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Technical note

X-ray fluorescence spectroscopy for accurate copper estimation

P. Escárate [a,*], R. Hein [b], M. Durán [c], P. Ramaciotti [c,d]

[a] Departamento de Electrónica, Universidad Técnica Federico Santa María, Av. España 1680, Valparaíso, Chile
[b] Ingenieros Matemáticos Consultores Asociados S.A. (INGMAT), Av. José Miguel de la Barra 412 Piso 4, Santiago, Chile
[c] Escuela de Ingeniería, Pontificia Universidad Católica de Chile, Av. Vicuña Mackenna 4860, Macul, Santiago, Chile
[d] CMAP, École Polytechnique, CNRS, 91128 Palaiseau, France

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ABSTRACT

This work presents a technique for a rapid and accuracy measurement of copper content using X-ray fluorescence spectroscopy (XRF). This approach improves the accuracy and shortens the measuring time with respect to the current laboratory procedures from hours to 30 s.

The models were calibrated and validated via the correlation coefficients (R_c^2 and R_v^2), the error of prediction (*RMSEP*) and the error of calibration (*RMSEC*). The calibration and validation were performed for copper content ranges of 0.04–2.9%. An R_v^2 value of 0.9886 and a RMSEP value of 0.0890 were obtained, showing the accuracy of this method for continuous, real-time and on-line estimation of copper content.

1. Introduction

The need of quantitative methods to determine the copper content present in copper ore samples is necessary for adequately planning the mining process. Especially in the 0–2.9% copper concentration, which the minimum concentration of economically extractable copper is located.

To determine copper content, analytical methods are available, but they require a previous preparation of the sample (Rubinson and Rubinson, 2000). During the last decades, extensive research using spectroscopy techniques has been carried out for mineral analysis (Bish and Chipera, 1988; Clark, 1999; Pour and Hashim, 2012). Although, their application to continuous, real-time and on-line monitoring seems unlikely. To be applied to copper mining industry, it is important that the technique could be used directly on the exploration site (Escárate et al., 2006; Escárate et al., 2010), with a high accuracy level near to the cutoff copper concentration (<100%).

The XRF technique, due to the ability of X-ray radiation of passing through the samples, is a good candidate for such an application.

The great development in the last few years of X-ray sensors working at ambient temperature has allowed the industrial implementation of XRF. Also, there are commercial XRF portable analyzers, but there are based on lineal regression models and preprocessing techniques to estimate the elements concentration. In this work, a non-lineal model based on artificial neural network is used to estimate the copper content from the XRF data without pre-processing.

2. Materials and methods

2.1. Mineral samples

Samples of copper ore minerals were taken from three different locations in Northern Chile's mining area. Their copper content was initially analyzed in a chemical laboratory using the US-EPA 3050B standard to be used as reference values for the later calibration process.

2.2. Hardware

The X-123SDD Amptek X-ray spectrometer was used to get the X-ray fluorescence spectra. It incorporates a silicon drift detector (SDD), a preamplifier, a digital pulse processor (DPP) and a multichannel analyzer (MCA), giving a resolution between 125 and 140 eV. The X-ray source was an Amptek Mini-X-Ag emitting in the range from 5 keV to 50 keV.

2.3. Optical design

The optical configuration generates X-ray fluorescence resulting from an angle of 45° ($\theta = 67.5°$) between source and detector (see Fig. 1).

As observed in Fig. 1, the X-ray source excites the sample, which in turn emits characteristic X-rays. The characteristic X-rays are

* Corresponding author. Tel.: +56 32 2652920.
E-mail address: pedro.escarate@usm.cl (P. Escárate).

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produced from a transition of an electron from the L to the K shell (K_α) or produced from a transition of an electron from the M to a K shell (K_β).

Finally, the spectrometer receives the photons and generates the spectrum. The vector containing the spectrum is transmitted via a USB port into the computer for mathematical processing.

The X-ray source was set to 40 kV and 100 μA to excite the characteristic X-rays of the ore sample between 0 and 40 keV.

