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Optical characterization of amber of Chiapas

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We show the refractive index value is a vulnerable test to discriminate true amber from false amber. In this sense, the fluorescence spectral signal is also a vulnerable test if the illuminating source has a broad spectral emission. We present results that allow us to conclude the Raman spectroscopy is a reliable test to distinguish amber of Chiapas from amber of the Baltic regions, and from false amber. We suggest the inclusion of the Raman spectroscopy to the Official Mexican Norm, NOM-152-SCFI-2003, to authenticate the amber of Chiapas.

Keywords: Optical properties of amber; polarization; fluorescence; Raman spectroscopy.

Mostramos que el valor del índice de refracción es una prueba vulnerable para discriminar ámbar verdadero de ámbar falso. En este sentido, la señal espectral fluorescente es también una prueba vulnerable si la fuente de iluminación posee un amplio espectro de emisión. Presentamos resultados que permiten concluir que la espectroscopia Raman es una prueba confiable para distinguir ámbar de Chiapas de ámbar de las regiones del Báltico o de ámbar falso. Se sugiere la incorporación de la espectroscopia Raman a la Norma Oficial Mexicana, NOM-152-SCFI-2003, para autentificar el ámbar de Chiapas.

Descriptores: Propiedades ópticas del ámbar; polarización; fluorescencia; espectroscopia Raman.

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1. Introduction

Amber and copal are the names given to the natural tree resin to distinguish one from the other, in terms of age. Amber is a resin with millions of years of formation while the copal comprises as much several thousand of years from formation. Amber is located in several countries around the world, in America is located mainly in the Caribbean region [1]. Amber of the Baltic regions has been known from long time ago and has been studied extensively from the recent years, using different techniques. Of particular importance for this work, is the use of the Raman spectroscopy, where a complete differentiation from the amber of the Baltic regions and the copal resins has been reported, including studies about the maduration processes [2-4].

Amber has been located also in México, being Chiapas the state with the highest number of mines from which this gem is extracted. Traditionally, amber (with ages up 2 million years) and copal (with ages down 2 million years) have been associated to mystic and medicinal uses. For scientists, amber represents a source of natural information about the ancient climate and the biological conditions of the places where it has been found. A special interest represents the presence of small tree leaves or animal species like mosquitoes, frogs, and lizards inside amber pieces, which act like natural memory keepers from ancient times. Now amber of Chiapas is used as a touristic attractor for jewelry lovers due to its beauty, hardness, vivid colors, and high light transmittance. Its relative low price makes it a very accessible item for almost any people. Unfortunately, the recent incorporation of amber imitations (artificial resins and glasses) to the commerce chain tends to damage the image and prestige of this natural resin, to affect the buyer's investment, and to decrease the tourist visitors searching for special pieces in Chiapas.

With the intention to protect the prestige of this gem, several social and government sectors have created an Official Mexican Norm, NOM, [5] and an Origin Denomination criterion for the amber of Chiapas. However, actually there is not a physically certified organism where the corresponding NOM can be applied to authenticate the amber. The NOM considers several mechanical, electrical, and optical tests. The optical tests are related to the determination of color, transmittance, fluorescence, and refractive index.

In this work, we show the refractive index is a vulnerable test, because false amber samples and true amber of Chiapas can reach similar values. We also show the fluorescence emission signal can be a vulnerable test if the samples are illuminated with a broad spectral light; however, it can be a reliable test if the illumination is associated to a sharp spectral source centered around 400 nm. Finally, we show the Raman spectral signal is a very reliable test to distinguish amber of Chiapas from amber of the Baltic and from the false amber. We conclude by suggesting the Raman spectroscopy be considered into the NOM [5] to authenticate the amber of Chiapas. To our knowledge, this is the first work where amber of Chiapas from the Simojovel de Allende region has been characterized by Raman spectroscopy.

