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Neural network-based matrix effect correction in EDXRF analysis

TUO Xianguo* CHENG Bo MU Keliang LI Zhe
Chengdu University of Technology, Chengdu 610059, China

Abstract In this paper we discuss neural network-based matrix effect correction in energy dispersive X-ray fluorescence (EDXRF) analysis, with detailed algorithm to classify the samples. The method can correct the matrix effect effectively through classifying the samples automatically, and influence of X-ray absorption and enhancement by major elements of the samples is reduced. Experiments for the complex matrix effect correction in EDXRF analysis of samples in Pangang showed improved accuracy of the elemental analysis result.

Key words Self-organizing mapping neural network, Cluster analysis, Matrix effect, Sinter mineral
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1 Introduction

In energy dispersive X-ray fluorescence (EDXRF) analysis, matrix effect can be caused by different factors. For a thick sample that consists of multiple elements in considerable contents, such as in mineral samples, photon numbers of characteristic X-rays of a high Z element can be reduced by edge absorption of the adjacent lower Z element. And the effect differs from element to element. Besides, samples of the same type collected from different cites often have different amounts of major and minor elemental contents[1].

The complex matrix effect may make the EDXRF technique ineffective. Therefore, it is important to establish a matrix effect correction model for such kind of samples in their EDXRF analysis. And derivation of a standard curve for the elemental analysis depends on the sample classification to correct the matrix effect.

2 Model

As shown in Fig.1, the neural network-based matrix effect correction model (NNBMECM) consists of four layers from left to right: 1) the input layer, 2) the sample classification layer, 3) the non-linear layer, and 4) the output layer. The input of non-linear layer relays on the output of sample classification layer.

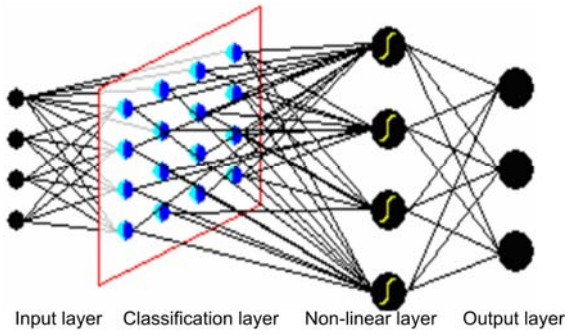

Fig.1 Neural network based matrix effect correction model.

The input layer is X-ray fluorescence counts of different elements in the sample. The sample classification layer is based on the self-organizing mapping (SOM) neural network[2]. It provides sample result to the non-linear layer, which calculates the elemental contents with different standard curves of respective samples. The output layer gives results of the analysis.

3 Algorithm

The sample classification layer has two sublayers: the input layer consisting of N input neural cells and the competition layer consisting of $M \times M$ output neural

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* Corresponding author. *E-mail address:* txg@cdut.edu.cn
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cells, hence the formation of a planar plane array, in which the neural cells of the input and competition layers are connected one to another, The neural cells in the competition layer are connected, but border side of the neural cells restrain each other. The NNBMECM catches the sample character by training the input mode repeatedly, so as to perform classification of the samples and to show the classification result of the input modes in the competition layer. When the classification layer receives an input similar to a subsistent mode, it will recall the modes for the classification. For nonexistent modes, it will remember the character for new samples, without affecting the memory. Consequently, a new kind of classification will be added to classification layer.

According to mechanism of the matrix effect in XRF analysis, input parameters of the NNBMECM are XRF counts of the elements in the sample. Given the number of elements to be detected is *N*, input mode of the sample classification layer is

$$X_k = \left(x_1^k, x_2^k, \cdots, x_n^k \right) \qquad k = 1,2,...,M \tag{1}$$

The NNBMECM decides the sample kind according to Eq.(2), and finds its corresponding standard work curve, so as to perform quantitative analysis of the element.

$$\begin{aligned} &Y_g = 1, d_g = \min d_j,\ j = 1,2,...,M \\ &b_i = 0, i = 1,2,...,M, i \neq g \\ &d_j = \left[\sum_{i=1}^{N} \left(a_i - w_{ji} \right)^2 \right]^{1/2} \end{aligned} \tag{2}$$

With a series of standard samples, the NNBMECM can be trained to resolve the sample characteristic into the classification layer connection during the course of demarcating phase for EDXRF analysis. For samples of similar characteristics, each group has a corresponding standard curve. When the NNBMECM completes the training phase, it analyzes easily element's contents of new mineral samples.

