Relative K X-ray energy shifts in Fe, Cu and Zn metals and their compounds with EDXRF set-up

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HIGHLIGHTS

► It explores the EDXRF set up and statistical method for energy shift measurements.
► Comparison of shift with errors in energies supports fluctuation free set up.
► Scientific explanation for energy shifts supports the method.
► Work recommends the use of economical EDXRF for shift measurements.

ARTICLE INFO

ABSTRACT

Energy Dispersive X-ray Fluorescence (EDXRF) set-up comprising low power X-ray tube and Si(PIN) detector has been used for chemical shift measurements in X-ray energies following a statistical method that involves division of measurement time into sub-divisions and in each sub-division the XRF spectra of element and its compound have been recorded. A polynomial fit to the photo-peak energies of recorded spectra determines the non-statistical fluctuations of the data due to instability of apparatus and environmental factors. Afterwards, the data was corrected for non-statistical errors. The method has been used for shift measurements in K X-ray energies of 8 pairs of 3 metals Fe, Cu and Zn; Fe and $FeSO_4 \cdot 7H_2O$, Fe and FeS, Fe and $Fe(NO_3)_3 \cdot 9H_2O$, Cu and CuO, Cu and $CuCl_2$, Cu and $CuSO_4 \cdot 5H_2O$, Zn and ZnS and Zn and $ZnBr_2$. The t-test for statistical significance of final results clearly supported the reliability of these shift measurements.

1. Introduction

The changes in fine features of X-ray emission spectrum of an element with its different chemical combinations can be classified into three groups: (a) shift in X-ray energy; (b) distortion of line shape and (c) change in X-ray intensity (Grieken and Markowicz, 2002). The measurement of shift in energy of element X-ray peak ($\sim$ a few eV) in its different compounds known as chemical shift involves great precision. Generally, the wavelength dispersive technique has been used to measure the chemical shift in different compounds (Oz et al., 2009; Baydas and Oz, 2010). Though it has fine resolution but it involves angular error and temperature variations of the analyzing crystal. On the other hand, EDXRF spectrometers with comparatively poor energy resolution in the range 135–250 eV at 5.9 keV may not seem

suitable for chemical shift measurements of the order of a few eV (Grieken and Markowicz, 2002) but they offer advantage of simultaneous multi-element detection with high efficiency. Considering the capability of EDXRF system to produce the normal Gaussian peak for X-rays with excellent energy and resolution stability that leads to its ability to detect the chemical shift, Kallithrakas-Kontos (1996) and Kallithrakas-Kontos and Moshohoritou (1998) have applied EDXRF system to detect the chemical shift of K X-rays of Cr and Mn in their compounds.

While recording the change in the line positions with the changing chemical environment, the measured data is generally accompanied with statistical and non-statistical fluctuations. Since, X-ray emission (a radiative decay) is a random process, therefore, its decay measurements are always associated with statistical fluctuations that can be reduced either by increasing the counting rate or by increasing the counting time (Knoll, 2000). The non-statistical error in positions of the recorded line is due to fluctuations caused by the environmental factors, apparatus instability and some unpredictable factors. To overcome the problem of instability of Si(Li) detector and of the associated electronics encountered in processing of the detector output in

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Kontos's work, Xiao et al. (1998) suggested a statistical data processing method that involves the partitioning of measurement time into many sub-divisions in EDXRF measurements. The statistical treatment of the data obtained from EDXRF set-up removes the statistical and non-statistical errors in the data on energy. The method does not require complicated spectroscopy as well as monochromatic X-ray source. Xiao et al. (1998) have theoretically and experimentally explored the application of the method for the EDXRF set-up with resolution 150 eV at 5.959 keV Mn K X-rays for Mn metal and its compound $KMnO_4$. On the similar lines, present work is an attempt to explore the capability of our existing EDXRF set-up (Gupta et al., 2010) for energy shift measurements in Fe, Cu and Zn metals and their compounds. To start with the work, first the energy stability of the set-up for energy measurements has been explored.

2. Energy stability of experimental set-up for energy measurements

The precision and accuracy of measure of shift in the peak positions depend upon the resolution of the detector. Moreover, there is an optimum value of channel width (energy per channel) of the multi-channel analyzer that gives the best precision (Greaves et al., 2005). The present set-up with low power Neptune X-ray tube, AMPTEK Si(PIN) detector and ORTEC Multi-Channel Analyzer (MCA) has FWHM 220 eV at 5.959 keV Mn K X-rays that corresponds to a standard deviation $(S_E) = 93$ eV. The amplifier gain settings for dead time losses of counting system $< 1\%$ produced the energy/channel in the range 12–15 eV. The theoretical discussion and data processing of Xiao et al. (1998) very much supports the present energy/channel, 12–15 eV in the energy stability range of the set-up.

3. Experimental observations

The EDXRF set-up comprises a 100 W Neptune X-ray tube set-up with Rh anode and Si(PIN) detector (AMPTEK model XR-100CR) Fig. 1. Photons coming from the X-ray tube were incident on the target. The fluorescent X-rays produced by the target elements were detected in the Si(PIN) detector which was at 90° to the source in single reflection geometry made from a single iron piece. The arrangement of tube, target and detector was such that detector could not see the direct photons coming from the tube.