2. Basic principles and optical techniques

The law of refraction (Snell's law) describes the path followed by an optical ray when interacts with a plane interface that separates two media. This path, defined by the transmis-

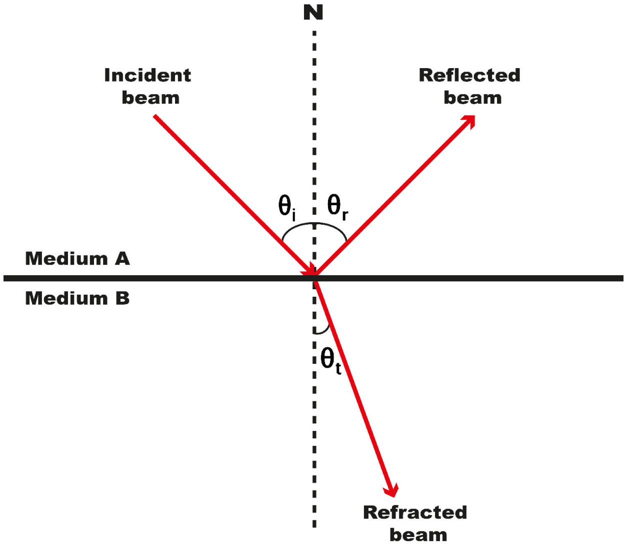

FIGURE 1. Schematic representation of the Snell's law.

sion and the reflected angles measured from the normal, is determined by the relative propagation velocity of light in the medium with respect to the propagation velocity at the vacuum (refractive index), and the angle of incidence. It is given as:

$$n_i \sin\theta_i = n_t \sin\theta_t \tag{1}$$

where the sub-index denotes the incident (i) or the transmitted (t) medium. Note that the knowledge of the refractive index associated to one medium, allows the determination of the refractive index of the second medium (see Fig. 1).

This simple rule, Eq. (1), is also responsible of the polarization behavior associated to the reflected and the transmitted light and is the core of several optical techniques. Other important derivations are associated to the chromatic response of the medium with the incident wavelength.

When light is incident at the critical angle, all the transmitted light travels through the interface, and if this angle is increased, all the light is reflected. This situation occurs when

$$\begin{aligned} &n_i > n_t \quad \text{and} \quad \theta_t = 90^\circ, \\ &\theta_i \equiv \theta_c \quad \Rightarrow n_t = n_i \sin\theta_i \end{aligned} \tag{2}$$

The transmission of light through waveguides and optical fibers is possible due to this principle. The Abbe refractometry is also another technique based in the critical incidence angle, used to measure an unknown refractive index [6], where an index-matching medium is employed as the reference. This method, even when precise, has some important limitations like the requirement of having a plane-polished face and an opposite-side rough-polished for the sample. This makes the technique invasive. It requires also of a matching liquid, and the measurement depends greatly of the user eye's sensitivity (when a telescope configuration is employed). This technique is considered into the Official Mexican Norm [5] to measure the refractive index of amber from Chiapas.

If un-polarized light is incident at the Brewster angle, only the perpendicular components of the electric field are reflected, and the beam transmitted is partially polarized. Several optical devices are based in this principle to generate linearly polarized light. The determination of the refractive index through the angle of Brewster is an easy, accessible, and precise technique. For a linearly polarized light parallel to the plane of incidence, incident at the polarization or Brewster angle, the refractive index is derived directly from Eq. (1):

$$\begin{aligned} &n_i < n_t \quad \text{and} \quad \theta_i + \theta_t = 90^\circ, \\ &\theta_i \equiv \theta_B \Rightarrow n_t = n_i \tan\theta_B \end{aligned} \tag{3}$$

On the other hand, the fluorescence is originated when light of lower wavelength (higher energy), usually in the UV-region, is absorbed by some medium which re-emits at higher wavelengths (lower energies), usually in the VIS-IR regions [7]. Unlike phosphorescence, fluorescence occurs only when the stimulus that causes exist. That is, the disappearance of the irradiation, the issue disappears, since the process is extremely fast.

