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Gamma radiation-induced thermoluminescence emission of minerals adhered to Mexican sesame seeds

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HIGHLIGHTS

- Blue TL emission of polymineral phases from sesame seeds from Mexico is studied.
- The polymineral phases are quartz, feldspars, calcite, gypsum and clinochlore.
- Samples exhibit high sensitivity, TL intensity and high TL stability during storage.
- Blind tests confirm the validity of TL to detect irradiated samples up to 15 months.

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ABSTRACT

The thermoluminescence (TL) emission of minerals isolated from Mexican sesame seeds appear as a good tool to discern between irradiated and non-irradiated samples. According to the X-ray diffraction (XRD) and environmental scanning electron microscope (ESEM) data, the adhered dust in both samples is mainly composed of different amounts of quartz and feldspars. These mineral phases exhibit (i) enough sensitivity to ionizing radiation inducing good TL intensity, (ii) high stability of the TL signal during the storage of the material, i.e. low fading, and (iii) are thermally and chemically stable. Blind tests were performed under laboratory conditions, but simulating industrial preservation processes, allow us to distinguish between 1 kGy gamma-irradiated and non-irradiated samples even 15 months after irradiation processing followed the EN 1788 European Standard protocol in sesame samples.

1. Introduction

Irradiation is an accepted method and authorized in almost 40 countries (Chauhan et al., 2009) to make food more safe since it contributes to prolong shelf life of the products removing bacteria, parasites, insects and fungi harmful to health, and delaying the maturation. The given dose depends on the type of the food; particularly water-rich products (i.e. tomatoes, onions or fruits) can be only irradiated with low doses, from 10 Gy to 1 kGy, to prevent the appearance of water free radicals (H_2O^+, $H^\bullet$ or $OH^\bullet$). Such doses avoid sprouting, postpone ripening and inactive some parasites. Medium doses, in the range of 1–10 kGy, are supplied to some vegetables, cereals, dried fruits and vegetables, spices, seasonings, meat, raw poultry or seafood in order to eliminate microorganism and pathogenic organisms, except viruses; this process is known as radicidation where the dose ranges are from 2 to 8 kGy. If the application of ionizing radiation is to increase their keeping quality, usually at lower temperatures, that induces a decrease of the spoilage microorganisms, the process is called radurization or radiopasteurization since is very similar to heat pasteurization. It is used to treat foods with high moisture content and a high pH. The dose for radurization is in the range of 1–10 kGy. Higher doses, up to 100 kGy, are usually employed to achieve total sterility making possible longer periods of storage without refrigeration, similarly to thermal canning. This method, known as radappertization, is applied to sterilize food for astronauts as well as immune-compromised hospital patients, for instance bubble children (IAEA, 2002). The quality control of the food irradiation processing, needs of an adequate methodology to discriminate irradiated foodstuffs or to verify the absorbed dose. In this sense, EN 1788 European Standard (EN 1788, 2001) based on the thermoluminescence (TL) emission from polymineral phases (quartz, carbonates, feldspars and clays) isolated from herbs, seeds, spices and seasonings appear as a suitable method to discriminate irradiated foodstuffs (Beneitez et al., 1994; Calderon

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et al., 1995) and, occasionally, to estimate the total absorbed dose (D'Oca et al., 2007, 2009). Nevertheless there are some uncertainties in the dose estimation, mainly due to, the food processing and the mineralogical composition. In food processing the irradiation: (i) is combined with freezing, heating, etc. (Kim et al., 2008); (ii) is sometimes provided in different steps, (iii) changes the dose-rate or; even, (iv) uses many sources. Related to the mineralogical composition, different amounts of quartz and Na or K-rich feldspars could change the intensity and the shape of the TL curves (Correcher and Garcia-Guinea, 2011). The conditions of storage (temperature, daylight) or the time elapsed since the irradiation took place could be also a limitation for the dose evaluation since modify the luminescence signal (Aitken, 1985; Goulas et al., 2008; McKeever, 1985). The main advantages of this technique is that it does not depend on the type of foodstuff and that the isolated minerals generally exhibit high sensitivity to radiation, high TL intensity, high stability of the TL emission during the period of storage, i.e. low fading, and are chemically and thermally stable (McKeever, 1985). TL is a method based on the emission of light from a solid sample (insulator or semiconductor) when it is heated after being irradiated by X-rays, gamma rays, electron beam, cosmic rays, etc. During the heating, the TL signal is detected by a photomultiplier tube and recorded as a function of the temperature or wavelength. The resulting curve is called a glow curve; the luminescent intensity and the shape of this glow curve are functions of radiation dose and heating rate.

The main aim of this work is to determine the time for the validation of the EN 1788 European standard protocol in two different sesame samples from Mexico. For this purpose, the isolated mineral phases from the samples were firstly characterized by ESEM, XRD and TL to check the mineralogical composition and the luminescence behavior. Secondly, blind tests on samples irradiated at random simulating industrial processes (similar room temperature and moisture, and presence of daylight); were performed to determine the suitability of the protocol in irradiated samples in the range of 1–10 kGy stored up to 15 months.

