied to seven different spectra with variable shapes, including a theoretically constructed test spectrum, and three time series spectra. Fig. 1 shows a ED-XRF sample spectrum with the background fitted using the "Rolling ball" technique. The original spectrum, background and resulting peaks are illustrated. This shape of spectrum has proven difficult to completely fit using any of the traditional methods. All spectra fitted with the present technique to-date have been successful. The number of iterations required to achieve adequate fits is also reduced. After the first iteration for all spectra the error for all areas of the spectrum with more than 10 counts per channel was less than 10% while in areas with only 1 to 10 counts of noise per channel errors with less than 5 counts per channel.

Fig. 2 shows a traditional aerosol PIXE thin film spectra with the "rolling ball" background. Resulting peaks are shown in Fig. 3 as well as the result of one iteration of peak fitting of the adjusted Gaussian peaks (beginning with 20 selected elements for fitting).

Spectra have been tested that were not derived from X-ray generation. These spectra were time series pollutant concentration spectra. Fig. 4 is an example of a pollutant time series which has a erratic compoenent that is slowly variable representative of regional pollutant levels with rapidly varying peaks caused by local pollution. The background model successfully separated the slowly varying and rapidly varying components of the pollutants investigated and for all changes, except one very sharp peak caused by a passing cold front, good separation was achieved. For the passing of the cold front

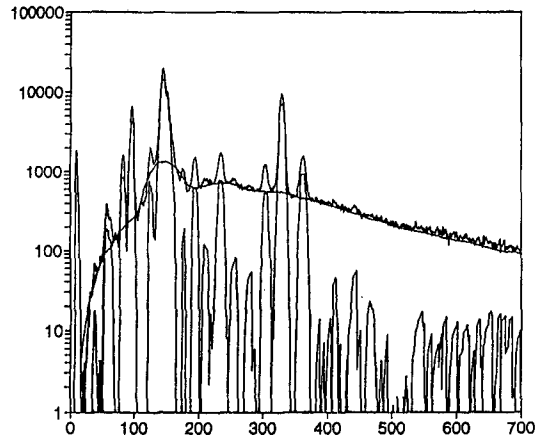

Fig. 1. ED-XRF spectra with a "rolling ball" background fit. The spectrum was collected at 20 kV and 2350 mA for 10 minutes. The original spectrum, the background fit and resulting peaks are shown.

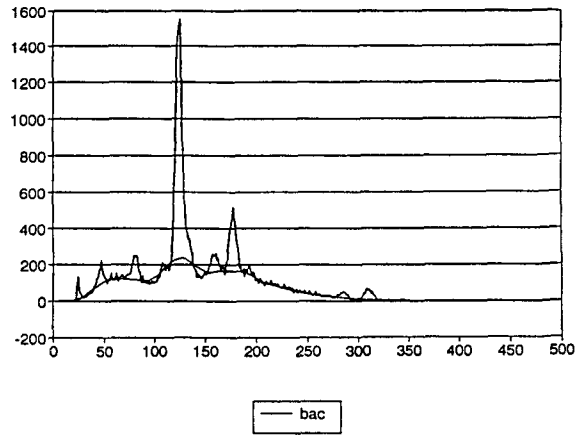

Fig. 2. A traditional aerosol PIXE thin target spectra with results of a "rolling ball" background fit.

an adequate fit was achieved but visual inspection showed some discrepancy between slowly varying compoents which were sharply ended and calculated components. As these samples are of widely varying background shape they were a good test for the overall flexibility of the model.

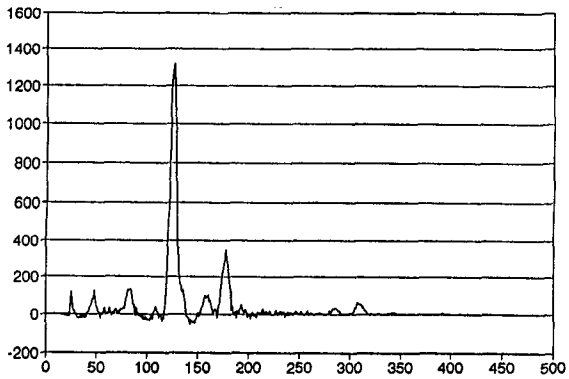

Fig. 3. The resultant peaks from the first iteration, with filtered Gaussian peaks, used during the fit to the spectrum in Fig. 2.

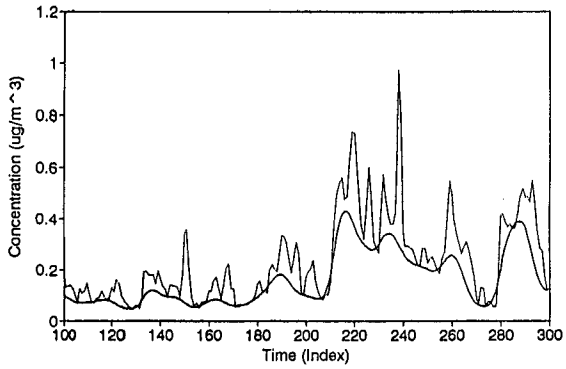

Fig. 4. A time series spectrum shows the effect of the "rolling ball" fitting technique on the various shapes underlying the regional pollutant levels for potassium from biomass buring.

5. Conclusions

A promising fitting technique has been identified for the generic fitting of a wide range of spectra covering most of the spectra shapes generated by various X-ray analysis techniques. Initial testing is giving fast accurate fit results for a wide range of spectra shapes. Mathematically the model is widely applicable without being excessively complex. If the final tests for reliability and mathematical rigour are successful then this technique could provide an elegantly simple solution to PIXE and other spectra background fitting independent of shape.

References

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[3] C.L. Dym and E.S. Ivey, Principles of Mathematical Modeling (Academic Press, New York, 1980).