

Investigation of The Chemical Effect on The Lines of Bromine K_{α} And K_{β} X-Ray Emission Spectra Using EDXRF Spectrometry

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Abstract

Bromine is used in many areas such as agricultural chemicals, dyestuffs, insecticides, pharmaceuticals and chemical intermediates. Some uses are being phased out for environmental reasons, but new uses continue to be found. In this work, the effects caused by different chemical environments in several bromine compounds were studied using EDXRF spectrometry. The samples were excited by 59,5 keV gamma rays emitted from Am-241 radioisotope source and characteristic K X-rays emitted from the samples were counted by Si(Li) detector. Modifications in values of energy of X-Ray line, full width at half maximum (FWHM), asymmetry index (AI) were determined. In conclusion, the results of the present paper demonstrate that the Bromine K_{α} and K_{β} emission energies depend on the Br chemical state and, therefore, their determination allows the chemical state speciation of Br in a given sample.

Keywords: EDXRF, Chemical Effect, Bromine, X-Ray line, Full width at half maximum (FWHM), Asymmetry index (AI)

1. INTRODUCTION

It is well known that the K X-rays (K_{α} and K_{β}) are produced when vacancies in the K shell created by incident radiation particles are filled by electrons from higher shells through radiative process. X-ray fluorescence (XRF) spectrometry experiments have been widely used for studying the chemical environment and the electronic structure of a wide variety of materials [1-4]. This information can be obtained by measuring changes in some spectral features, such as energy shifts, possible satellite lines, line shape and relative intensities.

Many researchers [5-8] discussed the K_{α} and K_{β} X-ray emission spectra profiles of fluorine, sulfur, bromine and chlorine compounds to study their chemical state behavior using different analytical techniques. But most of them not provide sufficient and systematic information on the cause of chemical effects in the compounds. Using WDS-PIXE technique, Kavcic et al. [9] showed significant differences in spectral shape of the sulfur $K_{\alpha 1,2}$ line emitted from S compounds in aerosol samples. There were lots of X-ray studies including sulfur and chlorine in different oxidation states and other elements in universe [10-12]. The $K_{\alpha 1,2}$

diagram lines and satellites of sulfur were investigated by the crystal spectrometer and it was demonstrated that the S K X-ray emission energies depends on the chemical state of sulfur.

The chemical environment has a strong effect on the transitions originated in valence band and its influence could clearly be observed in the emission spectrum structure. The P- K_{β} spectrum has been studied by many authors [13-14], who used both single-crystal and two-crystal spectrometers with conventional X-ray sources. These authors showed some modifications in the K_{β} spectra and its relation with P chemical environment. Compounds with oxygen as ligand atom, a relationship between the ratio of the K_{β} line intensity to the total intensity of the K_{β} line, and the energy shift of the $K_{\alpha 1,2}$ lines. Fichter [15] discussed the K_{α} -line shifts related to the oxidation number of the P-atom. The chemical shift of X-ray emission lines is usually interpreted with the effective charges or oxidation number of the X-ray emitting atom [16-17].

In this paper, we demonstrate possibility of chemical state analysis of Br-compounds by using the Energy Dispersive X-Ray Fluorescence (EDXRF) system. The literature survey shows that there is limited number of studies about the investigation of bromine K X-ray emission lines by using energy dispersive X-ray fluorescence since it has low resolution for the separation of $K_{\alpha 1}$ and $K_{\alpha 2}$ X-ray lines. To acquire more information about the structure of bromine electronic shells, it should be supply more experimental data.

2. METHOD AND MATERIALS

The measurement of shifts in Br K_{α} and $K_{\beta 1,3}$ X-ray emission lines of bromine in various compounds are carried out on a EDXRF. The detailed description of this spectrometer is reported elsewhere [18-19]. The experimental setup consist of a Si(Li) detector, Am-241 radioactive source and electromagnet as shown in Fig. 1.

