



Anal. Bioanal. Chem. Res., Vol. 9, No. 2, 183-190, April 2022.

Discrimination of Different Kinds of Iranian-made Kohl by Excitation-Emission Matrix Fluorescence Spectroscopy

Neda Chavoshi and Bahram Hemmateenejad*

Chemistry Department, Shiraz University, Shiraz, Iran

(Received 15 June 2021 Accepted 28 October 2021)

Kohl is a traditional eye cosmetic used as eyeliner in different parts of Iran. They have different natural sources such as oils, nuts and leaves, and so on. They possess different physical and chemical properties and, usually they have lead toxicity. The characterization of Kohl is evaluated as an important issue since it is directly affecting human health. So, in this study, kohl samples from various sources were characterized by different analytical methods such as scanning electron microscopy (SEM) and Energy-dispersive X-ray (EDX). Moreover, the sources of kohl samples were analyzed by three-dimensional (3-D) fluorescence spectroscopy. The fluorescence spectra of samples were evaluated by chemometrics methods to discriminate between different kohl sources. Principal component analyses (PCA) as unsupervised and extended canonical variates analysis (ECVA) as supervised classification methods were employed. PCA made relative discrimination between the various kohl samples and could only discriminate kohl stones from the others. Instead, more accurate classification results were achieved by ECVA and it represented sufficient ability for classification of all kohl samples. This study is the first study on Iranian-made kohl discrimination through 3-D fluorescence spectra and multivariate methods.

Keywords: Kohl, Excitation-Emission matrix fluorescence, Discriminant analysis

INTRODUCTION

Ancient civilizations adorned their eyes with colorful compounds [1]. One of the traditional eye cosmetics is kohl that is widely used in different parts of the world since 500 BC [2]. It is an ophthalmology and ophthalmic product known as surmah in Iran, kohl or cohol in Arabic countries, kajal in India and tiro in Nigeria. Moreover, kohl has been used for the prophylaxis and treatment of eye diseases such as blepharitis, trachoma, chalazion, pterygium, and cataract [3,4]. It is typically prepared from natural substances and ore in many cities of Iran and can be purchased as a powder and solid rock. In general, there are two main types of kohl: soot and minerals [4,5]. Studies have shown that kohl contains toxic heavy metals, such as lead and to be a potential source of lead toxicity in children and women [6-9]. Lead as a highly toxic metal can affect the brain, kidneys, bone marrow, and other body systems; high levels

cause convulsions, coma or, even death [10]. Food and Drug Administration (FDA) has announced the minimum permissible limit for heavy metals to be used in cosmetic products *e.g.* lead must be less than 20 ppm [11]. Therefore, analysis and investigation of cosmetic products especially kohl samples have drawn attention in recent years. Adulteration of kohl products is also an important issue for consumers such as using expensive raw materials and the replacement of high-cost ingredients with cheaper substitutes.

In previous researches, the analytical methods such as acid digestion (EPA 3050B) [5], X-ray powder diffraction (XRPD), electron microscopy (SEM) [1], energy-dispersive X-ray (EDX) microanalysis [4], atomic absorption spectrophotometer (AAS) [12,13], Laser-induced breakdown spectroscopy (LIBS) [14], confocal Raman microscopy [15] and high performance liquid chromatography (HPLC) [16] have been used for analyzing kohl samples. Among different analytical methods, fluorescence spectroscopy is a rapid, sensitive, and non-

Corresponding author. E-mail: hemmatb@sums.ac.ir

destructive analytical technique that can be used as a fingerprint. It is also simple concerning instrumentation, possesses high optical information, and benefits from ease of operation. Between various fluorescence techniques, 3-D fluorescence excitation-emission matrix (EEM) obtains more information about the fluorescent species present in the sample [17-19]. Because of spectral overlapping, EEM fluorescence spectroscopy should be combined with chemometrics tools (multivariate statistics) to extract the fingerprint of the analytes or properties from the total signals [20,21].

Among the numerous chemometrics tools, pattern recognition methods have found prevalent applications. The most commonly used pattern recognition technique is principal component analysis (PCA), which extracts the classifier features (called principal components; PCs) from data to visualize the data and show the clustering pattern of various groups of samples [21-23]. Extended canonical variates analysis (ECVA) is a supervised classification method, which maximizes the differences between classes and minimizes the differences within known classes concurrently. ECVA was used for spectroscopic data in which the number of variables is larger than the number of samples significantly [24].

Because of the importance of cosmetic products especially kohl in daily life, some researches have been devoted to this product [1,3,5,9,10,14]. However, according to the best of our knowledge, characterizing and classification of Iranian-made kohl samples using 3-D fluorescence spectroscopy and chemometrics data analysis has not been reported. In the present research, we evaluated for the first time the potential of EEM fluorescence spectra using multivariate statistical methods to discriminate Iranian-made kohl samples. Towards reaching this aim, we used multivariate classification methods such as PCA and ECVA. Among these methods, all kohl samples were successfully classified by ECVA. Also, the chemical composition of Iranian-kohl samples was investigated by various analytical methods such as SEM and EDX.