On the other hand, the Raman spectroscopy is a well-established optical technique, based in the molecular vibrations with the exciting incident wavelength. This phenomenon stems from the interaction of electromagnetic radiation with a deformable electron cloud. When a photon, whose energy is hν_0, from an external incident electromagnetic field interacts with a molecule, it is electrically polarized and oscillating dipole moments appear with different frequencies respect to the incident photon. During an inelastic impact of the photon with the molecule, the vibrational energy hν_v can change. Thus, the photons can be scattered with low (Stokes) or higher energies (anti-Stokes), according to the equation hν_d = hν_0± hν_v. A vibration is Raman active if the polarizability of the molecule change with the vibrational motion [8,9]. In a Raman spectrum the difference (hν_d -hν_0) is plotted and in many cases this signal is accompanied with the fluorescence signal of the same molecule, which is considered as a background noise. To reduce the fluorescence background in a Raman spectrum, exciting sources of greater wavelengths like the near infrared (NIR) are used; but for samples like a glass when are excited with a NIR wavelength, the fluorescence effect is very notorious. So this effect can be used to obtain great differences from true and false amber.

3. Equipment employed and results

The equipment employed to measure the refractive index through the critical angle, is an Abbe refractometer (Bausch & Lomb, Cat. No. 33 46 10), at a wavelength of 589 nm (according to the NOM requirements, one side of the samples was polished and the opposite was frosted). A value of n = 1.548 for amber of Chiapas, n = 1.558 for amber of Baltic, and n = 1.544 for false amber were obtained. The NOM considers a refractive index value of n = 1.552, measured using this technique.

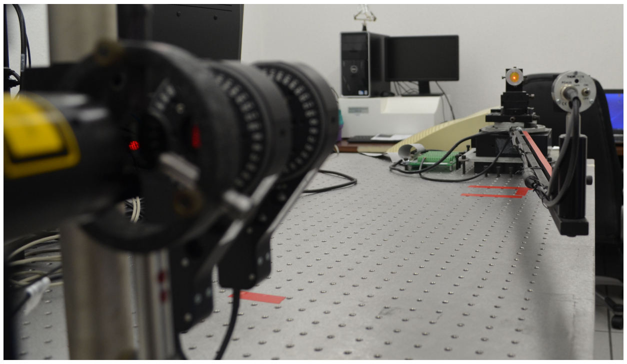

FIGURE 2. Angle resolved scattering used to determine the Brewster angle.

With the intention to suggest an easier and accessible technique, non-destructive with the samples (does not require any cut or to frost them), the refractive index by the Brewster angle was determined by the use of an Angle Resolved Scatterometer, where a He-Ne laser emitting at 632.8 nm and a linear polarizer with transmitting axis parallel to the incidence plane were employed to illuminate the samples (see Fig. 2).

A value of n = 1.539 was found for both, amber from Chiapas and amber of Baltic, and n = 1.510 for false amber.

In this work, the samples have been illuminated with a tunable Ar-laser at 457 nm, 488 nm, 514 nm, and multi-line outputs (Flexible, M-Stellar PRO, 150 mW) and the fluorescence generated was detected with a commercially available sensor (Ocean Optics, model USB4000). Figures 3a and 3b show the fluorescence spectra emitted by amber of Chiapas and amber of the Baltic, respectively, when they are excited by each of the four wavelengths available. Figure 3c shows the results obtained when the false amber is exposed to each of the four illuminating outputs from the tunable Ar-laser. The NOM [5] considers an excitation wavelength of 352 nm which generates a maximum in the fluorescence spectra at 463 nm (blue color).

Observe the maximum intensities of the fluorescence spectrum for amber of Chiapas occur around 525 nm (see Fig. 3.a) and for the amber of the Baltic regions, the maximum are located around 535 nm (see Fig. 3.b), for all the wavelengths considered here.

On the other hand, Fig. 3c shows there is not fluorescence spectrum for the false amber, for all the Ar-laser wavelengths employed here.

The maximum intensity peaks shown in Figs. 3 were normalized to a same value (the output power varies for each wavelength), they are associated to the incident wavelength. Note that if a broad spectrum source were employed, the incident signal would superpose to the fluorescent response.