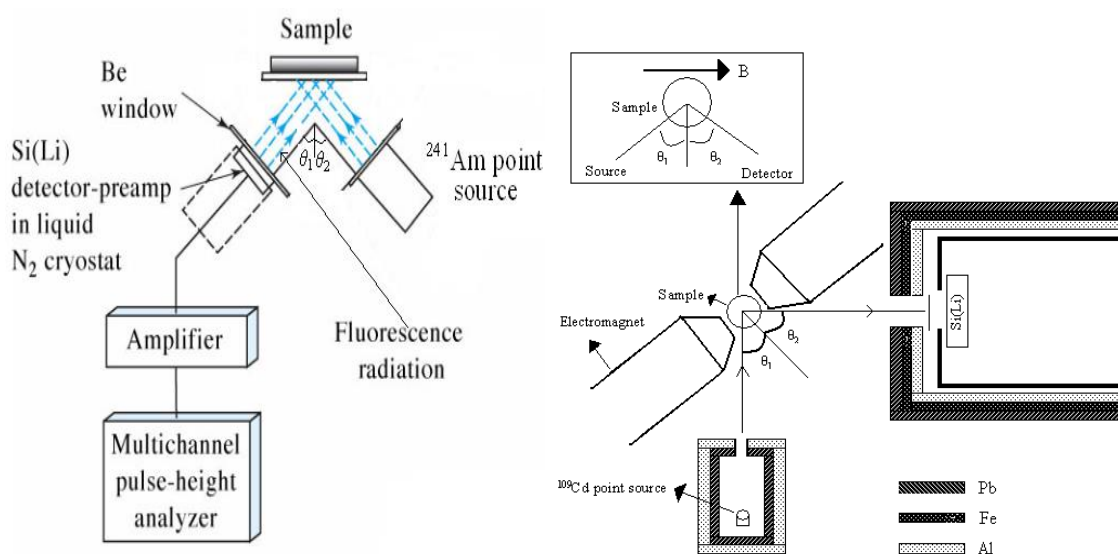


FIG 1. The experimental arrangement and the geometry

A graded conical shield of Al and Pb was used between the sample and the detector to obtain a large beam of emergent radiation and to avoid the interaction of the x-rays emitted by the component elements of the radioactive capsule and detector. The detector was shielded by a graded filter of Pb, Fe and Al to obtain a thin beam of photons scattered from the target and to absorb undesirable radiation shielded the detector.

For Br K_{α} spectrum, one channel is from 11.9242 keV to 11.8776 keV and for Br $K_{\beta_{1,3}}$ spectrum, channel is 13.2914 keV for all samples. The data were collected into 16384 channels of a digital spectrum analyzer DSA-1000. Each compound is analysed at least three times to check the reproducibility. For all samples, at least three spectra are recorded and average has been taken to give better accuracy and reduce statistical error. All given samples are analysed under same conditions. The typical acquisition time for each spectrum are taken as 60 min.

3. SAMPLE PREPARATION

All the fine powder samples are pressed at a pressure of 10 KN/m² using pelletizer machine with a uniform thickness into a thin pellet of 13 mm diameter. The pellet was kept in the 10-15 mg cm⁻² range. All the samples namely as VBr₃, CrBr₃.6H₂O, MnBr₂, FeBr₂, CoBr₂, NiBr₂, CuBr, ZnBr₂, YBr₃, ZrBr₄, RuBr₃, PdBr₂, SnBr₂, PrBr₃, NdBr₃, SmBr₃, ErBr₃, GdBr₃.6H₂O and TmBr₃ are purchased from Sigma Aldrich. . During the sample preparation, particle size effect should be kept in mind. It is worth mentioned that the thickness of the all samples should be taken as unity during the whole experiment. In order to circumvent particle size effects all samples were grounded and sieved through a -400 mesh (<37 μ m) sieve.

4. DATA ANALYSIS

The data analyses of X-ray emission of bromine compounds have been analysed with available computer software package Origin 8.0. This program offers including linear and non-linear curve fitting, model validation, dataset comparison tools, and multi-dimensional data analysis. To find the chemical shift in K_{α} and K_{β} spectrum, the line parameters, i.e., full width at half maximum (FWHM), index of asymmetry and integrated intensity were determined. Parameters such as FWHM and asymmetry index, defined in Fig. 2, were evaluated using the smoothed data.

