Characterization of table salt samples from different origins and ESR detection of the induced effects due to gamma irradiation.

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Abstract. Three nominated types of table salt samples are obtained from different sources: “cok” rooks table salt, “sal” red sea marine table salt, “Dr.salt” table salt with low sodium content prepared for hypertensive patients to procedure in this work labeled C, S and D respectively. Characterization of the table salt types using X-ray diffraction (XRD) analyses and the energy dispersive X-ray (EDX) analysis was carried out. EDX analyses show a difference in sodium and chloride content percentage atomic ratio between the three salt types. Also, potassium is apparent in the salt type D. The positions of each diffraction peak maximum intensity were obtained and compared with the corresponding peak in the database. Also, to discriminate the diffraction peaks of the impurities. Samples were irradiated with gamma source using Co60 at room temperature. Electron spin resonance (ESR) has been studied in the three different commercial table salt samples. The aim of the present study is to investigate the sensitivity of the naturally occurring table salts to gamma radiation, using the ESR technique. The ESR results represent the signal intensity of the salt types C is higher than S than D. The results also indicate that, the ESR intensity of the table salt and the sensitivity to gamma radiation increases with increasing the percentage of sodium and also some other impurities in each content type.

1. Introduction
The alkali halide NaCl (common salt) exhibits: linearity of the thermoluminescence (TL) emission with the dose in the range of interest (up to 20 Gy), high sensitivity to radiation, high stability of the TL signal during the storage of the material (i.e. low fading), thermal stability and discrete trap distribution [1]. The common commercial household salts are used in (TL) dosimetry examination [2]. Salt is sensitive to ionizing radiation, readily available [3,4,5]. Light induced fading announce that storage in the dark during and following exposure is needed (use of salt irradiated in packaged material) to reduce uncertainties in the assessment of the delivered dose [2].

ESR study of several Fe+ centers at various sites in X-irradiated NaCl (Tl, Fe) crystals are reported [6]. The centers are observed below 32 K, only in crystals freshly quenched from 700K before irradiation. Such crystals X-irradiated at 77K exhibit ESR transitions from Fe+ions situated on substitutional sites with either octahedral, axial or orthorhombic symmetry. The axial crystal field component is due to a negative ion vacancy trapped in the neighborhood of a Fe+ ion. ESR spectra of two new sulfur centers in NaC1, created after suitable doping and exposure to X-rays at room temperature, are analyzed. One of the defects, is likely a mono atomic S- centre, the other one is probably a substitutional S2- molecular ion [7].

The electron spin resonance (ESR) parameters for the tetragonal Ir2+ center in NaCl are theoretically observed [8] from the perturbation formulas of the parameters for a 5d7 ion in tetragonally elongated octahedra. The impurity center refers to the alternative [IrCl6]4-, cluster on host Na+ site. In spite of the ionicity of host NaCl, the [IrCl6]4-, cluster as yet exhibits moderate covalency and moreover spin-orbit coupling and the ligand orbital assistances should be taken into account. ESR spectra of two new sulfur centers in Na2O-Li2O-B2O3-K2O (R = Zn, Mg, Sr and Ba) glass Systems. The spin-Hamiltonian parameters were evaluated from the
ESR spectra. The bond parameters were evaluated from the ESR and optical data. In the case of VO$_{2+}$ ions, the covalency rates were estimated [9].

Differential scanning calorimetry on rock-salt samples represents a decrease in the latent heat of melting of sodium colloids during subsequent low temperature irradiation, while the stored energy increases slowly, denoting that the process of radiolysis continues. The model is formulated [10] to depict the nucleation kinetics and the development of the sodium colloids and distribution of chlorine precipitates in NaCl after high dose irradiation.

The electrical conductivity and optical and ESR absorption of KC1: Mn and NaCl: Mn crystals, colored electrolytically, additively and by X-irradiation was studied [11]. The results indicate that the valence state of the Mn$^{2+}$ center changes after X-irradiation. The ESR absorption of electron-irradiated crystals of NaCl: Mn were studied and at low temperature the ESR spectrum with large splitting were obtained [12].