4 Experiment

In the experiment, we used material mixtures in sinter process (such as titanium ore concentrate, iron ore concentrate, titanium gangue, iron gangue and original mine，from tens of factories home and abroad) and artificial mixtures. Therefore, great changes in elemental content of the samples, and evident matrix effect, would be expected. Nineteen groups of core sample, coded as K1 to K19, were analyzed for main elements of Fe, Ti and Si， with the minor elements of Ca, V, Ni, Cu, Zn, As, Pb and Cr.

All samples were treated by 1 h drying at 110℃ ground into powder and 180 mesh sieved. They were measured by EDXRF under the same environment with the same detection geometry.

We have a demarcating to the X-ray tube XRF analyzer. Major elements of the mineral samples were detected. They are Fe, Ti, Si, Ca, V, Ni, Cu, Zn and Cr, hence the classification layer input vector of X_i(i=1,…,9) for their X-ray count rates, respectively.

In classifying the 19 core samples using the SOM neural net, the samples that touch off the same neural cell were in the same type, and six classifications were obtained, as shown in Table 1. Type I has four groups of titanium ore concentrate containing Fe, Ti and V. Type Ⅱ has three groups of titanium gangue containing Fe, Ti, V and Zn. Type III has four groups of iron ore concentrate containing Fe, Ti, Cr, Cu, Ni and V. Type IV has three groups of iron gangue containing Fe, Ti, Cu and V. Type V has two groups of original mine containing Fe, Ti, Cr, Cu, V and Zn. Type VI has three groups of sinter mineral containing Fe, Ti and V. It is well classified by neural net to identify right type of core samples. This will provide a suggestion to establish different analysis mathematic models or equations to analyze different types of the samples. Table 2 shows the major element contents in the core samples analyzed by chemical analysis and artificial neural network (ANN) analysis methods or cluster analysis[4].

From Table 2, it is clear that results of the neural network based method agree with the actual contents of the samples, with absolute errors being less than 10 mg/g for Fe in the samples. In type VI sample groups (sinter mineral), absolute errors of the Si、Ca、Fe are just 0.152, 0.142, 0.245 (10 mg·g^{-1}), respectively, while those of the cluster method are 0.322, 0.412, and 0.504 (10^{-2} g·g^{-1}), respectively. This illustrates that by combining the SOM neural network based sample sorting with the new generation tube excitation XRF analyzer, the matrix effect can be better corrected. This makes a good base for applying the XRF analysis to mine and iron & steel industries.

Table 1 Results of auto-classification of the samples

Types	Groups and Ab.	Major elements	Type of raw material
I	K1/K15/K9/K18	$Fe_2O_3/TiO_2/V$	Titanium ore concentrate
II	K2/K5/K14	$Fe_2O_3/TiO_2/V/Zn$	Iron gangue
III	K3/K6/K7/K10	$Fe_2O_3/TiO_2/Cr/Cu/Ni/V$	Iron ore concentrate
IV	K8/K11/K13	$Fe_2O_3/TiO_2/Cu/V$	Titanium gangue
V	K4/K16	$Fe_2O_3/TiO_2/Cr/Cu/V/Zn$	original mine
VI	K12/K17/K19	$Ca/SiO_2/Fe_2O_3$	Sinter mineral

Table 2 Major element content (in 10^{-2} g·g^{-1}) in different types and groups of samples by different analysis methods