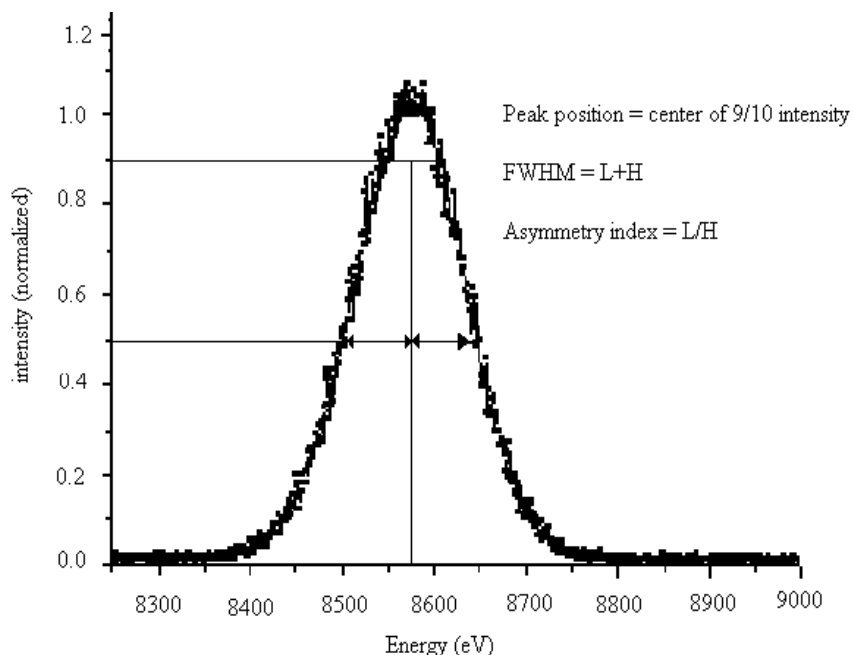


FIG 2. Definition of asymmetry index, FWHM and peak position determined from 9/10 intensity

The peak position was determined at the center point of the 9/10 intensity of the smoothed line shape. In the present measurements, given CuBr K X-rays emission lines in different chemical forms are fitted with Gaussian functions (Fig. 3.).

