AN ARTIFICIAL NEURAL NETWORK ANALYSIS OF LOW-RESOLUTION X-RAY FLUORESCENCE SPECTRA

Xianguan Long, Ning Huang, Taihua Li, Fuqing He and Xiufeng Peng
Institute of Nuclear Science and Technology
Sichuan University, Chengdu 610064, China

ABSTRACT

An artificial neural network approach was used for the analysis of low-resolution XRF spectra. Instead of peak analysis and fitting the experimental results to a mathematical function as used by the conventional algorithms, the artificial neural network method takes the spectrum as a whole, comparing its shape with the patterns learned during the training period of the network. This method was tested experimentally by the XRF spectrum analysis using both x-ray tube excitation and radioisotope source excitation. A multi-element analysis of geological samples with this method was carried out and satisfactory results were obtained.

I. INTRODUCTION

X-ray fluorescence spectroscopy is a well-established technique for qualitative and quantitative element analysis of materials, in both research and industrial environments. In the later case, the XRF information is to monitor the composition of samples or to classify samples. This type of application is often carried out in the field with much less sophisticated instrumentation. A low resolution x-ray detector, such as a gas-filled proportional counter is used to detect and count the emitted x-ray in these situations. Because of the low resolution of the detector, overlapping of the photo-peaks of adjacent element in the XRF spectrum often occurs. In early portable XRF analyzers, the balanced edge-filter method was used to discriminate between x-ray lines of adjacent elements. A major drawback of the balanced filters method is its poor sensitivity, as the analyte net intensity is a difference of two count rates which are usually high. In modern portable XRF systems, special proportional counters with sufficient energy resolution are used for multi-element analysis without balanced filters[1]. The analysis of x-ray spectrum is to set up the element windows about the appropriate peaks in the x-ray spectrum, and to measure the spectral overlap factors. Adjacent elements are determined using simple window integration methods[2].

In recent years, an approach to the solution of the automatic radiation spectrum analysis problem based on the use of a processing system known as artificial neural network (ANN) was presented by Olmos et al. and tested successfully in the analysis of several spectra, taken with a NaI spectrometer[3,4].

In the present work, the artificial neural network approach was used for the analysis of low-resolution x-ray fluorescence spectra. The details of the ANN approach were described and tested experimentally by the XRF spectrum analysis using both x-ray tube excitation and radioisotope source excitation. A multi-element analysis of geological samples with this method was carried out and satisfactory results were obtained. This method is useful in those cases in which a simple operation and a fast
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response are needed, but precise quantification is less important.

II. DESCRIPTION OF THE METHOD

In this method, each XRF pulse-height spectrum is considered to be an \( n \)-component vector \( X \) in an \( n \)-dimensional pattern space, where \( n \) is the number of channels and \( x_i \) is the counts of channel \( i \):

\[
X = [x_1, x_2, \ldots, x_n]^T
\]  

(1)

where a notation \([ ]^T\) is used for the transpose of \([ ]\).

A reference spectrum is a XRF spectrum produced by a reference material composed of a single element and is denoted as a vector \( r \). The set of \( k \) reference vectors will be referred to as the reference set, and it must be known in advance for solving the problem. This set may be seen as a matrix \( R \) composed of the reference column vectors:

\[
R = [r_1, r_2, \ldots, r_k]
\]  

(2)

An unknown XRF spectrum can be considered as a vector formed by a linear combination of a set of reference spectra, their coefficients \( c_i \) being a measure of the intensity of each component relative to the intensity of the reference spectrum taken as the unity:

\[
X = \sum_i c_i r_i
\]  

(3)

denoting as matrix product, then

\[
X = RC
\]  

(4)

where \( C \) is \( k \)-dimension vector

\[
C = [c_1, c_2, \ldots, c_k]^T
\]  

(5)

In a model of artificial neural network, known as Linear Associative Memory, \( X \) is the input vector of the network and \( C \) is the output vector of the network, as presented in Figure 1, they are related by a weighting matrix \( W \) as follows

\[
C = WX
\]  

