



A SPECTROSCOPIC INVESTIGATION OF ORPIMENT (YELLOW ARSENIC), USED AS A DEPILATORY

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Research Article

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ABSTRACT

Orpiment another name yellow arsenic, known as bath grass in public, is a sulfide mineral. Anciently, orpiment was evaluated as a pigment and dye in arts and industry for painting dolls and toys, and still is widely used as a depilatory. It is known that the bath grass (orpiment) used for depilatory, involve arsenic, may has a toxic effect on human health. In this study, we aimed to analyze the sample obtained commercially in order to see whether there can be a toxicity effect or not. Several spectroscopic techniques (Electron paramagnetic resonance, X-ray diffraction, Fourier-transform infrared spectrophotometer, Scanning electron microscopy-Energy dispersive spectroscopy) were applied to the sample and obtained results were evaluated in detail.

Keywords: Orpiment, arsenic, spectroscopic techniques, depilatory.

ÖZET

Diğer bir adla sarı arsenik, halk arasında hamam otu olarak bilinen orpiment, bir sülfid mineralidir. Eskiden, orpiment, sanatta ve endüstride bebekleri ve oyuncakları boyamak için bir pigment ve boya olarak değerlendirildi ve hala yaygın olarak tüy dökücü olarak kullanılıyor. Epilasyon için kullanılan, arsenik içeren hamam otunun (orpiment) insan sağlığı üzerinde toksik etkiye sahip olabildiği bilinmektedir. Bu çalışmada, toksisite etkisi olup olmadığını görmek için ticari olarak elde edilen numuneyi analiz etmeyi amaçladık. Numuneye çeşitli spektroskopik teknikler (Elektron paramanyetik rezonans, X-ışını kırınımı, Fourier dönüşümlü kızılötesi spektrofotometre, Taramalı elektron mikroskobu-Enerji dağılımlı spektroskopisi) uygulanmış ve elde edilen sonuçlar detaylı olarak değerlendirilmiştir.

Anahtar Kelimeler: Orpiment; arsenic; spektroskopik teknikler; tüy dökücü.

1. INTRODUCTION

Two of the sulfur sprouts of arsenic in nature are realgar and orpiment. Orpiment which is also known as yellow arsenic is a sulfide mineral with the formula As_2S_3 . It is found in volcanic regions and hot springs. Orpiment, due to its golden color, was used in ancient times as a pigment and dye, and is still commonly used in the worldwide, which is known as bath grass in public, as a depilatory. Hair removal agents containing arsenic are produced under unsuitable conditions. Depilatory agents consist mainly of 25% arsenic sulfide. If the material interacts with water, arsine and arsenic acid, which have the toxicity effect, are produced (Ozakın et al., 2013). In previous years, orpiment composed the most of depilatory mixtures, but in recent years the toxic arsenic compounds have been changed by alkali or alkaline earth sulphides (Murrer, 1938). One of these sulphides used for depilatory is BaSO_4 (Lev, 2010). “Yellow arsenic” or orpiment is also used commonly in Arabic pharmacology and medicine (Levey, 1973). In addition to the medicinal features of orpiment, its toxicity was also familiar (Arantegui et al., 2011).

In this study, we aim to investigate the yellow arsenic (orpiment) by determining the elemental composition, magnetic and structural properties. For this purpose, we used electron paramagnetic resonance (EPR) technique to see the paramagnetic features of the sample. X-ray diffraction (XRD) was performed to determine the crystalline property. Functional groups and the state of the bonds in the structure were seen by Fourier-transform infrared spectrophotometer (FTIR). Scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) results were obtained for understood the surface morphology and elemental composition. To the best of our knowledge, any report about the application of spectroscopic techniques to yellow arsenic used for depilatory has been given by previous studies. It will be important to learn about the structure, which is widely used as a hair removal agent, in terms of toxicity effect.

2. MATERIAL AND METHODS

Yellow arsenic (orpiment) in the powder form was purchased commercially from an herbalist. An X-band JEOL JESFA-300 EPR spectrometer with 100 kHz modulation field and ≈ 9.20 GHz frequency was operated for EPR spectrum of the sample taken at room temperature. The XRD spectrum of the sample was recorded by BRUKER D8 ADVANCE XRD, used at 40 kV and 40 mA with a scanning speed of $2.5^\circ/\text{min}$. Cu K- α radiation of wavelength $\lambda = 1.54060 \text{ \AA}$ was used and

results were obtained for the 2Θ range of 3° - 90° . The scanning electron microscope photographs and EDS results of the sample were taken by JEOL JSM-6610 SEM spectrometer. Bruker VERTEX 70v system was used for the FT-IR analysis.

