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Characterization of a hazardous eyeliner (kohl) by confocal Raman microscopy

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Abstract

A new method of analyzing kohl, a cosmetic eyeliner, using confocal Raman microscopy is reported. This technique offers an important alternative to conventional spectroscopic techniques that provide elemental/atomic composition. Raman spectra of three kohl samples have been measured between 150 and 3000 cm^{-1} at room temperature. The main component of two kohl samples was found to be lead(II) sulfide (PbS). Kohl is used as a traditional cosmetic and remedy in the Middle East, Far East, and Northern Africa. Since kohl products contain very high concentrations of lead, they constitute a risk for public health, particularly for children.

Keywords: Confocal Raman microscopy; Kohl; Lead(II) sulfide; Toxicity; Antimony(III) sulfide

1. Introduction

Kohl (from the Arabic kuhl, kohhel, kohol, and cohol) is a traditional eyeliner which has been widely used as an eye cosmetic in the Middle East, Far East, and Northern Africa [1]. It is both used for beautification and as a traditional ethnic remedy to relieve eyestrain, pain, or soreness. In addition, kohl is known to prevent sun glare, thus it was used by Bedouins in the Arab Peninsula. Previous studies [2–4] have shown that kohl contains toxic heavy metals, such as lead, and case studies have revealed that blood levels were significantly higher in individuals who used kohl compared to ones who did not. It was also shown that blood levels in infants of kohl using mothers were considerably higher than those of non-kohl using mothers (5.2 μg/dl versus 2.8 μg/dl) [5].

In this study, the presence of lead(II) sulfide (PbS) or galena in kohl samples will be tested using confocal Raman spectroscopy. Of the techniques [2,3], such as energy dispersive X-ray analysis (EDAX) and X-ray powder diffraction (XRPD) that have been used to characterize the chemical content of kohl, many require the introduction of vacuum and energy (high excitation source), thus modifying the sample to be analyzed. In contrast, Raman spectroscopy is non-destructive and may be performed under ambient conditions. Furthermore, the molecular vibrational signatures obtained for a Raman spectrum are very sensitive to chemical structure and bonding, rather than just atomic composition. PbS is a relatively weak Raman scatterer at room temperature as it has high absorptivity and is therefore susceptible to laser-induced degradation when intensely irradiated. Previous studies have applied conventional Raman spectroscopy [6] and not confocal Raman spectroscopy to analyze PbS. The advantages of confocal Raman microscopy over conventional Raman spectroscopy can be summarized as follows: both axial and lateral resolutions are improved; stray light is rejected, so only the desired Raman signal is passed to the detector; finally and most importantly, confocal Raman microscopy exhibits superior rejection of fluorescence. Among the studies that successfully accessed portions of the Raman spectrum of

