



Sulfur- and phosphorus- $K\beta$ spectra analyses in sulfite, sulfate and phosphate compounds by X-ray fluorescence spectrometry

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Abstract

Several sulfite, sulfate and phosphate compounds were studied by X-ray fluorescence spectrometry. Sulfur- and phosphorus- $K\beta$ spectral profile modified by the number of bonding hydrogen and oxygen atoms were analyzed. As it could be confirmed, the molecular orbital theory provides a suitable explanation of the origin and properties of the satellite $K\beta'$ lines. Also, for the compounds analyzed, it was found that sulfur- and phosphorus- $K\beta$ spectra present two main components and two secondary ones which exhibit a different behavior depending on the number of bonding hydrogen and oxygen atoms. Particularly, the peak corresponding to satellite $K\beta'$ line increases its intensity and moves away from the main peak when the number of oxygen atoms combined with the sulfur atom is increased. The energy differences between the main peak and the satellite peak found in the analyzed compounds were in average 14.2 ± 0.4 eV, thus being demonstrated that such a separation is a characteristic of the bonding atom, in this instance oxygen.

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1. Introduction

X radiation can remove inner orbital electrons of the atoms and the outer shell electrons can fill the vacancies with the consequent emission of characteristic X-rays [1]. These spectra, originating

from electron transitions between the valence band and the inner shells provide a powerful technique for obtaining information on the electronic structure in the valence band or the chemical bonding state [2]. Frequently associated with the main frequencies (whose origin can be easily accounted for) there are many satellite lines. These lines can have higher or lower energy than that of the main-

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line, their intensities being usually very significant. The origin of those with energies larger than that of the main line is well known [3]. A well-accepted proposal states that lower energy satellite lines are derived from a very strong bond between the valence band orbitals of an atom chemically linked to that of interest. O'Brien and Skinner [4] were the first to propose this explanation.

In a previous article [5], Al, Si, and S emission spectra were studied by X-ray fluorescence spectrometry (XRF). Among the results obtained, it was found that emission energies and relative transition probabilities for $K\alpha$ lines are slightly modified when considering an oxidized state compared to a pure element, while $K\beta$ and satellites exhibit a modified energy and relative intensity with different valence states and bonding atoms. The energy and relative intensity of the $K\beta'$ line appearing in oxidized states can be used to characterize them.

In this article, we analyzed $K\beta$ spectra of sulfite, sulfate and phosphate compounds by XRF. The main line and the associated satellites were analyzed, in particular, studying their dependence on the number of bonding hydrogen and oxygen atoms.

2. Experimental and results

Measurements were performed using a Philips PW 1400 wavelength-dispersive X-ray spectrometer. Spectra were obtained by employing a Ge ($2d=6.532 \text{ \AA}$) analyzer crystal, a 0.15 mm collimator and in step scan mode, during time periods long enough to obtain high-resolution spectra. Goniometer step was 0.01° . Spectrometer calibration (in energy) was checked before every set of measurements.

2.1. Sulfates

In the ions of polyatomic compounds, the individual ionic groups, such as SO_4^{2-} , are essentially isolated anions, as a whole, and are not significantly affected by the cations [6]. Sulfate ion has tetrahedral (T_d) symmetry and the valence atomic orbitals are made up of: $2s$, $2p$ and $3s$, $3p$, $3d$. Therefore, the T_d molecular orbital symmetry of

the sulfate ion has seven occupied orbitals in the valence band: $4a_1$, $3t_2$, $5a_1$, $4t_2$, $1e$, $5t_2$ and $1t_1$ [7].

The $K\beta$ spectrum of sulfate ions has two main components ($K\beta_{1,3}$ and $K\beta'$) [8,9]. Transitions into the $1s$ -level are allowed only from the t_2 orbital by the dipole-selection rule [10,11]. The population of the $4t_2$ orbital consists mainly of the $3p$ population of sulfur and the $2p$ population of oxygen. The $4t_2 \rightarrow 1s$ transitions give rise to the main peak known as $K\beta_{1,3}$. The other component, $K\beta'$, originates from $3t_2 \rightarrow 1s$ transitions [12]. The $3t_2$ molecular orbital has the $3p$ population of sulfur and the $2s$ population of oxygen [13,14].