2.4. The regression method

The regression models for calibration and prediction are based on Artificial Neural Networks (ANN), which are mathematical models inspired by biological neural networks consisting in a series of interconnected simple processing elements called neurons or nodes. Each neuron receives a series of data from the preceding layer, transforms it locally using weights and an activation or transfer function, and sends the result to one or more nodes in any of the following layers, until the output neurons are reached.

2.5. Experiment

The ore samples used for calibration contained copper contents ranging from 0.04% to 2.9%. Two models for different content ranges were developed: 0–1% and 0–2.9%. The purpose was to verify whether the shorter of the two behaved better for smaller copper content values, this being an important issue in the mining industry to determine the economic feasibility of copper extraction.

A total of 360 samples were used for the calibration of the full range model (0–2.9%). For the short range model (0–1%), 145 samples were processed. The set of samples was randomly separated for calibration (70%), validation (15%) and testing (15%). The calibration set was used to train the ANN, the validation and test set were used to measure the performance of the ANN in new ore samples not included previously in the calibration set.

Fig. 2 shows an example of the resulting X-ray fluorescence spectrum for an ore sample.

3. Results and discussion

3.1. Data analysis

3.1.1. Selection of spectral regions

In order to reduce the noise originated in X-ray regions with poor information or spurious contributions, the region were narrowed to test their performance under such conditions, although no energy zones were necessary to discard in the X-ray fluorescence spectra.

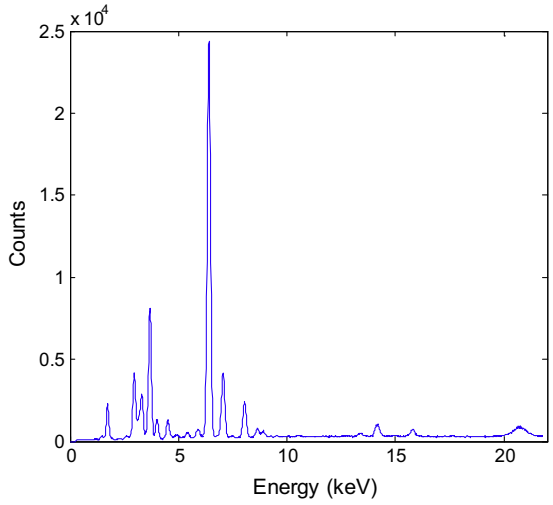

Fig. 2. X-ray fluorescence spectrum.

3.2. Calibration data

Two ANN were trained, one for the full range model (0–2.9%) and one for the short range model (0–1%). The aim was to find the best copper content estimation model when compared with the reference data obtained from the chemical laboratory. Also PLS models were used without success.

The group of spectra for each ANN was randomly separated in three groups: the first used for calibration or training (70%) and the other two for validation (15%) and testing (15%). No outliers were found in the data sets.

The validation and test data sets, which were not previously used for calibration, allow a rigorous evaluation of the model performance.

The performance of the two ANN models was assessed in terms of the root mean square error of calibration (RMSEC), the root mean square error of prediction (RMSEP) and the correlation index (R). These values are given by:

$$\mathrm{RMSE}(C/P) = \sqrt{\frac{\sum_{i=1}^{N}(\hat{y}_i - y_i)^2}{N-1}}, \tag{1}$$

$$R = \left(\frac{Cov(y_i, \hat{y}_i)}{\sigma_y \cdot \sigma_{\hat{y}}}\right), \tag{2}$$

where y_i and $\hat{y}_i$ are respectively the reference and predicted values of the sample.

The optimal number of neurons in the hidden layer to include in the ANN was determined by minimizing the RMSEC and RMSEP

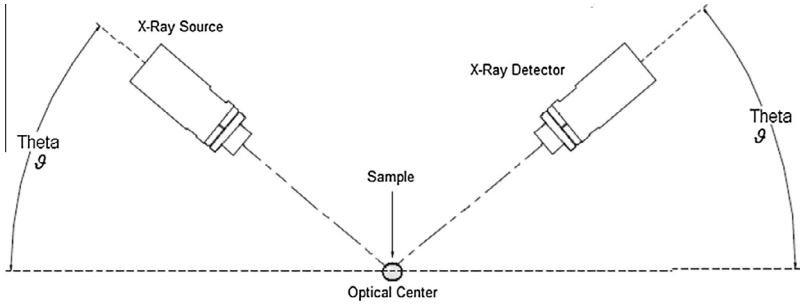

Fig. 1. X-ray fluorescence setup.