3. RESULTS AND DISCUSSION

EPR is a specific and significant technique that enables to detect free radicals and paramagnetic centers containing unpaired electrons in the presence of an external magnetic field (Aygun, 2019). From the scanned EPR spectrum, obtained EPR lines are recognized by g values, where g is a unitless constant that is a typical property of the studied sample. These g values are determined by the equation $h\nu = g\beta H$, where H the magnetic field, ν the microwave frequency, h the Planck constant and β the electron Bohr magneton.

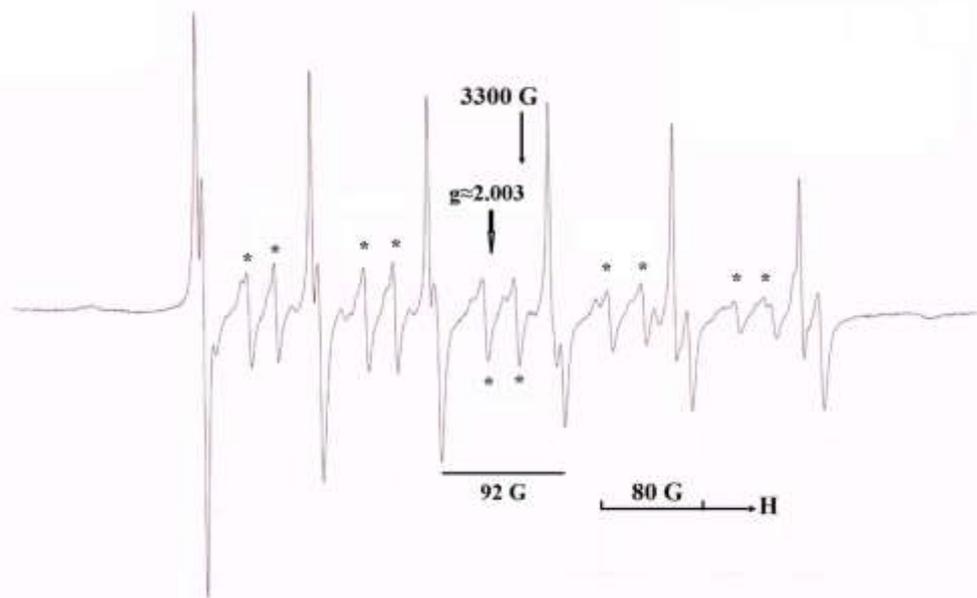


Fig. 1. EPR spectrum of the sample scanned at room temperature.

EPR spectrum obtained by room temperature EPR experiment is given in Figure 1. We have observed EPR lines with $g \approx 2.003$ and ≈ 92 G line width attributed to Mn ($I = 5/2$) six hyperfine lines. These sextet lines have been associated with the allowed transitions ($\Delta m_s = \pm 1$, $\Delta m_l = 0$). We have also seen five weak doublets (indicated with asterix) of Mn ($\Delta m_l = \pm 1$), forbidden transition lines, between main six peaks (Aygun and Yarbasi, 2019). This kind of Mn spectrum obtained by EPR has been related to the lower Mn concentration, due to the lower dipole-dipole interaction.

XRD pattern obtained by room temperature XRD experiment has been shown in Figure 2. XRD result with sharp peaks clearly shows the crystalline property of the sample. It can be said that the

sharp and clear peaks may be related to bigger crystallite size. The most intense peak centered at $\approx 29^\circ$ has been assigned as calcite (CaCO_3) (Aygun, 2017). Barium and barium sulfate peaks labeled at $\approx 23^\circ$, 40° , 43.5° , 58° , 65° were also seen in previous studies (Bafghi, 2011; Dera et al., 2017). Peak observed at $\approx 18^\circ$ can be assigned as Mn_3O_4 (Ramachandran et al., 2018). We can also observe Si and Ti peaks as seen in Figure 2 (Hossain et al., 2018).