MATERIALS AND METHOD

Synthesis of Iranian-made Kohl Samples

Three types of Iranian-made kohl (hazelnut kohl, bovine bone marrow oil kohl and butter oil kohl) and one type of

mineral stone kohl were used in this investigation. Mineral stone kohl is an inorganic compound; however, the others are based on organic compounds. The carbon-based kohl (CBK) was prepared in our lab and synthesized from incomplete combustion of hazelnut, butter oil, and bovine bone marrow oil. Hazelnut kohl was prepared by burning one medium size hazelnut to create black soot. For synthesizing butter oil and bovine bone marrow kohl, a 100.0 g portion of butter or bovine bone marrow oil was melted to become oily. Immediately, the cotton was used as wicker and the oil was poured on the cotton wool and burned. The black soot from burning hazelnut or oils was collected on a glass plate placed at 50 cm top of the flame. The soot was scraped out with a spatula and stored in sample tubes.

The inorganic kohl sample being a special stone comes from Mecca. It was provided from local shops in Shiraz (south of Iran).

Apparatus

All fluorescence spectra were recorded on an LS50B fluorescence spectrophotometer from Perkin-Elmer (Waltham, MA, USA) equipped with a thermostat water bath from Peco Company (Shiraz, Iran). The pH values were adjusted using a Metrohm pH-meter model 827 (Herisau Switzerland). Scanning electron microscopy (SEM) and Energy-dispersive X-Rays (EDX) analyses were carried out using VEGA 3-TESCAN (Brno, Czech Republic).

Fluorescence Measurements and Data Collection

A 0.12 g portion of each kohl sample was added to 5.0 ml NaOH (1 M), and the mixture was sonicated for 30 min. The smaller-sized particles were collected by centrifugation at 12000 rpm for 30 min. At that point, the solution was filtered with a 0.22 μ M syringe filter and the resulting solution was utilized for fluorescence measurements. The 3-D fluorescence spectra of four different types of kohl samples were collected with subsequent collecting of the emission spectra from 340-450 nm at 0.5 nm increments by varying the excitation wavelength from 240-320 nm at 10 nm increments. For these measurements, the widths of both excitation and emission slits were set to 5 nm. The scan rate was 500 nm min⁻¹.

Fluorescence measurements resulted in an excitation-emission matrix (EEM) sizing (220×9) for each kohl sample. Each treated EEM data was then unfolded into a vector (1×1980). Synthesizing of the organic kohl samples was repeated three times, and three samples of kohl stone were purchased from different shops. Finally, twelve kohl samples were utilized in this investigation. Therefore, the fluorescence responses can be represented as a data set matrix [$(3 \times 4) \times 1980$ wavelength]. Each row of the matrix represents excitation-emission fluorescence characteristics of each kohl sample. Since the kohl samples represented different fluorescence intensities and to ignore variations in source intensity among different samples, autoscaling to unit variance and zero mean was utilized as data preprocessing.

Data Analysis

The pre-processed data were submitted to advance chemometrics analysis such as PCA and ECVA. Data analyses were run in MATLAB (Mathwork, Inc., version 8) environment. The MATLAB Statistics Toolbox and the ECVA Toolbox, version 2.02, developed by the Technology and Quality Research Group at Copenhagen University (available at <http://www.models.life.ku.dk>) were utilized [25].

The employed chemometrics methods are the well-known methods in chemometrics literature but are briefly described below:

Principal Component Analysis (PCA) is one of the most common methods for pattern recognition and is widely utilized for data reduction [21,26]. As the result of PCA, the m -dimensional space of a matrix D can be reduced to a significantly lower-dimensional space including a few (*e.g. f*) latent variables or principal components (PCs):

$$D = TP' + E \quad (1)$$

Where T is the score matrix containing PCs in the direction of the samples, P is the loading matrix carrying in the direction of the wavenumbers and E is the residual matrix. The superscript ($'$) denotes matrix transpose. The calculated PCs represent the compressed information, demonstrating the fine difference in instrumental signal relating to various samples and being used for discrimination purposes [27,28].

Besides PCA, supervised classification methods use class markers and extract features from the data matrices that are covariate with the class markers. Fisher's discriminant analysis (known as linear discriminant analysis; LDA or canonical analysis; CVA) is a kind of supervised classification, in which a weight matrix is defined to minimize the ratio of within-class variances to the between-class variances [21]. LDA fails to give a stable model in the presence of colinear variables, especially when the number of variables is larger than the number of objects. ECVA is an extension of LDA, which uses partial least squares (PLS) as its inner modeling method [21,24,27] to handle collinearity among variables. So, ECVA can be considered as an ideal candidate for the analysis of spectroscopic data. Like other data modeling methods, in ECVA a calibration step is done using a training set with known classes (source) and it then is applied to predict samples with unknown sources. More theoretical details of ECVA can be found in the literature [29].