2. Objectives and methodology.

In previous work, the characteristics of thermoluminescence (TL) have been studied [13] for four different commercial table salt samples (NaCl) obtained from different sources. Samples were irradiated with Gamma source using Cs$^{137}$. One prominent glow peak is observed in the glow curve at around 216 - 222 °C of the commercial salt samples. By comparison, the TL intensity for all salt samples could be arranged concerning with their radiation sensitivity. The most sensitive and preferable one has a linear response with the dose for a broad range from 250 mGy to 20 Gy. The post-irradiated fading rates are investigated and show stability after 8 days. The fading at room temperature was monitored during 24 days. In conclusion, this type of salt may be a candidate for using as a Gamma ray retrospective dosimeter.

In the current work, Three types of commercial table salt C, S and D were obtained from different sources. Characterization of the salt types using EDX and confirmation of the results using XRD analyses were done. The three salt types were gamma Irradiated at room temperature with a dose of 5 kGy. ESR was used to investigate the radiation induced radicals due to gamma irradiation. Arranging the salt types according to their sensitivity to radiation and studying the relationship with the ratio of sodium, chloride and other associated minerals in each type.

3. Materials and method.

3.1. Materials

Three types of salt were selected to contribute in this work, C, S, and D salts. Commercially available domestic salt and rock salt, were collected from various locations. The salt samples are passed through sifting nets, to obtain salts with low grain size. All the samples are kept in desiccators which contains silica gel to absorb the moisture at room temperature.

3.2. methods

The investigations were done on a commercial natural samples, i.e. without changing on its physical properties. For the purpose of structure study, the salt samples were heated to 300 °C for 30 minutes in the furnace. The structural study for C, S and D salt was done by X-ray diffraction method in an XRD-Shimadzu diffractometer 6000 X-ray diffraction spectrometer using a copper target ($\lambda = 1.542$ A$^0$). The measurements were done at room temperature, in the 2θ range, between 4 to 90 degrees. The irradiation was carried out at room temperature with radiation dose of 5 kGy. Gamma irradiation of the sample has been carried out by means of CO$^{60}$ gamma source “4000 A, Indian gamma chamber” at a dose rate of 2 kGy/h.

ESR signals were recorded at room temperature using a Bruker X-band spectrometer under the following conditions: Microwave power = 1.008 mv and modulation frequency = 100 kHz. The spectrum was recorded as the first derivative signal. Before recording sample spectra, empty tube spectrum was measured so as to assure the purity of the obtained signals. In order to correct for the change in the spectrometer sensitivity, readings were corrected to the peak-to-peak of the material reference standard,
which was listed before and after each single spectrum of the salt samples. Sample weight was about 0.38 ± 0.05 g on average. Sample mass normalization was done for each gained signal intensity. The spectrum of each single sample was achieved three or more successive times, each spectrum is from a single scan.

The elemental analysis of the salt samples was performed using Scanning Electron Microscope (SEM) (JEOL-6510-LA), made in Germany and Energy Dispersive X-ray (EDX) analyzer. In EDX spectrometer, each specimen was subjected to an energetic electron beam (20 keV) resulting in the production of characteristic X-rays from the specimen surface. The emitted X-ray spectrum was used to determine the composition of the C, S and D samples qualitatively and semi-quantitatively.

X-ray diffraction (XRD) is an analytical technique used for identifying whether the material is a crystalline or amorphous material. X-ray diffraction (XRD) patterns were registered using XRD-6000 x-ray diffraction Shimadzu spectrometer with a copper target (λ = 0.1542 nm) at an electric current of 30 MA and an operating voltage of 40 KV. The pattern was recorded with a scanning rate of 2°/min at the (2θ) scan range of 4° to 90° and with scatter slit 1°, divergence slit 1°, and receiving slit 0.3 mm with a 0.02° sample pitch. These operating conditions were applied all over the examination.