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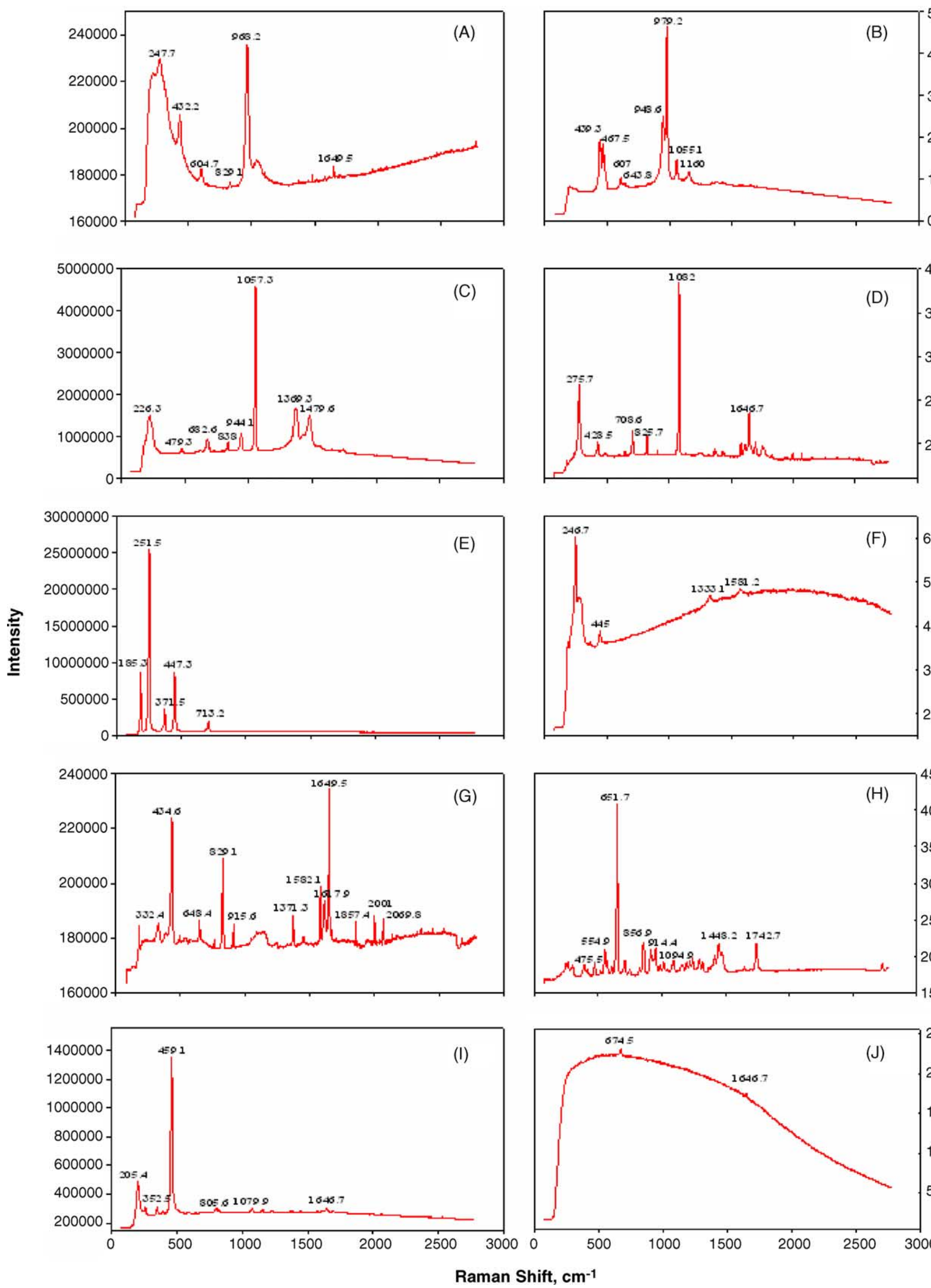

Fig. 1. Raman spectra of (A) lead(II) sulfide, (B) lead(II) sulfate, (C) lead(II) carbonate, (D) calcium carbonate, (E) antimony(III) oxide, (F) antimony(III) sulfide, (G) zinc oxide, (H) camphor, and (I) silicon dioxide.

PbS, differences existed regarding the number of vibrational bands claimed to be observed [7–9].

2. Methods and material

2.1. Samples

Three samples of kohl were obtained from local herbalists in the United Arab Emirates markets. Two of these samples were manufactured in India and the third was a Pakistani product. High purity powders including lead(II) sulfide (+99.9%), lead(II) sulfate (98%), lead(II) carbonate (+99%), antimony(III) sulfide, antimony(III) oxide (<5 μm), calcium carbonate (+99.9%), copper(I) oxide anhydrous (99%), talc (350 mesh), camphor (96%), zinc oxide (nano powder), and sand (white quartz 70 mesh) were obtained from Sigma–Aldrich (USA).

2.2. Instrumentation

Raman spectra of the samples were collected using confocal Raman spectroscopy. The sample was globally illuminated by a 20 mW helium neon (He–Ne) laser operating at 632.5 nm with only 5 mW reaching the sample field of view. The laser radiation is focused on the sample by means of a high-power ×10 microscope objective after passing through a narrow band-pass filter (BPF). The BPF has a transmission of 84% for laser radiation. The BPF reflects the Raman scattered light (reflection coefficient >98% in the spectral interval 150–3000 cm^{-1}). The light is focused in the image plane of the microscope objective, where a pinhole is positioned in order to suppress the fluorescence from out-of-focus regions of the sample under study. Finally, the signal is detected by a liquid nitrogen charge coupled device (CCD). The resolution is 0.45 ± 0.05 μm in the lateral direction and 1.3 ± 0.1 μm in the axial direction. The signal integration time was 2 s taken 400 times in order to improve the signal-to-noise ratio.