The metals and their compounds were taken in pairs; Fe and $FeSO_4 \cdot 7H_2O$, Fe and FeS, Fe and $Fe(NO_3)_3 \cdot 9H_2O$, Cu and CuO, Cu and $CuCl_2$, Cu and $CuSO_4 \cdot 5H_2O$, Zn and ZnS and Zn and $ZnBr_2$. Fe,

Cu and Zn being transition metals are more electronegative and are more prone to form covalent compounds. The status of element in question in the pair, metal and its compound, may differ because of its oxidation state, number of attached ligand atoms, number of oxygen atoms bound to a central atom and/or electro-negativity etc. Chemical shift is strongly correlated to all these factors and varies with changes in one or more of these factors (Oz et al., 2009; Baydas and Oz, 2010). As far as differences in their structures are concerned, iron (II) sulfate, $FeSO_4 \cdot 7H_2O$ and iron (III) nitrate, $Fe(NO_3)_3 \cdot 9H_2O$ both have octahedral coordination geometry whereas iron (II) sulfide, FeS has hexagonal coordination geometry; two of the copper compounds copper (II) sulfate $CuSO_4 \cdot 5H_2O$ and copper (II) chloride $CuCl_2$ both with valence 2 have octahedral coordination geometry, copper (II) oxide CuO has square planar coordination geometry and Zinc sulfide ZnS forms a tetrahedral geometry and Zinc bromide $ZnBr_2$ forms a super tetrahedral crystal structure.

Thus, in pairs, metals Fe, Cu, and Zn were selected as reference sample (R) and $FeSO_4 \cdot 7H_2O$, FeS, $Fe(NO_3)_3 \cdot 9H_2O$, CuO, $CuCl_2$, $CuSO_4 \cdot 5H_2O$, ZnS and $ZnBr_2$ as analyte sample (A). All the metals and compounds were of spec pure grade. The metals were in the form of foils. Most of the analyte samples were in briquette form from their powdered materials of analytical grade. Iron foil was preserved from rusting in a closed container. Moreover, it was properly cleaned up with acetone before using it in the experiment. In spite of all this, if oxidation layer remains at the surface, it did not interfere much with the results as XRF measurements are bulk phenomenon including surface. Iron nitrate, a deliquescent, was in crystal form with plain surface enclosed in plastic sheet. Powdered iron sulfide is pyrophoric, so it was in solid form with plain surface.

A 2 min time was spent to collect a pair of spectra of samples R and A. First half of the time (60 sec) was used for sample R, out of which 30 sec was used for acquiring the spectrum and 30 sec for saving the spectrum and changing the sample. Similarly, rest half (60 sec) was utilized for sample A. A manual controlled sliding mechanical system (Fig. 2) that comprises a long rod ending with base of target holder was used in the experiment to change the targets R and A alternately at the target position.

The procedure of acquiring and saving the spectra and changing samples was repeated 40 times. So, the whole experiment performance time was 80 min.

The anode voltage of the tube was set above the K edge energy of the element for exciting its K shell electrons in the samples (8 kV for Fe, 12 kV for Cu and Zn excitations). The filament current was set accordingly to reduce the dead time losses of the counting system $< 1\%$. The gain of the detector was adjusted to optimize the precision of measurements as discussed earlier under the energy stability of the set-up for energy measurements. The spectra were
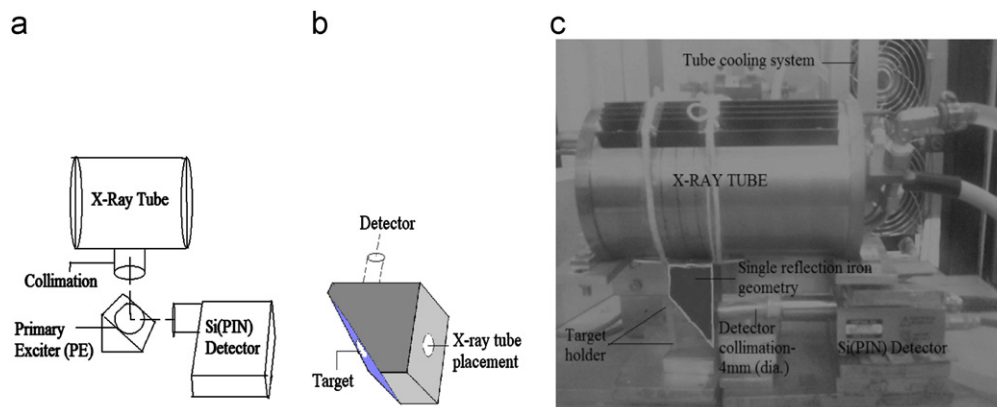

Fig. 1. (a) A schematic arrangement of tube, geometry and detector. (b) Geometry from single piece iron with provisions for X-ray tube, target and detector. (c) A view of single reflection iron geometry with X-ray tube as photon source, target and Si(PIN) detector.