

## **Inclusion of the Radiative Auger Effect X-ray emission spectra in fitting K-spectra of elements in the range $Z = 26-35$**

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The X-ray team, part of CSIRO Mineral Resources Business Unit develop X-ray fluorescence (XRF) instruments designed to measure trace concentrations of precious metals such as gold and platinum in mineral samples and slurries, where these elements are often accompanied by low-value base metals such as iron, nickel and copper present at significantly higher quantities. The low intensity L-shell lines of gold and platinum overlap with the high intensity K-shell lines of light elements commonly found in ore in the Z-range of 26 to 35. It is standard to fit K-shell spectra with only the diagram lines. However, as the accuracy of measuring precious metals in minerals samples approaches parts per billion, it is crucial to fit the full K-shell signatures to better resolve the overlapping low intensity precious metal L-shell lines.

The photoelectric effect occurs when photons eject an inner-shell electron from an atom, leaving the atom in an excited state. The transition of a higher-shell electron into the vacancy can lead to the emission of either a characteristic X-ray or an Auger electron. The Radiative Auger Effect (RAE) accounts for the emission of a photon and an Auger electron simultaneously. The energy of de-excitation is shared between the auger electron and the photon. This allows the photon to have any energy value in the range of 0 to the total energy of the standard Auger electron emission. The unique energy distribution of RAE photons results in a tail feature, most prominent on the low energy side of the  $K\beta$  peak which is predicted to have an intensity of up to 5% relative to the  $K\beta_{1,3}$  peak in the Z-range of 26 to 35.

When an excited atom is multiply ionized, resulting in more than one vacancy being present, the transition of a higher-shell electron into the inner-shell vacancy causes the emission of satellite and hyper-satellite lines, present as weak lines surrounding the main diagram lines. The satellite line energy positions and intensities can be predicted by theory and extensive studies have been conducted both calculating and measuring these values for low Z elements.

We have measured wavelength dispersive XRF spectra for five different elements with Z between 26 and 35. These spectra have been carefully fitted with the diagram, satellite and RAE peaks. While the satellite and hyper-satellite lines are well documented in literature, there is only limited theoretical information available for the RAE peaks, and experimental measurements reported in literature use inconsistent line-shapes to fit the RAE profile. We have fitted the RAE peaks with different line-shapes, including wide Gaussian profiles and exponential tails, and measured the resulting intensity of the RAE features relative to the main diagram line. We present a comparison of our results with other studies that measured values for both the satellites and the RAE peaks. We discuss the significance of improving the fitting of low-intensity spectral features in relation to improving the measurement of low concentration elements in complex mineral samples.