Table 1
Calibration results for both models.

	R_c^2	R_v^2	RMSEC	RMSEP
Short range model (0–1%)	0.9634	0.9566	0.0381	0.0398
Full range model (0–2.9%)	0.9882	0.9896	0.0886	0.0890

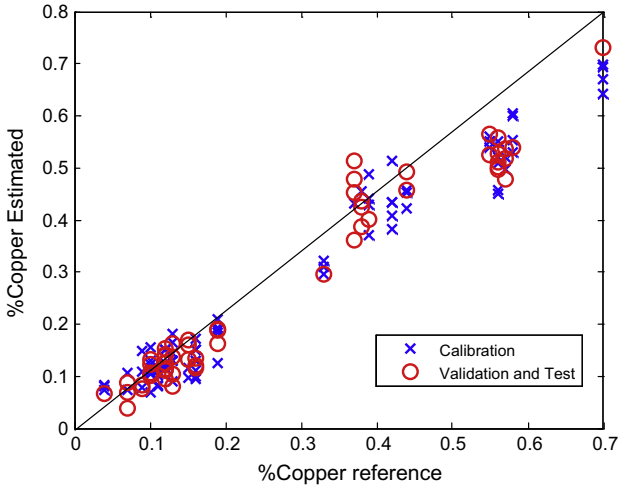

Fig. 3. Short range model.

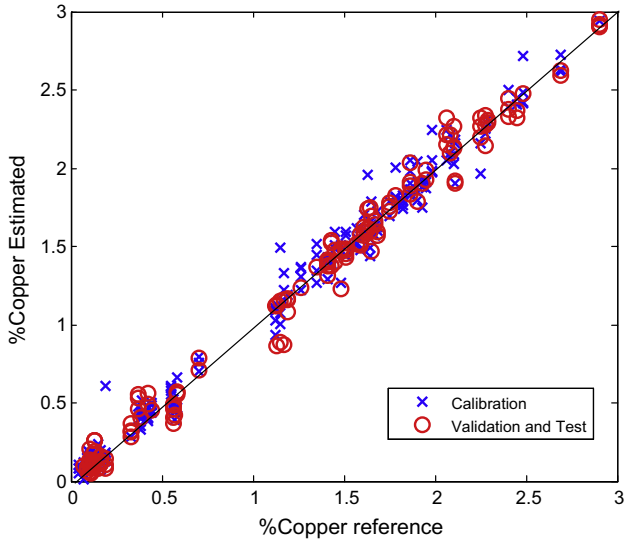

Fig. 4. Full range model.

indices and by maximizing the correlation coefficients for both calibration and validation (R_c^2 and R_v^2).

The calibration and validation results obtained for the models are summarized in Table 1.

The results from the table above show that the performance of the short range model is better in terms of the root mean square error and that the full range model has the best performance in terms of R_v^2.

Figs. 3 and 4 show the validation plot for the 0–1% and 0–2.9% models, respectively.

4. Conclusion

The results show that the technique can provide an accurate and rapid estimation of copper concentration in ore samples.

The RMSEP obtained shows that it is possible to use ANN models with the raw XRF spectra to estimate the copper concentration with a excellent accuracy (RMSEP < 0.0890). Also, the use of the raw spectra has the advantage of requiring a smaller amount of calculations for the copper estimation, by this means enabling its potential use in continuous, real-time and on-line measurements, either in conveyors or piles.

Regarding future work, reduction of reading variation should be sought using spectral averages of the samples. Further reductions in processing time could be achieved by increasing the X-ray source current and more sensitive detectors.

Although this development was meant for a mine site located in a desert region, its impact could be extended to other geographical areas.

Further work should also be done in order to seek a better accuracy in the short range, due to the interest of the mining industry.

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