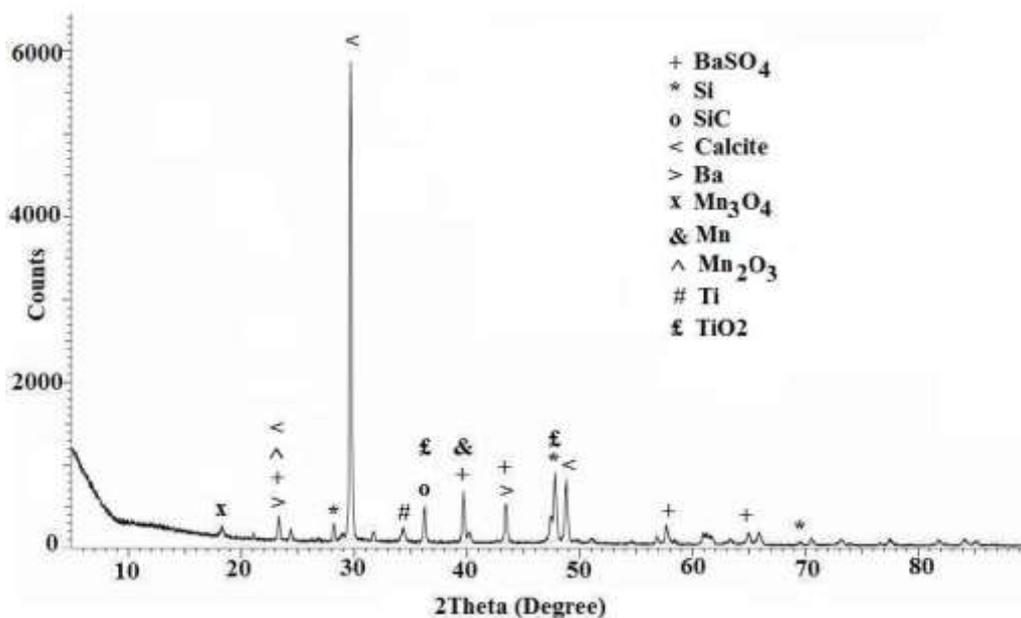


Fig. 2. Room temperature XRD spectrum of the sample.

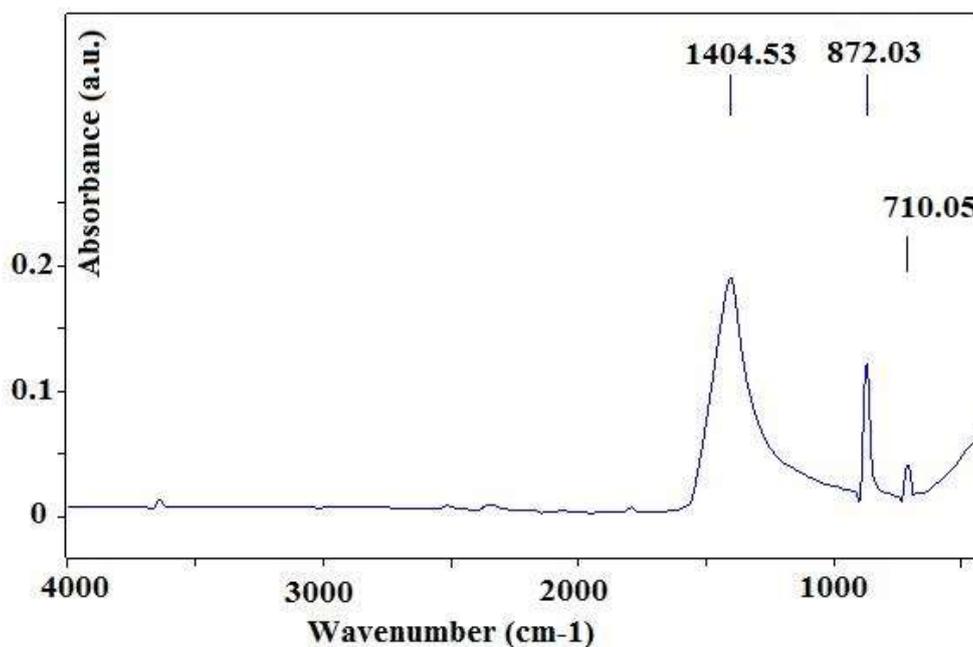


Fig. 3. FTIR spectrum of the sample taken at room temperature.

Room temperature FTIR spectrum has been given in Figure 3. According to the obtained spectrum, we are able to say that the bands at $\approx 1404\text{ cm}^{-1}$, 872 cm^{-1} , and 710 cm^{-1} have been associated with asymmetric C-O stretch and C-O out-of-plane and C-O in-plane bends in the CO_3^{2-} , respectively (Vahur et al., 2016). As stated in a previous research by Hodson et al., (2016), the recorded spectrum is a typical FTIR spectrum of a crystalline calcium carbonate (calcite).