RESULTS AND DISCUSSION

Chemical Analysis of Iranian-made Kohl

The physical and chemical properties of different types of Iranian-made kohl were investigated by SEM and EDX. In addition, the Surface texture and morphology were affectedly studied by SEM (Fig. 1). In general; there are two types of Iranian-made kohl: (i) mineral base (mineral stone kohl) and (ii) amorphous carbon-based (hazelnut, bovine bone marrow oil, and butter oil kohl). As shown in SEM images (Fig. 1), the mineral base kohl has crystalline nature with a particle size of about 300 nm; however amorphous carbon-based kohl samples have fibrous nature with a particle size of about 60 nm. The results are shown that kohl samples mainly consist of particles sizing less than 1 μm . Furthermore, a portion of kohl samples were nanometer-size particles and they can adhere to the nail surface and easily absorbed into the human gut [4,30].

The EDX spectra over the scan regions are shown in Fig. 2. The organic-based kohls are mainly composed of carbon and oxygen. However, those made from hazelnut possess a significant amount of nitrogen. On the other hand, mineral-based kohl is composed of heavy metals such as

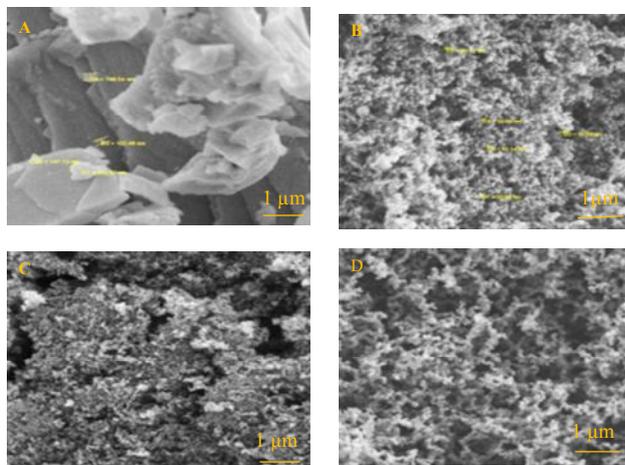


Fig. 1. SEM images of kohl samples of different sources observed at magnification ($\times 4000$): (A) mineral stone kohl, (B) Hazelnut kohl, (C) Bovine bone marrow oil kohl and (D) butter oil kohl.

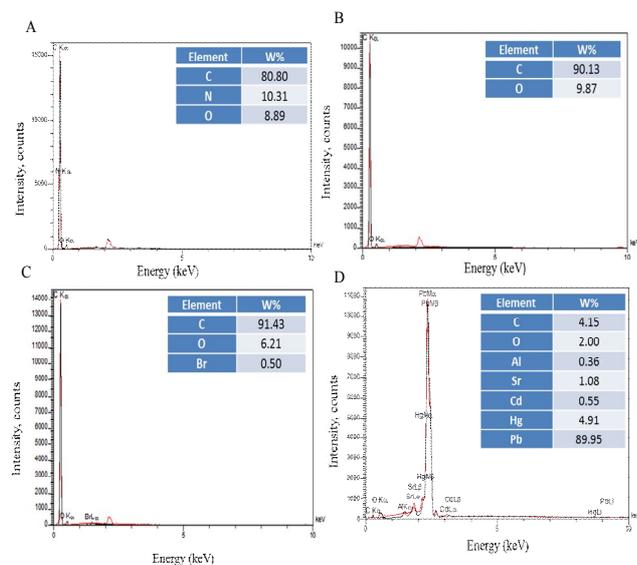


Fig. 2. EDX spectra of hazelnut kohl (A), butter oil kohl (B), Bovine bone marrow oil kohl (C) and mineral stone kohl (D)

lead, aluminum, cadmium, and mercury. The amount of Pb is significantly larger than carbon in this type of kohl sample. According to the World Health Organization [31], these heavy metals have developed the most public health concern [32]. The Federal Office of Consumer Protection and Food Safety (BVL) of Germany [33] suggested that the amount of lead, cadmium, and mercury in cosmetics should

be lower than $2.0 \mu\text{g g}^{-1}$, $0.1 \mu\text{g g}^{-1}$, and $0.1 \mu\text{g g}^{-1}$, respectively [33]. In this kohl, the amount of lead and other heavy metals are significantly higher than the allowed limit. So, mineral-based kohl samples are hazardous to health. Nanometer-size particles of lead-containing kohl samples may cause lead contamination in consumers (mostly women and children) in Iran. These results suggested that lead-containing kohl in this research is inhalable particles and harmful which may deposit in the respiratory system [30]. Consequently, more quality control on kohl products is required for the high level of toxic elements and their impact on the health of kohl users.