4. Results and Discussion.

4.1. EDX Analysis.

Before investigating the ESR measurements, the elemental analyses of the three types of salts under implementation were achieved by Energy Dispersive X-Ray Analyses (EDX). The given elemental analysis values are obtained in atomic percentage (at %) for every constituent element, with anticipated error less than ±0.1%. After normalizing to the unity of mass, the atomic weight percentages for each element are listed in the table 1. From the results it can be observed that: The atomic percentage (at %) is a relative value specified by the elemental presence as a number of atoms in the compositional form of the sample relative to the total number of ingredient elements, i.e. the change in the atomic percentage of every element affects the corresponding values of the other elements and therefore the total atomic percentage is standardized to 100% of the sample constituent elements.

**Table 1.** The energy dispersive X-ray analysis (EDX) for the three salt types.

| Element | Norm at. wt.% |
|---------|---------------|
|         | C (Rock salt) | S (Sea salt) | D (Dr. salt) |
| Cl      | 35.1          | 38.37        | 41.09        |
| Fe      | 2.59          | 1.84         | 0.22         |
| S       | 0.55          | 1.52         | -            |
| K       | 4.61          | 4.22         | 26.56        |
| Ca      | 4.38          | 3.97         | 0.88         |
| Na      | 41.81         | 39.55        | 28.75        |
| Mg      | 6.53          | 5.96         | 2.3          |
| Si      | 1.15          | 1.29         | -            |
| Ni      | 0.85          | 0.96         | -            |
| Cu      | 2.43          | 1.92         | 0.2          |

The results reveal that the atomic weight percentages of sodium and chloride are 36.31% and 33.1% of C salt, 34.55% and 39.84% of S salt and 27.4% and 41.09% of D salt respectively. Also, the other common constituent elements apparent with various atomic percentages in the three types of salts are (Fe, K, Ca, Mg). From the table 1, EDX analyses indicate the presence of Na, Cl, for the three salt types, and show the differences in Sodium and Chloride percentage ratio between the three salt types.
4.2. XRD
The structural study of the three commercial table salt (C, S and D) was done by X-ray powder diffraction method. The measurements were done at room temperature in the 2θ range between 4 to 90 degrees. The XRD spectra for C, S and D table salt are shown in Fig. 3.1: (a), (b) and (c) respectively.

![XRD spectra for C, S and D table salt](image)

**Figure 1.** XRD of the table salt, (a) C salt, (b) S salt and (b) D salt.

The data from *JCPDS 78-0751* for NaCl and the 2θ peak positions for the current salt types are reported in table 2. The position of each diffraction peak maximum intensity was obtained and compared with the corresponding peak in the reported JCPDS data.
Table 2. The comparison of angular positions of XRD of the three commercial table salt (C, S and D) and Data from *JCPDS 78-0751 for NaCl.

| Peak No. | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     | 9     |
|----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| * 2 theta (NaCl) | 27.42 | 31.76 | 45.54 | 53.98 | 56.59 | 66.37 | 73.23 | 75.46 | 84.19 |
| C        | 27.22 | 31.63 | 45.34 | 53.82 | 56.38 | 66.17 | 73.22 | 75.22 | 83.92 |
| S        | 27.64 | 32    | 45.76 | 54    | 56.64 | 66.13 | ------| 75.5  | 84.2  |
| D        | 27.7  | 31.29 | 45.22 | 53.48 | 58.12 | 66.06 | 73.4  | 76.92 | 84.34 |
| * h k l  | 1 1 1 | 2 0 0 | 2 2 0 | 3 1 1 | 2 2 2 | 4 0 0 | 3 3 1 | 4 2 0 | 4 2 2 |
| Peak No. | 10    | 11    | 12    | 13    | 14    | 15    | 16    | 17    | 18    |
| C        | 28.36 | 39.62 | 59.54 | 64.02 | 67.62 | 70.34 | 71.52 | 78.42 | 81.36 |
| S        | 28.58 | 36.4  | 59.3  | 64.18 | 68.82 | 69.94 | 70.62 | 78.82 | 81.26 |
| D        | 28.18 | 31.86 | 36.26 | 40.42 | 49.69 | 65.8  | 77.26 | 81.52 | 86.92 |