Fig. 1 shows $SK\beta$ spectra of sulfate compounds: K_2SO_4 , Na_2SO_4 and $\text{CoSO}_4 \cdot 8\text{H}_2\text{O}$. The positions of the peaks A and C ($K\beta'$ and $K\beta_{1,3}$, respectively) are not significantly affected by the kind of cation. It can also be seen that the $K\beta$ spectrum has two secondary components: the small peak D, on the right side, known as $K\beta''$ and the peak B on the lower-energy side of the main peak. Peak D originates from the transitions of the $5t_2$ molecular orbital, which consists of the $3d$ population of sulfur and the $2p$ population of oxygen [14,15]. Peak B probably originates from the $5a_1$ molecular orbital, whose main populations are $3s$ of sulfur and $2p$ of oxygen. The transition into the $1s$ level is not allowed from the a_1 orbital by the dipole-selection rule. Nevertheless, if the molecule symmetry is distorted and the $5a_1$ molecular orbital contains the $3p$ population, an electronic transition into the $1s$ level will be allowed. Therefore, it seems that the peak B is influenced by the chemical bonding conditions and the kind of cation. Peak D seems to be very little affected by the kind of cation.

Fig. 2 shows the effect of replacing a cation by the hydrogen ion. In general, the $SK\beta$ spectrum reveals no significant changes, except for the peak B. The intensity of peak B increased upon replacing a potassium ion by a hydrogen ion. Peaks A and D also increased their intensities although less significantly. Consequently, there was a decrease in the intensity ratio of the two main components of the spectrum. At the same time, there was an increase in the FWHM value of the peak composed by the contributions of peaks B, C and D (see Table 1). It thus seems that hydrogen contributes

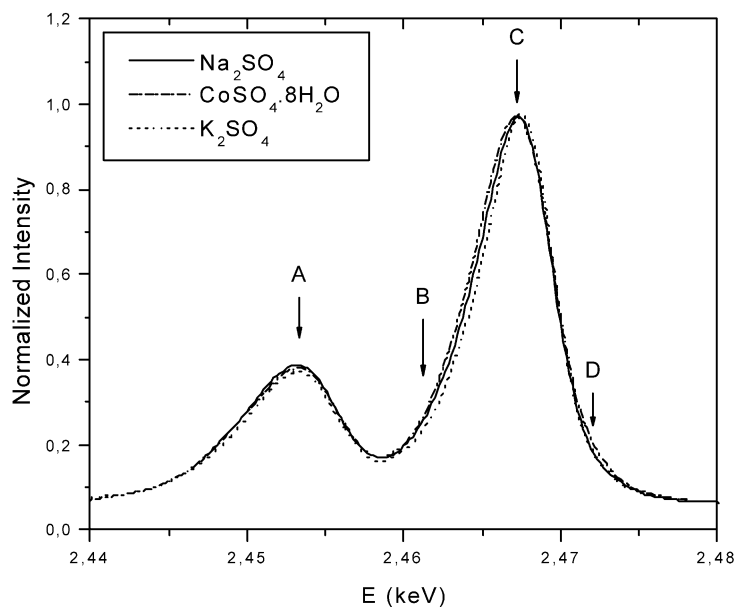


Fig. 1. $SK\beta$ spectrum of sulfate ions linked to different cations. Arrows indicate the approximate positions of peaks A, B, C and D. Table 1 shows the main characteristics of the spectra.