3. Results and discussion

Raman spectra of the high purity chemical powders and the three kohl samples (sample one, sample two, and sample three) collected using the confocal Raman microscopy, are shown in Figs. 1–4, respectively. The spectra of the reference powders will help in identifying the chemical compounds present in the kohl samples, since a recent study [3] showed using XRPD and EDAX that kohl might contain these chemical powders shown in Fig. 1. Raman peaks corresponding to phonons from sample one (Indian made kohl) shown in Fig. 2 appearing at 967.1, 830.2, 605.5, 432.1, and 234.5 cm^{-1} are evident. Comparison of the spectra of pure PbS (Fig. 1A) and sample one clearly demonstrates the similarity of both spectra and indicates that the main chemical compound present in sample one is PbS. Raman spectrum of sample two

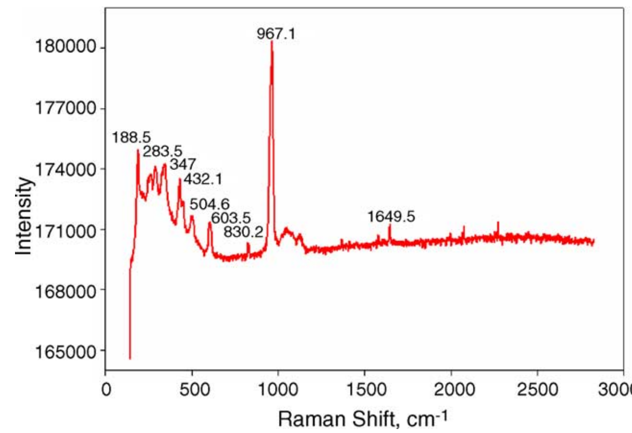

Fig. 2. Raman spectrum of sample one of kohl.

(Indian made kohl) is shown in Fig. 3 with peaks appearing at 1368.9, 1056, 966.3, 826.3, 606.7, and 434 cm^{-1}. It can be concluded that sample two is made up of both PbS and lead(II) carbonate ($PbCO_3$) since the observed peaks in sample two spectrum at 966.3, 826.3, 606.7, and 434 cm^{-1} can be assigned to pure PbS (Fig. 1A) and the ones appearing at 1368.9 and 1056 cm^{-1} can be assigned to pure $PbCO_3$ (Fig. 1C). The Raman spectrum of sample three (Pakistani made kohl) showed the absence of lead based chemical compounds with sharp features appearing at 1322.7 and 1597.1 cm^{-1}. The observed peaks can be assigned to pure micro-crystalline graphitic carbon and is confirmed by Nemanich et al. [10] and Knight and White [11] who both characterized carbon bonding in diamond and diamond-like thin films using Raman spectroscopy. Thus, sample three is an amorphous carbon/carbon (in an amorphous organic compound) based kohl. The three samples were also analyzed for total lead content using atomic absorption spectroscopy (AAS) and the results corroborated the findings obtained using the confocal Raman microscopy where both samples one and two contained lead (>85% total Pb content) and sample three did not (0% total Pb content) (data is not shown).

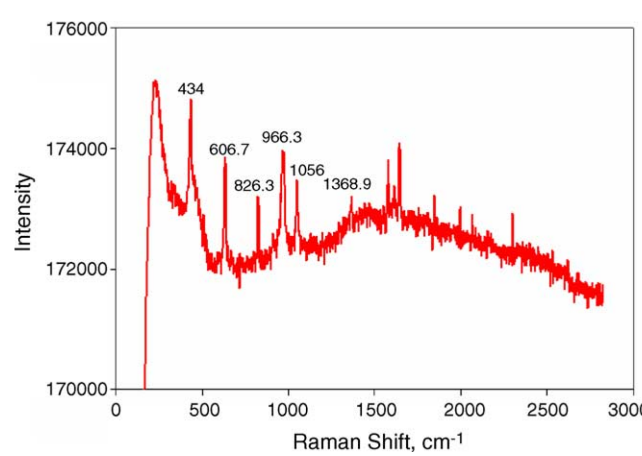

Fig. 3. Raman spectrum of sample two of kohl.

