

Separation of Effects due to Superimposition using the Rietveld Method in Spectra Obtained by WDXRF

V. L. R. Salvador¹, N. B. de Lima²

Instituto de Pesquisas Energéticas e Nucleares – IPEN/CNEN-SP

¹Centro de Química e Meio Ambiente

²Centro de Ciências e Tecnologias de Materiais

Caixa postal 11049. Pinheiros, CEP: 05422-970, São Paulo, Brazil

vsalvado@ipen.br

Keywords: WDXRF, Rietveld, GSAS

Abstract: This paper presents a new method to separate interfering spectra obtained in wavelength dispersive x-ray fluorescence spectrometry (WDXRF). This method permits improved results to be obtained, compared to conventional analytical results and enables the determination of chemical species of the same element without chemical separation. This is done by separation of the spectra due to electronic transitions of the valence electrons. The Rietveld method [11] overcomes the problem of superimposed peaks of the species present in the specimen and simultaneously enables determination of the species and does not require standard specimens and calibration curves. This signifies a marked improvement in comparison to other techniques. Specimen surface preparation to obtain spectra is a critical stage and its effects can be minimized by using Rietveld refinement, which permits the determination of intensity relationships of superimposed peaks with the aid of mathematical models. This establishes the basic conditions to obtain more accurate results in quantitative analysis. In the determination of chemical species, it is possible to separate, for example, Cr (III) and Cr (IV), with almost 100% superimposition.

Introduction

In response to increasing demand for safe analytical tools for quantitative and qualitative determination of chemical elements in a wide variety of materials, the field of analytical chemistry has contributed significantly with increasingly more sensitive methodologies that are selective and dependable.

This search for new alternatives that are safe and quick has resulted in the development of many instrumental analytical techniques. Besides representing a significant progress, these techniques have been used in the development of many applications in a variety of areas.

Among the new instrumental analytical techniques, X-ray fluorescence [4, 15, 6] has been prominent, mainly due to rapidity in the determination of major, minor and the micro constituents in a variety of materials. Often these constituents need to be identified quickly or quantified in exploratory analysis in areas such as chemistry, metallurgy, geology, archeology, the arts, materials science, biochemistry, polymer science, forensic science etc. Also, the number of users and applications has increased steadily.

Presently, with technological advances, there are increasing demands from users for the determination of specimen composition and the species present in them. In this context, the X-ray fluorescence technique has a drawback. Since it is normal practice to use inner electron electronic transitions to identify and quantify the chemical element, it is the total amount of the element present that is determined and not the species in the specimen. The spectra required for the identification of the species require electronic transitions involving electrons in the valence band, where peak superimposition is almost total.

In published literature, the papers reporting the determination of species of some chemical elements have done so by modifying accessories of WDXRF and by using difficult mathematical models, involving even deconvolution of interfering lines. *Asada et.al.* [1] studied the effect of oxidation state on the intensities of the $K\beta_5$ and $K\beta'$ lines that result from electronic transitions involving the 3d level in transition elements. *Urch and Wood* [14] studied variations in the valency of Mn in minerals. *Tanninen et.al.* [12] used the $K\beta$ emission spectra to determine the valency of Fe. *Iwatsuki and Furusawa* [3] used the $K\beta_2 / K\beta_{1,3}$ intensity to study the chemical states of Se and Br. *Klockenkämper and Koch* [5] determined the different phases of Al in steel and *Pinkerton et.al.* [10] studied the variation in valency of S.

The introduction of chemometry [9, 2], in X-ray fluorescence enabled the determination of species with the aid of powerful computing programs which require hundreds or thousands of data for processing, followed by laborious statistical interpretations.

In the new methodology presented here, the spectra separation process is simple, quick, and precise, requiring only knowledge about the crystallographic characteristics of the crystal analyzer used in the X-ray fluorescence spectrometer and that of the spectra of the specimen. To separate the spectra of the species, the Rietveld method [13,16,17] and the GSAS program (GSAS AND EXPGUI PACKAGES) created by *Larson and Dreele* [7] are used. These two, the Rietveld method and the program have been widely used in X-ray diffraction analysis to adjust crystallographic standard.

Methods and materials

Specimens in metallic form, as powder compact or as a solution can be analyzed.