(6)

![Figure 1. Scheme of ANN for x-ray spectrum analysis](https://example.com/figure1.png)
The weighing matrix can be obtained during the training period of the network by solving the matrix equation:

\[ I = WR \]  \hspace{1cm} (7)

where \( I \) is a \((k \times k)\) unit matrix. In the conditions that the vectors \( r_i \) of the matrix \( R \) are linearly independent, an exact solution \( W \) to the equation (7) exists and is the pseudoinverse matrix of \( R \), that is,

\[ W = R^+ \]  \hspace{1cm} (8)

Therefore, the vector \( C \) can be obtained by

\[ C = R^+ X \]  \hspace{1cm} (9)

Because of the properties of the pseudoinverse matrix \( R^+ \), this formula gives the solution in the sense of optimal least squares. In this work we have used the Greville algorithm for finding the pseudoinverse \( R^+ \).

III. EXPERIMENTAL

The method was tested by the XRF spectrum analysis using both radioisotope source excitation and x-ray tube excitation. The secondary x-rays were detected by a proportional counter. A standard nuclear spectroscopy amplifier was used to feed the pulse-height spectra into a personal computer-based 1024 channel pulse-height analyzer.

Several single element standards and one scatterer were used for the reference spectrum measurement. Each standard can be a pure element or a compound of the element and cast into a small disk. The powdered sample was compressed into a disc 25 mm in diameter and 3 mm in thickness. The disk was placed on a sample holder in air.

For samples of pentlandite, a 5 mCi \(^{109}\text{Cd}\) source was used to produce the primary exciting x-ray. The secondary x-rays were detected by a proportional counter, which has a 100 \(\mu\)m thick Be window and filling gas of xenon. The energy resolution (FWHM) of the counter is 17% for 5.9 keV Mn K x-ray. Reference spectra were measured for single element standard Ca, Fe, Ni, Cu and a scatterer and presented in Figure 2. The Fe spectrum, presented in Figure 2(b), clearly shows that, in addition to the 6.4 keV photopake, another peak at 2.1 keV (4.3 keV below 6.4 keV) is also present due to the escape of the 4.1 keV Xe L x-rays not absorbed by the filling gas.

The XRF spectra for samples of pentlandite were taken with the same instrument and experimental conditions and some typical spectra were presented in Figure 3. It is clear from Figure 3 that because of the poor resolution and the relatively high concentration of Fe in the samples, the peaks of Ni and Cu are overlapped with the peak of Fe.

For samples of V-Ti magnetite, a x-ray tube with a molybdenum anode operated at 11 kV was used to produce the primary exciting X-rays. The secondary X-rays were detected by a proportional counter, which has a 25 \(\mu\)m thick Be window and filling gas of neon-argon mixture. The energy resolution (FWHM) of the counter was 15% for 5.9 keV Mn K x-ray. Reference spectra were measured for single element standards Al, Si, Ca, Ti, V, Fe and a scatterer. The XRF spectra for samples of V-Ti magnetite were taken with the same instrument and experimental conditions and some typical spectra were presented in Figure 4. All spectra were taken in air and consequently elements lighter than Al were inaccessible due to the air absorption of their fluorescence x-ray. The same overlapping of peaks can be seen in Figure 4 as well. In these situations it is...
Figure 2. XRF spectra for single element Ca, Fe, Ni, Cu standard and scatterer, detected by a proportional counter with 100 μm Be window, excited by radioisotope $^{109}$Cd.

Figure 3. XRF spectra for samples of pentlandite, detected by a proportional counter with 100 μm Be window, excited by radioisotope $^{109}$Cd.
Figure 4. XRF spectra for samples of V-Ti magnetite, detected by a proportional counter with 25 μm Be window, excited by x-ray tube.

difficult to perform the peak analysis and fitting the experimental results to a mathematical function as used by the conventional algorithms.