Room temperature SEM images of the sample have been shown in Figure 4. The microcrystalline structure has been obviously seen from the photographs. Evaluation of the obtained surface morphology by SEM in conjunction with the observed XRD peaks, a compatible result can be achieved regarding the crystallite size. EDS results have been obtained at room temperature and given in Figure 5. We can see the Ba, S, Ca, C, O, Si, Ti, Mg elements in the spectrum, but the Mn element has not been obtained by EDS unlike by the EPR technique. This may be a result of the device's limitations about the element's amount. Also, we could not detect any arsenic by EDS.

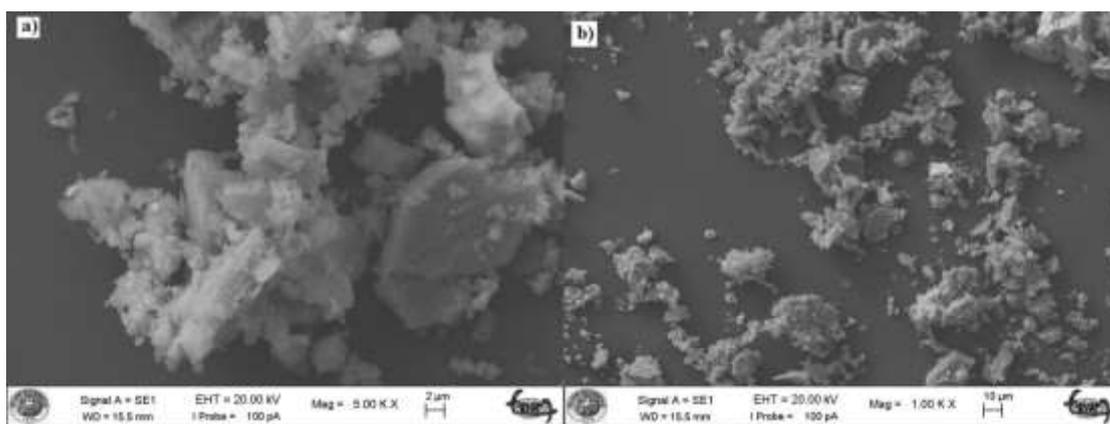


Fig. 4. SEM images of the sample taken at room temperature.

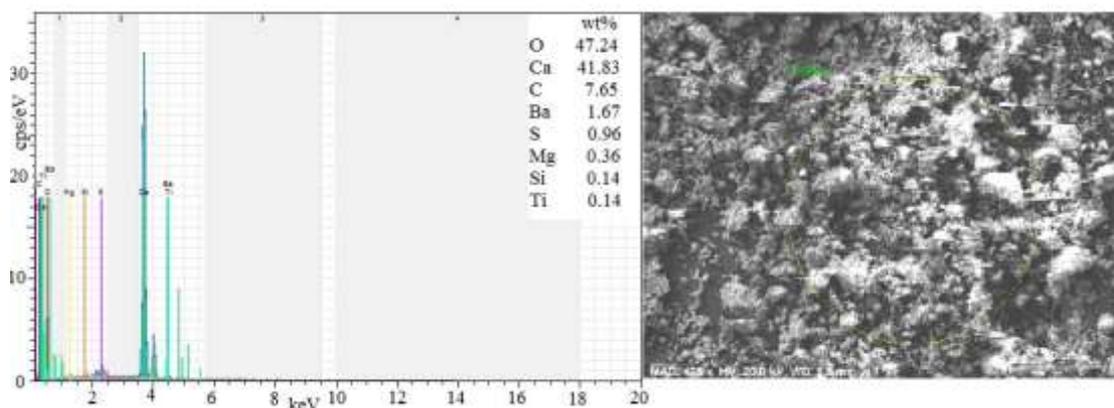


Fig. 5. Room temperature EDS pattern of the sample.

4. CONCLUSIONS

In the present study, we investigated yellow arsenic, in other name orpiment or known as bath grass in public. This sample is widely used as depilatory or medicinal in the world, especially in Arabic countries. There is also a common knowledge about the toxicity effect of the sample. Because of this, we interested in the structural and magnetic properties of the structure obtained commercially. For this purpose, EPR, XRD, EDS, FTIR and SEM analysis of the sample were carried out. According to the obtained results, arsenic was not determined by spectrometers. This may be because of the lower amount of the arsenic or as mentioned in previous studies alkali sulfates may be used instead of arsenic. For our examined sample, barium sulfate was detected by spectroscopic methods. It may be concluded that the toxicity effect of the arsenic can be removed by using barium sulfate content.

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Conflicts of interest

The authors declare that there are no potential conflicts of interest relevant to this article.

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