Types	Groups	Methods	Fe	Ti	V	Zn	Cr	Cu	Ni	Si	Ca
I	K1	Chemical	33.712	26.246	0.051	—	—	—	—	—	—
		ANN	34.512	26.869	0.053	—	—	—	—	—	—
	K15	Chemical	35.043	27.282	0.053	—	—	—	—	—	—
		ANN	34.602	26.939	0.053	—	—	—	—	—	—
	K9	Chemical	34.366	26.755	0.052	—	—	—	—	—	—
		ANN	34.483	26.846	0.053	—	—	—	—	—	—
	K18	Chemical	33.710	26.244	0.051	—	—	—	—	—	—
		ANN	34.502	26.861	0.052	—	—	—	—	—	—
II	K2	Chemical	14.849	3.316	0.046	0.010	—	—	—	—	—
		ANN	14.426	3.221	0.045	0.018	—	—	—	—	—
	K5	Chemical	14.563	3.252	0.045	0.010	—	—	—	—	—
		ANN	14.582	3.257	0.045	0.006	—	—	—	—	—
	K14	Chemical	14.285	3.190	0.044	0.01	—	—	—	—	—
		ANN	14.459	3.229	0.045	0.021	—	—	—	—	—
III	K3	Chemical	53.398	7.553	0.332	—	0.026	0.014	0.011	—	—
		ANN	53.614	7.584	0.334	—	0.026	0.016	0.011	—	—
	K6	Chemical	52.372	7.408	0.326	—	0.026	0.014	0.010	—	—
		ANN	52.378	7.434	0.345	—	0.028	–0.029	0.011	—	—
	K7	Chemical	53.389	7.552	0.332	—	0.026	0.014	0.011	—	—
		ANN	52.738	7.460	0.328	—	0.025	0.031	0.011	—	—
	K10	Chemical	52.386	7.410	0.326	—	0.026	0.014	0.010	—	—
		ANN	52.673	7.451	0.327	—	0.025	0.050	0.011	—	—

(To be continued in next page)

Table 2 (Continued)

Types	Groups	Methods	Fe	Ti	V	Zn	Cr	Cu	Ni	Si	Ca
IV	K8	Chemical	19.208	5.614	0.007	—	—	0.012	—	—	—
		ANN	19.128	5.591	0.007	—	—	0.012	—	—	—
		A-err.	–0.080	–0.023	0	—	—	0	—	—	—
	K11	Chemical	18.834	5.505	0.007	—	—	0.012	—	—	—
		ANN	18.947	5.538	0.007	—	—	0.012	—	—	—
	K13	Chemical	18.475	5.400	0.007	—	—	0.011	—	—	—
		ANN	19.814	5.791	0.007	—	—	0.012	—	—	—
		A-err.	1.339	0.391	0	—	—	0.001	—	—	—
V	K4	Chemical	30.570	6.266	0.156	0.019	0.012	0.015	—	—	—
		ANN	31.414	6.440	0.059	–0.081	0.012	0.015	—	—	—
	K16	Chemical	30.569	6.266	0.156	0.019	0.012	0.015	—	—	—
		ANN	30.892	6.332	0.357	0.220	0.012	0.015	—	—	—
VI	K12	Chemical	56.680	—	—	—	—	—	—	5.280	10.200
		Cluster	57.156	—	—	—	—	—	—	5.554	10.612
		ANN	56.985	—	—	—	—	—	—	5.412	10.332
	K17	Chemical	54.790	—	—	—	—	—	—	5.540	11.860
		Cluster	55.294	—	—	—	—	—	—	5.786	11.682
		ANN	55.033	—	—	—	—	—	—	5.638	11.848
	K19	Chemical	58.432	—	—	—	—	—	—	5.023	8.994
		Cluster	58.788	—	—	—	—	—	—	5.230	9.347
		ANN	58.655	—	—	—	—	—	—	5.175	9.097

5 Conclusion

The matrix effect correction model is based on self-organizing mapping neural network in EDXRF analysis. Comparing with conventional classifying and estimating methods, it has higher recognition ability to the samples, and has the characters of self-study and self-organizing. The neural network based sample classification layer is applied to the XRF analysis in an iron & steel company (Pan Gang) for correcting the matrix effect, and the analysis errors from conventional correcting methods were greatly reduced. But it has still some deficiencies. For example, the classifying arithmetic should be optimized to make it more efficient and dynamical, and the standard working curves should be founded automatically. Further programs are underway to solve the problems.

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