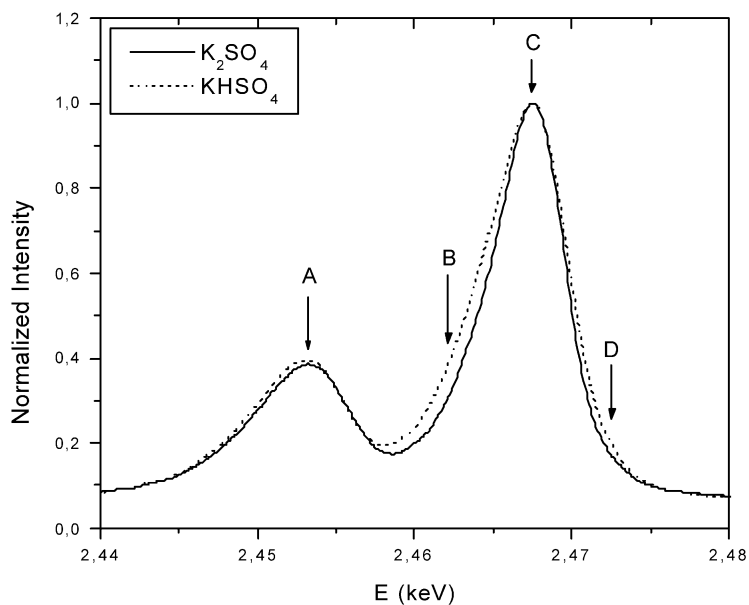


Fig. 2. Comparison of $SK\beta$ spectra of potassium sulfate and potassium bisulfate. Arrows indicate the approximate positions of peaks A, B, C and D. Table 1 shows the main characteristics of the spectra.

Table 1

Characteristic parameters of sulfate, sulfite, pyrosulfite and thiosulfate compounds (A, B, C and D subscripts refer to the peaks indicated in Figs. 1–4)

Anion	Compounds	E_C (eV)	E_A (eV)	$E_C - E_A$ (eV)	$I_A/I_{B,C,D}$ (%)	FWHM _{B,C,D} (eV)
SO_4^{2-}	K_2SO_4	2467.5	2453.4	14.1	41	5.5
	Na_2SO_4	2467.3	2453.1	14.2	38	5.6
	$CoSO_4 \cdot 8H_2O$	2467.1	2453.5	13.6	42	6.1
	$KHSO_4$	2467.6	2453.2	14.4	39	6.4
SO_3^{2-}	Na_2SO_3	2466.5	2451.9	14.6	24	5.9
	$NaHSO_3$	2466.2	2452.1	14.1	29	6.9
$S_2O_5^{2-}$	$Na_2S_2O_5$	2466.8	2452.4	14.4	31	6.7
	$Na_2S_2O_3 \cdot 5H_2O$	2466.7	2453.1	13.6	16	6.5

Estimated error for A and C peak positions is ± 0.2 eV.

to the peak B and its intensity increases according to the increase in the covalent interaction between the anion and the cation.

X-ray emission involves two levels, thus the whole chemical effect is the result of the shift of the core level as well as the structure of the valence band. A core-level change is expressed as an energy change in the emission spectrum, while the spectral features are related to the structure of

the valence band. Therefore, it seems reasonable that the core level of sulfur is not modified by the presence of hydrogen, since the 1s levels of sulfur and hydrogen are separated. This is the reason why no shifts are observed in the main peak (C) of the $SK\beta$ spectrum. Changes detected in the peak B are due to the presence of hydrogen affecting to some molecular orbital of the valence band.

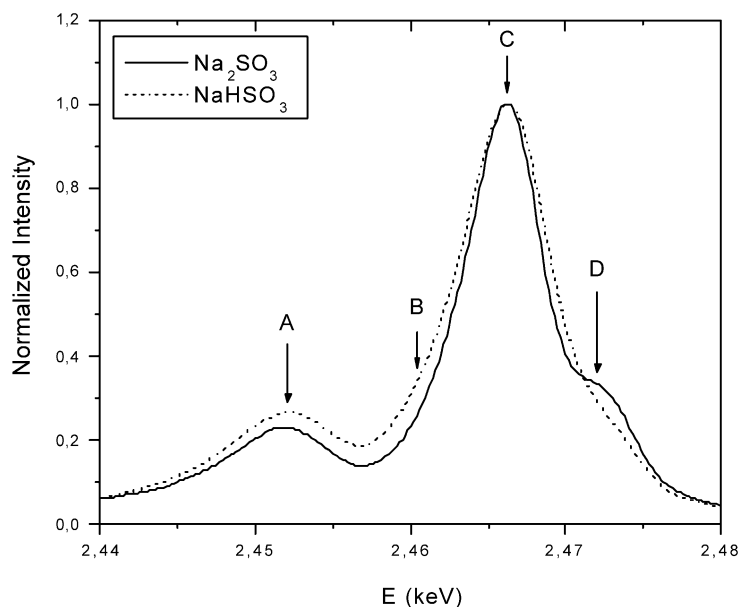


Fig. 3. Comparison of $SK\beta$ spectra of sodium sulfite and sodium bisulfite. Arrows indicate the approximate positions of peaks A, B, C and D. Table 1 shows the main characteristics of the spectra.