To obtain the spectrum containing the species Cr (III) and Cr (VI), the characteristic radiations of the 3d sublevel (electrons in the valence band) to K level electron transitions were used. Second order radiations were used as they rendered improved separation effects. The spectra of the interfering elements were obtained in the X-ray fluorescence spectrometer – model RIX-3000 of RIGAKU at the X-ray Fluorescence Laboratory of the Chemistry and Environment Centre of IPEN/CNEN-SP.

The data obtained with the spectrometer were transferred to an appropriate program to have “.dat” format files and subsequently in “.gsas” format to permit separation using the Rietveld Method [12] and the GSAS AND EXPGUI PACKAGES program created by *Larson and Dreele* [7].

Optimum conditions of the crystal analyzer

To determine the optimum conditions of the LiF(220) crystal analyzer, that was used to obtain the superimposed spectra, a spectrum containing the Cu $K\alpha_1 - CuK\alpha_2$ lines was used. This was introduced in the GSAS-EXPGUI program using the crystallographic conditions of the LiF (200) crystal analyzer. Through phase refinement, separation of the $K\alpha_1$ (65.48°) and $K\alpha_2$ (65.66°) lines was observed. After complete refinement of the phases the optimum conditions of the instrument for this crystal analyzer were obtained and used to refine the superimposed spectra obtained with this instrument.

Spectrum containing superimposed cr (iii) and cr (vi) peaks

The position of Cr (III) can be seen at 5847.9 eV and that of Cr (VI) at 5947.1 eV [8]. Transformation of these values in wavelength gave: Cr (III) at 2.0848 Å and Cr (VI) at 2.0850 Å. Figure 1 shows the superimposed spectrum of Cr (III) and Cr (VI) as obtained with the LiF 220 crystal.

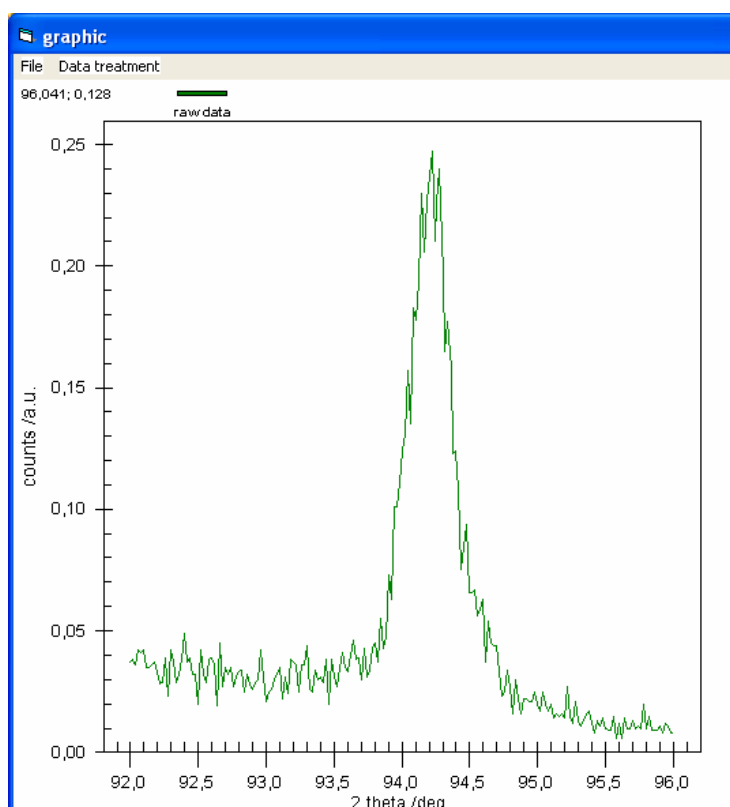


Figure 1 - The superimposed spectrum of Cr (III) and Cr (VI) as obtained with the LiF 220 crystal.

The spectrum shown in Figure 1 was introduced in the GSS-EXPGUI program using the optimum crystallographic conditions of the LiF (220) crystal analyzer and the conditions of the

two phases. After primary refinement of the phases (Figure 2) separation of the Cr (III) $K\beta_{1.3}$ and Cr (VI) $K\beta_{1.3}$ lines can be observed. At this stage of refinement, the minimizing values by least squares (CHI^{**2}) is 6.9.

Figure 3 shows the spectrum in which the zero of 2θ of the crystal analyzer and the ratios of the intensities of the Cr(VI) $K\beta_{1.3}$ / Cr(III) $K\beta_{1.3}$ have been adjusted. At this stage of refinement the minimizing values by least squares (CHI^{**2}) was equal to 0.2.