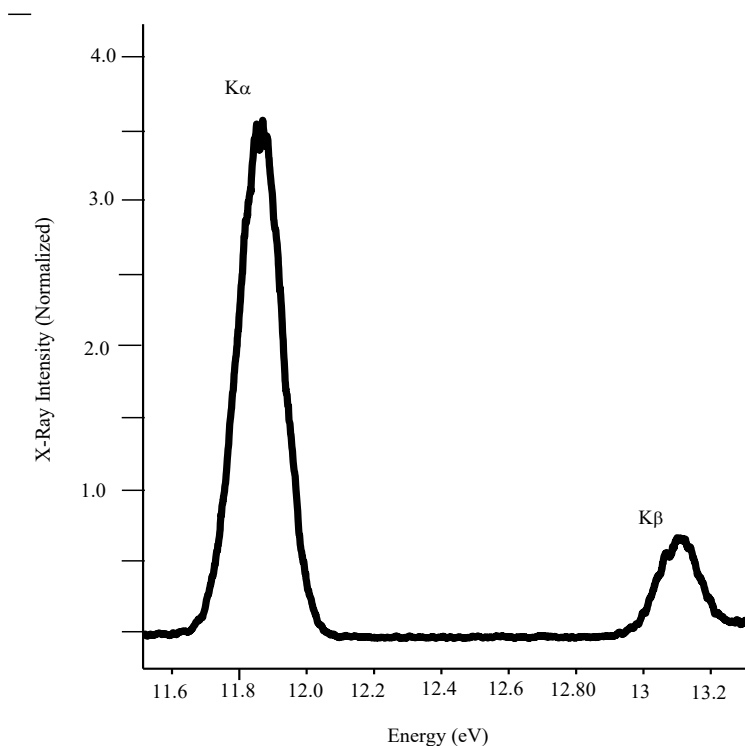


FIG 3. A typical K x-ray spectrum of CuBr

5. RESULTS AND DISCUSSIONS

Table 1 represents the collection of bromide compounds (VBr_3 , $CrBr_3 \cdot 6H_2O$, $MnBr_2$, $FeBr_2$, $CoBr_2$, $NiBr_2$, $CuBr$, $ZnBr_2$, YBr_3 , $ZrBr_4$, $RuBr_3$, $PdBr_2$, $SnBr_2$, $PrBr_3$, $NdBr_3$, $SmBr_3$, $ErBr_3$, $GdBr_3 \cdot 6H_2O$ and $TmBr_3$) whose oxidation state varies from +1 to +6. The present work deals with the study of chemical effects in Br K_α and $K_{\beta_{1,3}}$ X-ray emission lines of various chemical compounds. The measured energy shifts (ΔE), line-width and asymmetry index are given in Table 1 respectively. The relative intensity ratio and line-width are the more sensitive parameters to study the chemical effects in various unknown compounds. From Table 1, it is observed that line-width is found to be proportional with chemical shift (ΔE).

Moreover, from Table 1, it is also clearly seen that the value of chemical shift in Br $K_{\beta_{1,3}}$ emission peaks are slightly more than that of Br K_α emission peaks. This is due to the fact that $K_{\beta_{1,3}}$ ($2S_{1/2} \rightarrow 3P_{1/2}, 3P_{3/2}$) transition directly involves outermost valence electrons which affect the central peak position of the compounds as compared to the K_α ($1S_{1/2} \rightarrow 2S_{1/2}, 2P_{1/2}$) transitions. During the bond formation, the inner levels (1s) behave like an atom character while on the other hand, the outer levels (2p) refers to the molecular orbital characteristics in a given compounds which influences the quantum states and electron density around the surrounding atom.

From Table 1, it is seen that the $TmBr_3$ compound show large chemical shift than VBr_3 and YBr_3 compounds ($TmBr_3 > VBr_3 > YBr_3$) for all K emission lines. It is also observed that, chemical shift in all K shell emission lines gradually increases as the coordination number increases. K_α and K_β lines which are

broad in the case of PrBr_3 , SmBr_3 and CuBr_3 and then gradually becomes more and more sharp as the oxidation number of Br decreases. In CoBr and CuBr , where Br ions are in the hexavalent state, the emission lines are nearly sharp. In addition to the Br observations, there is a definite correlation between the FWHM ratio and coordination number of the Br ions in the materials studied in this investigation. The shift of cubic Br compounds (ZrBr_4) is significantly lower than that of a bicapped trigonal prismatic PrBr_3 and NdBr_3 compounds. For anomalous small difference of energy shifts in Br K_α and $K_{\beta 1,3}$ emission lines, it is believed that there is some basic physical phenomenon lies behind it which causes chemical shift in X-ray emission peaks.

Table 1. Full width at half maximum (FWHM), asymmetry index, chemical shift (ΔE), energy shift (δE) values of K_α and K_β emission lines in Br compounds

Element	FWHM (eV)		Asymmetry Index		ΔE (eV)	
	K_α	K_β	K_α	K_β	K_α	K_β
VBr₃	3.186	3.230	1.205	1.114	-1.253	-1.333
CrBr₃.6H₂O	3.223	3.406	1.005	0.979	-1.006	-1.215
MnBr₂	3.057	3.240	1.024	0.974	-0.996	-1.012
FeBr₂	3.351	3.525	0.989	0.968	-0.551	-1.168
CoBr₂	3.087	3.246	1.009	0.937	-0.981	-1.365
NiBr₂	2.954	3.528	1.272	0.986	-0.946	-1.555
CuBr	3.397	3.465	1.003	1.167	-0.863	-1.163
ZnBr₂	3.140	3.592	1.009	1.017	-0.958	-1.468
YBr₃	3.110	3.515	1.111	0.984	-1.202	-1.299
ZrBr₄	3.178	3.679	1.216	0.993	-0.911	-0.725
RuBr₃	3.329	3.599	1.139	0.948	-1.079	-1.897
PdBr₂	3.062	3.582	1.151	0.911	-0.956	-1.888
SnBr₂	3.306	3.542	1.099	1.098	-1.202	-1.203
PrBr₃	3.560	3.654	1.056	1.068	-0.957	-1.012
NdBr₃	3.318	3.443	1.006	1.041	-1.102	-1.222
SmBr₃	3.456	3.505	1.007	0.989	-0.939	-1.205
ErBr₃	3.403	3.555	0.969	1.004	-1.111	-1.658
GdBr₃.6H₂O	3.227	3.456	0.864	0.989	-1.009	-1.469
TmBr₃	2.997	3.006	0.964	1.105	-1.343	-1.878