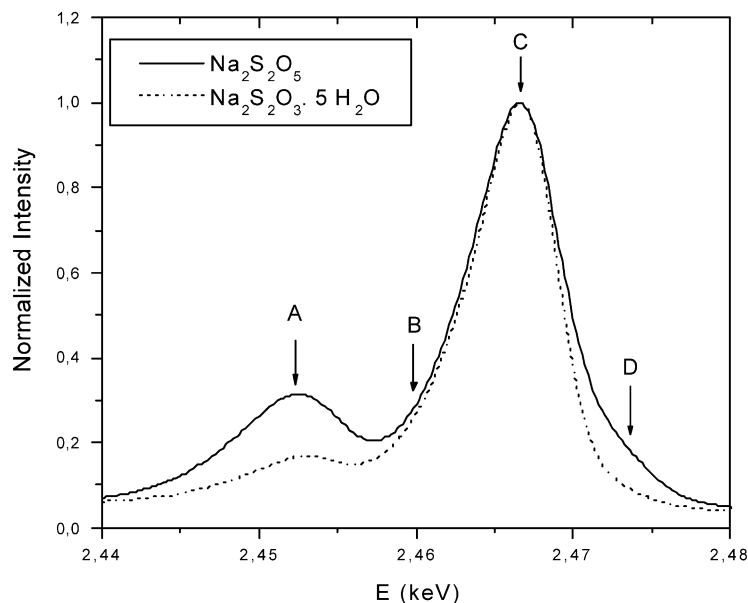


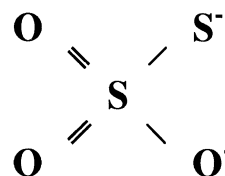
Fig. 4. Comparison of $SK\beta$ spectra of sodium pyrosulfite and hydrated sodium thiosulfate. Arrows indicate the approximate positions of peaks A, B, C and D. Table 1 shows the main characteristics of the spectra.

2.2. Sulfites

Fig. 3 shows a comparison of $SK\beta$ spectra of anhydrous sodium sulfite (Na_2SO_3) and sodium bisulfite (NaHSO_3). These compounds have cubic symmetry C_{3v} and the sulfur atom is in the oxidation state +4. Each of these spectra also has four components but they are different regarding the sulfate spectra. When a sodium ion is substituted by a hydrogen ion, the positions of the peaks A and C do not change significantly (Table 1), however, there is an increase in the peaks intensity. However, peak D intensity diminishes, which would seem to indicate that the sulfite (SO_3^{2-}) group exhibits an opposite behavior regarding the sulfate (SO_4^{2-}) group when a cation is substituted by a hydrogen ion. The changes in the $SK\beta$ spectrum have resulted in an important increase in the intensity ratio between the peak A and the main peak and, secondly, an increase of 1 eV in the $\text{FWHM}_{B,C,D}$ value (Table 1).

Fig. 4 shows a comparison of $SK\beta$ spectra of sodium pyrosulfite and hydrated sodium thiosulfate. The thiosulfate anion, $\text{S}_2\text{O}_3^{2-}$, is of a great

analytical interest because the two sulfur atoms in the ion are in different oxidation states: -2 and $+6$. The structural formula for the anion $\text{S}_2\text{O}_3^{2-}$ should be given as follows:



As can be seen in Fig. 4, peak A grows in proportion to the increase in the number of oxygen atoms combined with the sulfur atom. This result is in agreement with the previously mentioned origin of $K\beta'$ lines ($3t_2 \rightarrow 1s$), i.e. the greater number of oxygen atoms linked to the sulfur atom, the larger the population of the $3t_2$ orbital. Peak D exhibits the same behavior, growing with an increasing number of oxygen atoms. Table 1 shows that the peak A moves away from the peak C when the number of bonding oxygen atoms is increased, while the values of intensity ratio