The specimen that was analyzed was prepared by mixing 200 ppm of Cr (III) and 100 ppm of Cr (VI). A measured amount of 0.1mL of the mixture was deposited on a filter paper. Since the ratio observed was 0.49999, it indicated a deviation of 0.02%, confirming that the methodology was precise.

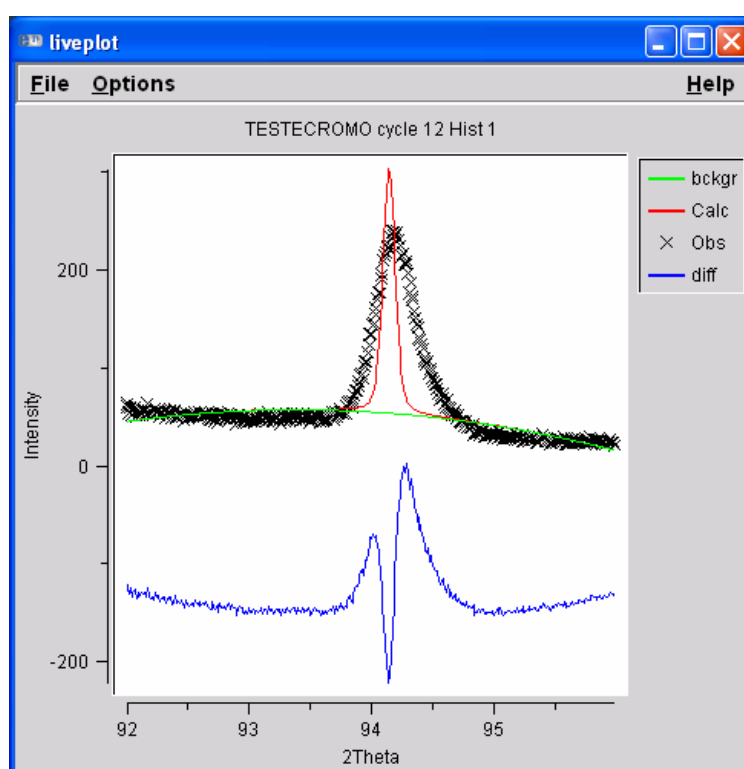


Figure 2 - Superimposed spectrum of Cr (III) and Cr (VI) obtained with a LiF 220 crystal and with separation of the Cr (III) $K\beta_{1.3}$ and Cr (VI) $K\beta_{1.3}$ lines.

CONCLUSIONS

The methodology presented here is quite simple, quick and precise and does not require a large amount of data as in chemiometric methods. The separations can be easily carried out with a program that can be obtained free of charge.

With the separations that have been proposed, it is possible to determine the composition of the specimen and the species present in it.

The drawback of the method is the necessity to know the crystallography of the crystal analyzer and separation of the lines with just one interference.

Using the X-ray fluorescence technique and the Rietveld method it is possible to easily resolve the problem of superimposed peaks of species present in the specimen. This enables the determination of the species simultaneously without the need for standard specimens and calibration curves. This is the main advantage, compared to other techniques.

In X-ray fluorescence, specimen preparation and its surface state are important factors to obtain the spectrum. The effects due to these factors can be minimized using Rietveld refinement.