IV. RESULTS AND DISCUSSION

A multi-element analysis using the ANN approach is carried out in the following steps:
1. The XRF spectrum of single standard is denoted as \( r_i \).
2. A set of reference spectra is referred as reference set \( R \).
3. Calculate the pseudoinverse matrix \( R^+ \).
4. The XRF spectrum of unknown sample is denoted as \( X \).
5. The intensity \( C \) is obtained by the matrix multiplication of \( R^+ \) and \( X \).

The results of the analysis by the ANN approach are presented in Table 1 and Table 2, respectively, where coefficient \( c_i \) is a measure of the intensity of each component relative to the intensity of the reference spectrum taken as the unity and the \( c_c \) is a confidence coefficient, defining the goodness of a given analysis by Olmos[31]. This value is the projection of the spectrum vector on a vector normal to the vectorial subspace defined by the database. The smaller this value is, the better the analysis is and a threshold of 0.15 is fixed for considering a given analysis as valid. Values higher than this limit indicate the presence of elements for which the network was not trained [4].

The results of multi-element analysis for geological samples of pentlandite and V-Ti magnetite are presented in Figure 3 and Figure 4, respectively, as well.

For visual inspection of the quality of the analysis, the best method is to plot the residuals of the fit, defined as

\[
r_i = (x_i - x(i))/\sigma_i
\]

where \( x_i \) is the experimental value, \( x(i) \) the analysis value and \( \sigma_i \) standard deviation of \( x_i \). The residuals are also plotted in Figure 3 and Figure 4, respectively, as an indicator of the quality of the analysis. Residuals in excess of 3 or -3 then indicate regions of bad
Table 1. Results of the analysis by the ANN for samples of pentlandite

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Ca</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Scatterer</th>
<th>cc</th>
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Table 2. Results of the analysis by the ANN for samples of V-Ti magnetite

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<th>Si</th>
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<th>Ti</th>
<th>V</th>
<th>Fe</th>
<th>Scatterer</th>
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<td>0.0000</td>
<td>0.0000</td>
<td>0.00</td>
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<tr>
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<td>Samples</td>
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</table>
fit, as can be seen in Figure 3 and Figure 4. So these results obtained are satisfactory.

The results show that the assumption of a measured spectrum of unknown sample can be described as a linear combination of spectra of a scatterer and pure elements constituting the sample holds very often. The coefficients can be obtained by using the ANN approach simply.

The advantage of this approach is that most of computation take place during the training period of the network to calculate the pseudoinverse matrix. Once the network is trained for a particular task, operation is relatively fast and spectrum analysis can be rapidly processed. The time to calculate a pseudoinverse of matrix, for example, a matrix with 1024 x 7 dimensions which due to the case of 7 x 1024 channels XRF reference spectrum, is about two seconds on a 40MHz Inter 386 based personal computer and any pre-processings of spectra are not needed.

Because this approach is based on the comparison of unknown spectrum with the patterns stored in the reference base, the effect of instrument drift will spoil the accuracy of analysis. It is very important that quite stable spectrometer is used. Recently a method that handles the drift problems using associative memory algorithms was reported [6].

The obtained results have demonstrated the benefits of the ANN approach in analyzing low-resolution XRF spectral data. The advantages over conventional analytical techniques include simplicity, real-time analysis, and automatic operation, which should make it ideally suited for application in field environments.

V. CONCLUSIONS

The artificial neural network approach was used for the analysis of low-resolution XRF spectra. In this approach an unknown XRF spectrum can be considered as a linear combination of a set of reference spectra, their coefficients are a measure of the intensity of each component relative to the intensity of the reference spectrum taken as the unity and can be obtained simply by calculating the pseudoinverse matrix. This method was test experimentally by the analysis of XRF spectra excited by radioisotope source or x-ray tube and detected by a proportional counter. A multi-element analysis with this method was carried out and satisfactory results were obtained. The algorithm can be easily implemented on a personal computer.

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REFERENCES