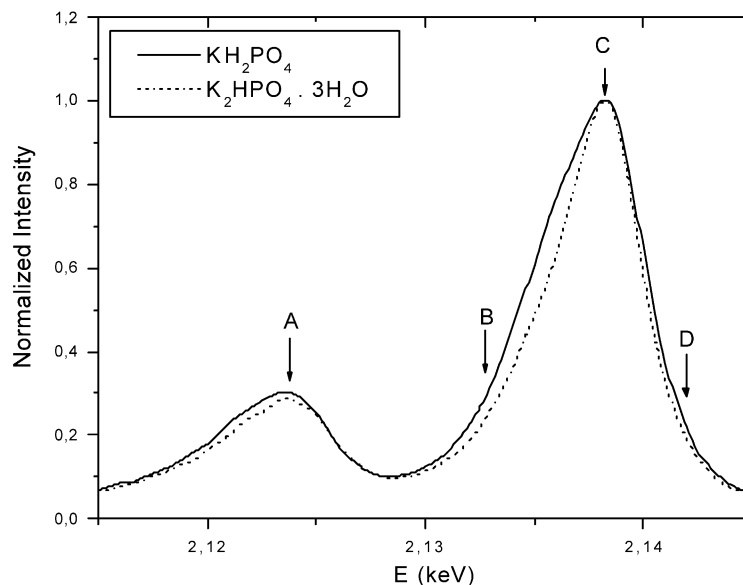


Fig. 5. Comparison of $PK\beta$ spectra of potassium phosphates when a cation is substituted by a hydrogen ion. Arrows indicate the approximate positions of peaks A, B, C and D. Table 2 shows the main characteristics of the spectra.

between the satellite and the main line can nearly double.

The $K\beta$ spectra shown in Figs. 1–4 were analyzed and the energy of the lines $K\beta_{1,3}$ and $K\beta'$ were determined (E_C and E_A in Table 1). The intensities (areas) of the main peak ($I_{B,C,D}$) and the satellite (I_A) were also calculated. Background subtraction was carried out, considering the absorption edge below the peak $K\beta_{1,3}$. Table 1 shows the main characteristics for the $K\beta$ spectra of the sulfur anions analyzed in this study.

2.3. Phosphates

Phosphates also have T_d symmetry and their behavior was found to be similar to that of sulfates. Fig. 5 shows the effect of replacing a potassium cation from dibasic potassium phosphate ($K_2HPO_4 \cdot 3H_2O$) by a hydrogen ion. The positions of the peaks A and C slightly modified with the consequent increase in the separation between them (see Table 2). The covalent interaction between the phosphate ion (PO_4^{3-}) and the cations

Table 2

Characteristic parameters of phosphate and pyrophosphate compounds (A, B, C and D subscripts refer to the peaks indicated in Figs. 5 and 6)

Anion	Compounds	E_C (eV)	E_A (eV)	$E_C - E_A$ (eV)	$I_A/I_{B,C,D}$ (%)	FWHM _{B,C,D} (eV)
PO_4^{3-}	$K_2HPO_4 \cdot 3H_2O$	2138.1	2123.8	14.3	30	4.8
	KH_2PO_4	2138.4	2123.3	15.1	28	5.8
$P_2O_7^{4-}$	$Na_4P_2O_7$	2138.1	2123.9	14.2	29	4.7
	$Na_3HP_2O_7$	2138.1	2123.8	14.3	27	6.1

Estimated error for A and C peak positions is ± 0.2 eV.