6. CONCLUSION

In the present work, X-ray fluorescence measurements have been carried out EDXRF. It has been found that in Br compounds, the energy shift varies in the range of (0.6 to 2) eV. This energy shift in given compounds with respect to pure metal/foil happens due to chemical effect. The observed spectral features, namely the asymmetry indices, FWHM values, chemical shifts, energy separations between K_{α} and K_{β} lines show an interesting correlation with crystal symmetries. There is a relation between the crystal structures and K X-ray emission rate because of the change in bond distance, inter atomic distance, the interaction between ligand atoms and the central atom, and the Auger electron and dipole transition. These situations cause a redistribution of the electron configuration in the molecule.

7. ACKNOWLEDGEMENTS

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REFERENCES

- [1] C. Mande, M.Y. Apte, Bull. Mater. Sci. 3 (1981) 193.
- [2] A.K. Nigam, M.K. Gupta, J. Phys. F: Metal Phys. 4 (1974) 1084.
- [3] H.K. Hinge, S.K. Joshi, B.D. Shrivastava, J. Prasad, K. Srivastava, Ind. J. Pure Appl. Phys. 49 (2011) 168.
- [4] S.K. Pandey, A.R. Chetal, P.R. Sarode, J. Phys. Soc. Jpn. 59 (1990) 1848.
- [5] J. Kawai, K. Fujisawa, Y. Gohshi, Spectrochim. Acta 42B (6) (1987) 729–743.
- [6] S. Wonglee, T. Tada, H. Fukuda, J. Hasegawa, Y. Oguri, Nucl. Instrum. Methods Phys. B 269 (2011) 3111–3114.
- [7] Z. Kertész, E. Furu, M. Kavčič, Spectrochim. Acta B 79–80 (2013) 58–62.
- [8] S. Nishibu, S. Yonezawa, M. Takashima, J. Fluorine Chem. 126 (2005) 1048–1053.
- [9] M. Kavčič, A. Karydas, C. Zarkadas, Nuc. Instr. and Met.s in Phys. Res. Sec. B (2004) 222(3-4):601-608.
- [10] T. Tada, M. Hayashi, H. Fukuda, J. Hasegawa, Y. Oguri, Nucl. Instrum. Methods Phys. B 266 (2008) 2292–2295.
- [11] R.M. Harrison, C.A. Pio, Environ. Sci. Technol. 17 (1983) 169–174.
- [12] S. Mirji, A.S. Bennal, N.M. Badiger, M.K. Tiwari, G.S. Lodha, Chem. Phys. Lett. 634 (2015) 271-276.
- [13] K. Taniguchi, Bull. Chem. Soc. Jpn., 57 (1984) 915-920.
- [14] T. Deluigi, M. Perino, E. Olsina, R. Riveros de la Vega, Spectrochim. Acta Part B, 58 (2003) 1699-1707.
- [15] M. Fichter, Spectrochim. Acta Part B, 30 (1975) 417-431.
- [16] G. Leonhardt, A. Meisel, J. Chem. Phys. 52 (1970) 6189-6198.
- [17] A. Meisel, G. Leonhardt, R. Szargan, (1989). Springer-Verlag, Berlin, Heidelberg.
- [18] O.K. Koksai, G. Apaydin, E. Cengiz, (2016). Spectroscopy and Spectral Analysis 36 (12), 4125-4129.
- [19] S. Porikli, Y. Kurucu, Instrumentation Science & Technology, 36:4, (2008) 341-354.