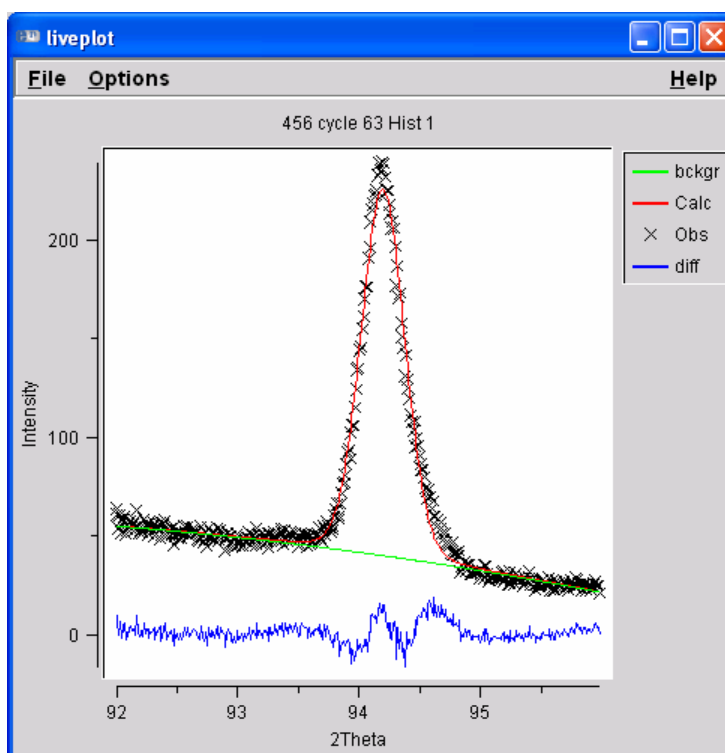


Figure 4 - The zero of 2θ of crystal analyzer has been adjusted and the ratio of the intensities of the Cr III) $K\beta_{1.3}$ and Cr (VI) $K\beta_{1.3}$ lines has also been adjusted.

References.

- 1 ASADA, E.; TAKIGUCHI, T.; SUZUKI, Y. The Effect of Oxidation State on the Intensities of $K\beta_5$ and $K\beta''$ of 3d-Transition Elements. **X-Ray Spectrometry**, v. 4, p. 186-189, 1975.
- 2 FERREIRA, M.M.C.; ANTUNES, A.M.; MELGO, M.S; VOLPE, P.L.O.; *Aplicação de Alguns Modelos Quimiométricos à Espectroscopia de Fluorescência de Raios-X de Energia Dispersiva*. **Quim. Nova** 1999, 22, 724.

- 3 IWATSUKI, M.; FURASAWA, T. $K\beta_2/K\beta_{1,3}$ X Ray Intensity Ratios of As, Se and Br in Various Chemical States. *X-Ray Spectrometry*, 16: 73-79, 1987.
- 4 JENKINS, R.; GOULD, R.W.; GEDCKE, D. **QUANTITATIVE X-RAY SPECTROMETRY**. New York, Marcel Dekker, Inc., 1981.
- 5 KLOCKENKÄMPER, R.; KOCH, K.H. Determination of Various Phases of Al in Steel by X-Ray Fluorescence Spectrometry. *X-Ray Spectrometry*, 18: 177-181, 1989.
- 6 LACHANCE, G.R.; CLAISSE, F. **QUANTITATIVE X-RAY FLUORESCENCE ANALYSIS: THEORY AND APPLICATION**. New York, USA, 1995
- 7 LARSON, A.C. and VON DREELE, R.B.. **General Structure Analysis System (GSAS)**. Los Alamos National Laboratory Report LAUR 86-748 (2004).
- 8 MAZZILLI, B. **“Chemical effects in X-ray emission spectra of transition metal compound”**. Tese de Doutorado, 1982.
- 9 NAGATA, N e Bueno, M.I.M.S. Métodos Matemáticos para Correção de Interferências Espectrais e Efeitos Interelementos na Análise Quantitativa por Fluorescência de Raios-X. *Quim. Nova*, Vol. 24, No. 4, 531-539, 2001.
- 10 PINKERTON, A.; NORRISH, K.; RANDALL, P.J. Determination of Sulphur in Plant Material by X-Ray Fluorescence Spectrometry. *X-Ray Spectrometry*, vol.19, p. 63-65, 1990.
- 11 RIETVELD, H.M.; A Profile Refinement Method for Nuclear and Magnetic Structures. *J. Appl. Cryst.* 2, p.65-71, 1969.
- 12 TANNINEN, V.P.; MIKKOLA, E.; HYVÄRINEN, K.H.; GREKULA, A., KALLIOMÁKI, P.L. Determination of the Valence of the Iron in Welding Fumes with the $K\beta$ Emission Spectrum. *X-Ray Spectrometry*, vol.14, n. 4, 1985
- 13 TOBY B.H., EXPGUI, a graphical user interface for GSAS, *J. Appl. Cryst.* 34, 210-213 (2001)
- 14 URCH, D.S.; WOOD, P.R. The Determination of the Valency of Manganese in Minerals by X-Ray Fluorescence Spectroscopy. *X-Ray Spectrometry*, vol.7, n. 1, 1978.
- 15 VAN GRIEKEN, R.E.; MARKOWICZ, A.A. **Handbook of X-ray Spectrometry: Methods and Techniques**. Marcel Decker, USA, 1993.
- 16 YOUNG, R.A.; *Using Rietveld Method*; School of Physics, Georgia Institute of Technology; Atlanta, 1994.
- 17 YOUNG, R.A. *The Rietveld Method*. I.U.C, Oxford University Press Inc., New York; 1995.