The obtained characteristic peaks of the analyzed samples of the table salts are very close to the corresponding reported sodium chloride peaks reported in the 78-0751 data at the same 2θ degrees. In figure 1(a) & 1(b) spectra of the XRD analysis of the salt samples (C, S) shows also other peaks which may be attributed to traces of other minerals. But, in figure 1(c), the spectrum of the XRD analysis of the salt samples (D) shows other intense peaks which may be attributed to potassium and other minerals. Since the XRD of C salt is measured and the 9th peak (i.e., 2θ at around 84 degrees) is missing as shown in Figure 1(a). On the other hand, in the XRD of S salt 2θ is analyzed as in Figure 1(b). The XRD results for C, S and D salt samples were compared directly with the JCPDS data. Most of the angular positions of the intense peaks are found almost matching with JCPDS 78-0751 for NaCl.

4.3. ESR analyses.

In the current section, the acquired ESR spectrum of the C, S and D samples will be discussed in the light of the compositional and structural knowledge acquired through EDX and XRD analyses. The electron and hole have two destinies: they will be either diffuse to the crystal lattice where they initiate the chemical reaction or trapped by interstitial sites [14]. They are the main mobile species on the very short time. Similarly, in the current work, the formed electron hole pair in NaCl lattice enhances the oxidation of metal ions leading to the change of the ESR signal after gamma irradiation. Figure 2, shows the ESR spectra for the three table salt types and their apparent concentration of sodium, chloride and the associated impurities irradiated using gamma rays. The type of impurities, Fe, O, K, Ca and Mg may have different behavior concerning of the trapping radicals or other precursor species. These species can play an important role in the radiolytic decomposition.
EDX analysis of table salt C, S and D samples table (1) indicate the presence of paramagnetic cations such as Na, Fe, O, Ca, K and Mg. It is known that gamma radiation can oxidize metal cations to higher oxidation states. So, the concentration of paramagnetic cations increases.

\[
\text{Mn} \xrightarrow{\text{Gamma Radiation}} \text{Mn}^{n+1} + \text{e}^-
\]

Where, M is a metallic ion and n is an integer number. \( \text{M}^{n+1} \) is the participate ion in the obtained spectra in figure 2. Therefore, ESR spectra of gamma irradiated table salt samples at room temperature with 5 kGy, may be related to \( \text{M}^{n+1} \).

**Table 3.** Shows the ESR peak intensity per gram of the salt samples.

| Sample name | Intensity/gm | g//   | g⊥    |
|-------------|--------------|-------|-------|
| Sample-C    | 20387.77908  | 1.98708 | 2.098992 |
| Sample-S    | 18479.53216  | 1.98732 | 1.99017  |
| Sample-D    | 1390.9224    | 1.98726 | 1.99027  |

The paramagnetic cations (\( \text{M}^{n+1} \)) can be formed by direct effect of gamma radiation on \( \text{M}^{n+} \), or by the radiation induced oxidation of \( \text{Na}^{+} \) to \( \text{Na}^{2+} \). It can be considered that \( \text{Na}^{2+} \) able to oxidize \( \text{M}^{n+} \) to \( \text{M}^{n+1} \).

As shown in figure (2), the ESR signal intensity may be related to the increase in the concentration of the paramagnetic cations. So, the highest ESR signals intensity related to the C samples, which contain the highest concentration of paramagnetic cations. The lower ESR signals intensity were related to the D samples, which contain a lower concentration of paramagnetic cations.

**5. Conclusions**

EDX analyses indicate the presence of Na, Cl, for the three salt types, and show the differences in Sodium and Chloride percentage ratio for the three salt types. Also, It shows the atomic percentage for the
contents of the rock, marine and the prepared salts. The most common impurities in the commercial salt are mixed alkali and alkaline earth (Fe, K, Ca, Mg). The obtained characteristic peaks of the analyzed samples of the table salts are very close to the corresponding sodium chloride peaks reported in the JCPDS 78-0751 data at the same 2θ degrees. XRD analysis of the salt types shows other intense peaks which may be attributed to potassium and other tinny peaks related to other impurities.

The high sensitivity to radiation of C salt may be related to the higher apparent concentration of sodium and the associated alkali metals like iron, copper, magnesium, calcium and calcium percentage ratio than the ratios in the other two types of salt used in the current work.

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