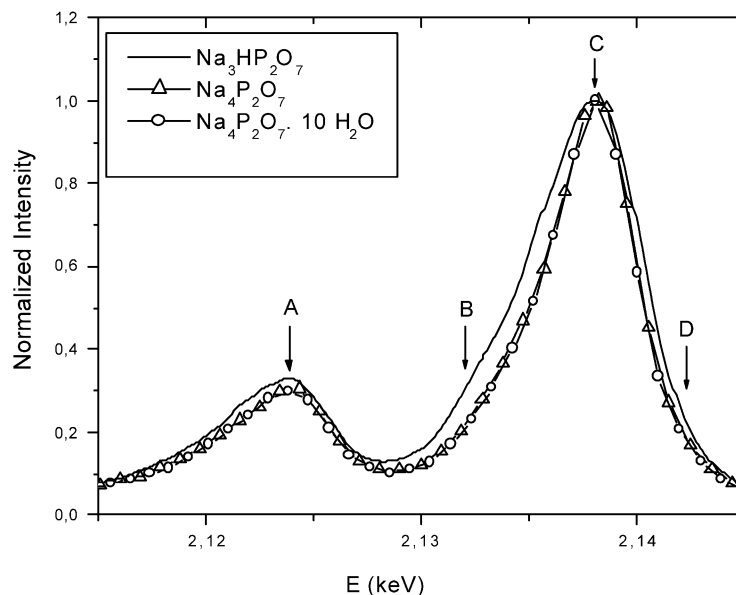


Fig. 6. Comparison of $PK\beta$ spectra of sodium pyrophosphates when a cation is substituted by hydrogen. Anhydrous and hydrated pyrophosphates spectra are also compared. Arrows indicate the approximate positions of peaks A, B, C and D. Table 2 shows the main characteristics of the spectra.

is relatively large. In the $PK\beta$ spectrum of KH_2PO_4 , the shoulder B grows according to the contribution of hydrogen and the increase in the covalent interaction between the anion and the cation. The intensity of the peak D also increased although less significantly. Consequently, there was an increase of 1 eV in the FWHM value as well as a decrease in the intensity ratio between peak $K\beta'$ and the main peak [composed by the contributions of peaks B, C and D (see Table 2)].

Fig. 6 shows the changes occurring in the $PK\beta$ spectrum when Na is substituted by H in sodium pyrophosphate. Peaks A and C nearly do not change their positions. The intensity of peak A increases, though peak (shoulder) B grows relatively more. Thus, as shown in Table 2, the intensity ratio decreases two units. As a consequence of this growth, there is an increase in the FWHM value. Fig. 6 also shows that water molecules do not modify the spectrum.

The main characteristics the $PK\beta$ spectra (Figs. 5 and 6) are shown in Table 2. Calculations of

integrated intensities were performed in the same way as $SK\beta$ spectra.

3. Conclusion

The experimental data obtained in this work (Tables 1 and 2), including the position of lines $K\beta_{1,3}$ and $K\beta'$ and the relative intensities of the satellites with respect to the main line, are similar to those values found by Schnell [16] and Wilbur and Gofman [17].

The molecular orbital theory provides a suitable explanation of the origin and properties of the satellite $K\beta'$ lines.

$SK\beta$ and $PK\beta$ spectra for the compounds analyzed exhibit two main peaks (A and C) and two secondary components (B and D). They show different spectral profiles depending on the number of bonding hydrogen and oxygen atoms.

$SK\beta$ spectrum for the SO_4^{2-} compounds is not significantly affected by the change of cations.

When a cation is replaced by hydrogen in sulfate compounds, there is an increase in the intensity of the peaks A, B and D.

In sulfite compounds, the peaks A and B increase their intensities when a cation is replaced by hydrogen. However, there is a decrease in the intensity of the peak D, which is the opposite effect regarding sulfate compounds.

When increasing the number of oxygen atoms combined with the sulfur atom, there is an increase in the intensity of the peak A. The latter also moves away from the peak C.

Like in sulfate compounds, when hydrogen replaces a cation in phosphate and pyrophosphate compounds, an increase in the intensity of the peaks A, B and D is observed. In phosphate compounds, the positions of the peaks A and C slightly modify, though they remain nearly constant in pyrophosphate compounds.

In all the analyzed compounds, it was found that energy differences between the satellite and the main line were in average 14.2 ± 0.4 eV (Tables 1 and 2). It is thus demonstrated that such a separation is a characteristic of the bonding atom [18]—in this instance oxygen. As can be seen, these energy differences are similar to the ionization energy difference for the oxygen atom from the 2s orbital (28.4 eV) and from 2p orbital (13.6 eV), which is agreement with the molecular orbital theory.

Finally, a better resolution spectrometer is required to resolve satellite B and D lines separating them from the main line C ($K\beta_{1,3}$) [19–23]. An improved resolution would allow a precise evaluation of the energy differences between lines.

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