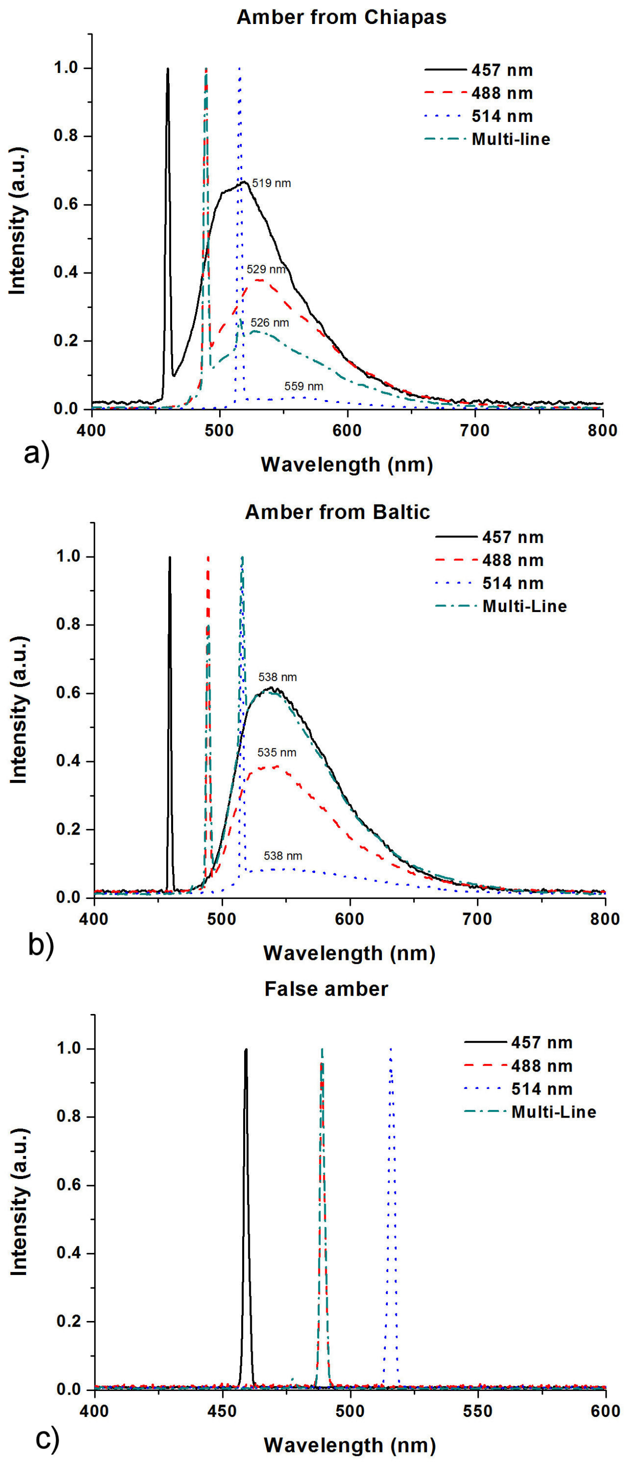

FIGURE 3. a) Fluorescence spectrum of amber of Chiapas illuminated at 457 nm, 488 nm, 514 nm, and multi-line outputs of a tunable Ar-laser. b) Fluorescence spectrum of amber of the Baltic region illuminated at 457 nm, 488 nm, 514 nm, and multi-line outputs of a tunable Ar-laser. c) Fluorescence spectrum of false amber illuminated at 457 nm, 488 nm, 514 nm, and multi-line outputs of a tunable Ar-laser.

Finally, the Raman spectra of the true and false amber samples were obtained, in the wave-number interval 200 to 1800 cm^{-1}, by using a Renishaw micro-Raman system 1000 equipment with a backscattering geometry. As excitation wavelength, the system has a diode laser emitting at 830 nm

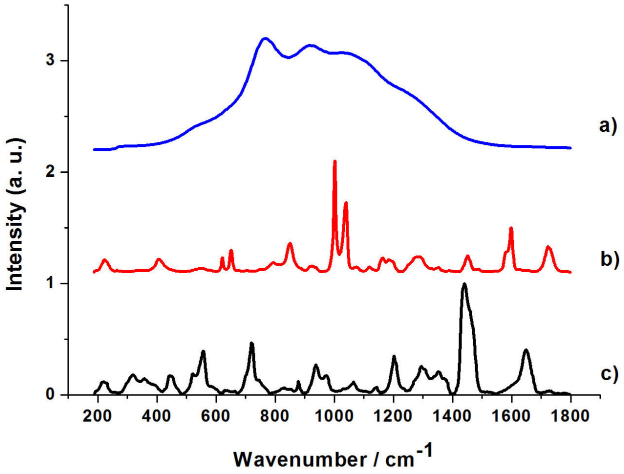

FIGURE 4. Raman spectra obtained for representative samples of a) false amber, b) amber of the Baltic, and c) amber of Chiapas.