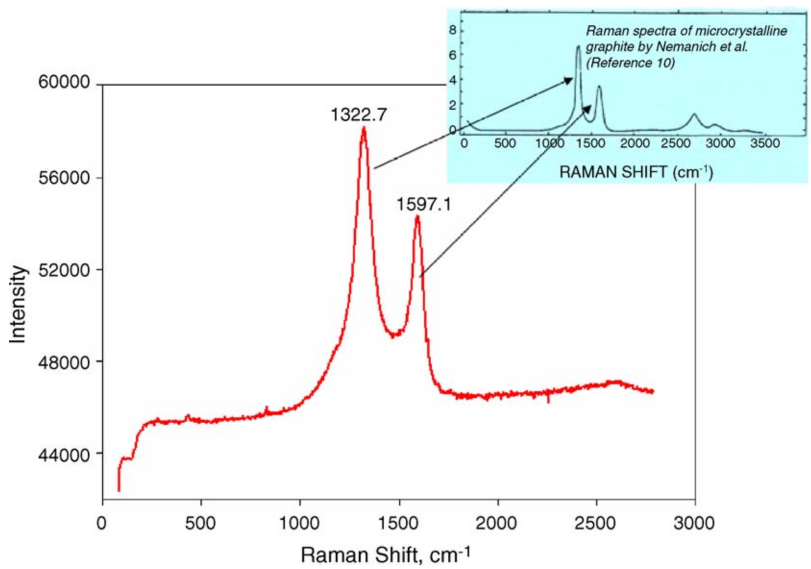

Fig. 4. Raman spectrum of sample three of kohl.

It has been known for centuries that most brands of kohl are made of antimony(III) sulfide (Sb_2S_3) (ethmid). This form of kohl was prepared by grinding ethmid stone. Antimony (Sb) ores are found in nature in the form of stibnite or antimonite composed of antimony(II) and antimony(III) oxide (SbO and Sb_2O_3) with traces of copper(II), silver, and lead sulfide [12,13]. Unfortunately, due to the expense and scarcity of Sb_2S_3, PbS having similar properties and cosmetic appeal was used instead in preparation of kohl. Raman spectra for both Sb_2O_3 and Sb_2S_3 are shown in Fig. 1E and F, respectively. Published studies showed that Sb_2S_3 is relatively benign when it comes to human toxicity [14]. On the other hand, lead compounds are very toxic and can be introduced into the body by ingestion, inhalation, and by skin exposure. Kohls with high lead concentration are frequently used by women as an eyeliner and also applied as an eyeliner and as a skin treatment product on infants. Higher blood lead levels in kohl using infants and in infants of kohl using mothers have been reported (5.2 μg/dl versus 2.8 μg/dl) [5] and blood lead levels in children that are greater than 10 μg/dl are now considered abnormal [15]. Abnormal blood lead levels are considered unsafe and have been shown to be associated with intelligence quotient deficits, behavioral disorders, slowed growth, and impaired hearings [16,17].

4. Conclusion

Confocal Raman microscopy was used to characterize kohl either as an unsafe and hazardous eyeliner (lead based) or as a safe eyeliner (non-lead based); thus introducing a relatively inexpensive, a user friendly (no vacuum, no sample preparation, and no high energy), and a non-destructive spectroscopic technique in analyzing kohl samples. Kohl products containing high levels of lead have a high reputation among the population in this part of the world due to their supposed therapeutic and cosmetic qualities. Increasing awareness of their serious toxic implications seems to be the only reliable means of ending or at least reducing the practice of these dangerous customs especially when children are involved.

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