2. Samples and experimental

Sesame seeds from Mexico have been used for this study. Separation of the dust from the seeds was performed attending to the different densities of inorganic and organic phases. The whole samples were dipped in a container with carbon tetrachloride (CCl_4), and stirred for 3–4 h. CCl_4 was selected because it is an inert solvent; it does not damage the sample and has an optimum density for the aim (1.59 g/cm^3). Subsequent centrifugation showed clearly two different layers, the sesame seeds being on the surface and the inorganic material at the bottom of the beaker. The two parts were separated by decantation and the mineral phase was washed several times using in every case CCl_4 (Correcher et al., 1998). Finally, the samples were stored at room temperature in a desiccator holder with silica gel in the presence of white light in order to extend the results obtained to the conditions usually employed by producers and dealers. This method of separation yielded about 4–5% of dust. When the inorganic phase was isolated, the samples were carefully crushed with a pestle and mortar to avoid triboluminescence (Garcia-Guinea and Correcher, 2000) and sieved to obtain a size of the grain under 50 μm to decrease the scattering of the TL results (Beneitez et al., 1994). The samples were analyzed using a FEI QUANTA 200 ESEM (40 kV electron microscope with a resolution of 70 Å) operating under high vacuum conditions and equipped with both secondary electron and backscattering detectors. The microscope also displays two X-ray detectors (Analytical-Inca Instruments) that could be used simultaneously or in alternating mode. The microanalysis detector was a Si–Li model, using a Tractor Northern Z2 computer. The mineral phases were characterized by XRD using a Phillips PW1710/00 powder diffractometer with a CuKα radiation source. Patterns were obtained by step scanning from 2° to 64° (2θ in steps of 0.020°; 4 s per step).

Thermoluminescence measurements were carried out using an automated Risø TL system model TL DA-12 (Botter-Jensen and Duller, 1992). This reader is provided with an EMI 9635 QA photomultiplier and the emission was observed through a blue filter (a FIB002 of the Melles-Griot Company) where the wavelength is peaked at 320–480 nm; FWHM is 80 ± 16 nm and peak transmittance (minimum) is 60%. All the TL measurements were performed using a linear heating rate of 5 °Cs^{-1} from RT up to 500 °C in a N_2 atmosphere. Aliquots of 5.0 ± 0.1 mg powdered samples were used for each measurement. The incandescent background was subtracted from the TL data.

Gamma irradiation was performed from the ^{60}Co radionuclide source placed at the NAYADE unit of CIEMAT, usually employed in food irradiation processes due to its high penetrating capability very effective for thick or dense products. The sample were exposed to 1, 5 and 10 kGy at a dose rate of 5.5 kGyh^{-1} calibrated by Fricke system that is based on the oxidation of ferrous ions to ferric ions in aqueous sulfuric acid solution by the effect of ionizing radiation. The change in the absorbance of the $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and NaCl dissolved in H_2SO_4 solution is measured by means of a UVISPEK UV spectrophotometer (supplied by Hilge & Wattsat) with matched quartz cells of 1 cm optical path length provided with a temperature control system. The absorbance was carried out at 25 °C on the 100 Gy irradiated solution (precision 1%).

3. Results and discussion

Mexican sesame samples rely on inorganic dust adhered on the surface (Fig. 1) that consists mainly on quartz 47.7%, feldspars 24.9%, calcite 9.1%, gypsum 10.4% and clinochlore 7.9%. This type of mineral phases has been also found in other species, seasonings and herbs although varying the percentage in each sample (Calderon et al., 1995; Correcher et al., 1998; Correcher and Garcia-Guinea, 2011). It is well-known that all of this inorganic dust may act as good TL dosimeters since exhibit a good TL response (Horowitz,

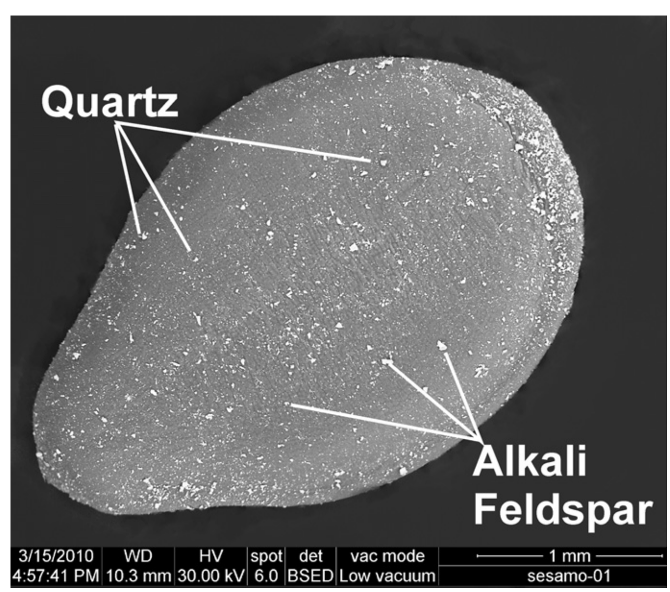

Fig. 1. Inorganic material detected on sesame seeds from Mexico by means of ESEM technique. Note that the dust material that is mainly composed by quartz and alkali-rich feldspars.