(the laser power at the sample was about of 15 mW). The laser beam was focused onto the sample with a 50X microscope objective (Leica, model DMLM) with numerical aperture of 0.75. For this numerical aperture and wavelength, the cylindrical excitation volume has a diameter and length of about 7 μm and 187 μm, respectively. The amber samples were prepared with a basic cleaning to remove grease and dust from the sample's surface, using warm water, liquid detergent, and compressed air. Then they were placed on the microscope stage of the Raman system, in which the microscope objectives were used with dual purpose: to focus the laser on the surface of amber and, at the same time, collect the Raman signal. The spectra were obtained from several points of the surface sample and only representative spectra are reported. The calibration of the Raman system was performed using the 520 cm^{-1} Raman line of a silicon wafer. Figure 4 shows the results obtained for representative samples of false amber (Fig. 4.a), amber of the Baltic (Fig. 4.b), and amber of Chiapas (Fig. 4.c).

4. Discussion and conclusions

The refractive index for the amber of Chiapas, according to the NOM [5] is 1.552, and the values obtained here are 1.548 (Abbe refractometer, at 589 nm) and 1.539 (obtained through the Brewster angle, at 632.8 nm). These results are experimentally consistent, even when they are determined by different wavelengths. The refractive index for the amber of the Baltic is 1.558 when the Abbe refractometer is used and 1.539 when the Brewster angle is determined. Observe the refractive index does not distinguish clearly between the amber of Chiapas and the amber of the Baltic regions. The refractive indexes obtained for the false amber were 1.544 and 1.510, respectively; these values can also be obtained for the pyrex glass. Taking into account the experimental errors associated to these techniques (±0.00025 for the Abbe refractometer and ±0.029 for the ARS setup employed here), but mainly to the fact that the false ambers are made from plastics or glasses, which have a broad range of refractive index values, ranging from (1.510-1.670), the refractive index is not a reliable parameter to discriminate true from false amber. The oligoclase minerals have a refractive index of 1.552, a similar visual aspect with the amber, and also present fluorescence.

On the other hand, even when the samples under test were illuminated with higher wavelengths than the considered in the NOM, figures 3a and 3b shows the fluorescence spectra associated to amber of Chiapas and amber of the Baltic, respectively, are notably different from the fluorescence spectrum associated to the false amber (Fig. 3c). This proof must be realized carefully, because if the samples are illuminated with a broad spectrum source, it is added to the response spectra and this technique could fail to distinguish the true from the false amber. Glasses, resins and plastics can be easily doped with colorants and nano-particles, which could have a similar fluorescent behavior as the true amber. In this sense this technique is also a vulnerable test.

Finally, Fig. 4 shows a drastic difference between the Raman spectrum of amber of Chiapas and the false amber. The broad bands in the false amber spectrum are characteristic for a glass sample when it is being excited with a near infrared wavelength that, in this case, was of 830 nm. It also shows there are common Raman bands to both amber samples, even when this technique can distinguish one of the other.

We can conclude by saying that we have measured the refractive index of samples of amber of Chiapas, amber of the Baltic regions, and false amber by searching three different optical responses. Even when the optical response depends on the wavelength used to illuminate the samples, results show similar values can be obtained for the amber of Chiapas and the false amber, indicating the refractive index is not a reliable criterion to distinguish one from the other. The fluorescence spectrum can be a reliable test but only if it is used at the appropriate exciting wavelengths to avoid superposition of the illuminating light with the emission signal (respecting the procedure indicated in the NOM). However, this is a test that can be violated easily by using doped artificial resins, glasses or plastics with fluorescent colorants. The most important result, is the evidence that the Raman spectroscopy can distinguish the amber of Chiapas from false amber and from amber of the Baltic regions. We suggest the Raman spectroscopy be incorporated to the Official Mexican Norm, NOM-152-SCFI-2003 as a reliable test for the amber of Chiapas.

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