Although SEM and EDX analysis represent the best information about the chemical composition and morphology of different types of kohl samples, the additional information can be obtained by the inherent fluorescence property of kohl samples which can be monitored by fluorescence spectroscopy.

FTIR spectroscopy has also been previously used for the analysis of Kohl [2]. However, EEM has not yet been used. The advantages of using fluorescence are firstly its higher sensitivity than FT-IR. Secondly, in fluorescence spectroscopy, we just focused on the carbon dots content of the Kohl [34], which may be unique for each Kohl source. Whilst FT-IR can provide a distinctive signature it is not unique and may be affected by cross-contamination from different sources. We also tried using FT-IR (results not shown here). However, within-group variances were much larger than those obtained by fluorescence spectroscopy.

Evaluation of Fluorescence Spectra of Different Kohl Samples

The ability of fluorescence spectroscopy in combination with chemometrics data analysis for discrimination between different kohl samples was investigated. According to a previous search, the black soot of kohl has a carbon dot (CD) structure and fluorescence properties [30]. The 3-D fluorescence spectra of 12 samples of different sources were provided. The average EEM for different kohl samples is represented in Fig. 3. The kohl samples from hazelnut, bovine bone marrow oil, butter oil, and mineral stone have exhibited excitation/emission fluorescence maxima (E_x/E_m) at 250/450, 250/475, 250/430, and 240/440, respectively. The excitation wavelength of the mineral kohl sample is

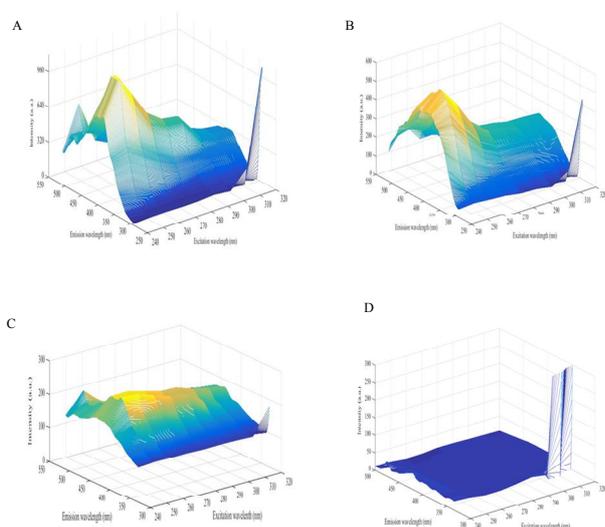


Fig. 3. Average EEM (three repeats) between $\lambda_{Ex} = 240$ -320 nm and $\lambda_{Em} = 290$ -500 nm of hazelnut kohl (A), butter oil kohl (B), Bovine bone marrow oil kohl (C) and mineral stone kohl (D).

significantly smaller than the organic kohl samples. On the other hand, the organic kohl samples share the same excitation wavelength whereas they differ in emission wavelength. As can be seen in Fig. 3, the highest and lowest fluorescence intensity was observed for hazelnut and the mineral kohl samples, respectively. The relative intensity and position of the peaks were varied by changing of kohl types. These differences were used to produce classification models that are used to identify different types of kohl. It should be noted that each emission spectrum is normalized before the application of chemometrics methods. It's typically used when ratios and spectral shapes are more applicable than quantitative measures in fluorescence spectroscopy [31]. After applying preprocessing methods, the data obtained by fluorescence analysis were analyzed by PCA as an unsupervised method and ECVA as a supervised method.

Unsupervised Cluster Analysis by PCA

PCA is a well-known method that reduces the dimensionality of the data matrix and provides the data structure that identifies grouping patterns [30]. The eigenvalues and the percent of variances explained by each eigenvector, obtained from the application of PCA are

summarized in Table 1. It shows that 95% of spectral information is retained when 1980-dimensional spectral space is projected into 3-dimensional space. The two and three-dimensional plots of principal components, which visualize the relative position of the kohl samples based on information included in their fluorescence spectra are given in Fig. 4. As can be seen, mineral stone kohl samples that were hazardous to health are discriminated from the others. It is clear from Fig. 4 that PCA has not shown good ability in the discrimination of whole kohl samples from different origins. This can be attributed to the high degree of similarity between their fluorescence spectra and hence more sophisticated methods may be required.

Table 2. Statistical Parameters (Cross-validation) of the ECVA Model Constructed for Kohl Samples

Kohl Source	Sensitivity	Specificity
Hazeknut	0.75	0.91
Butter oil	0.75	0.91
Bovin bone marrow	1.00	1.00
Mineral stone	1.00	1.00

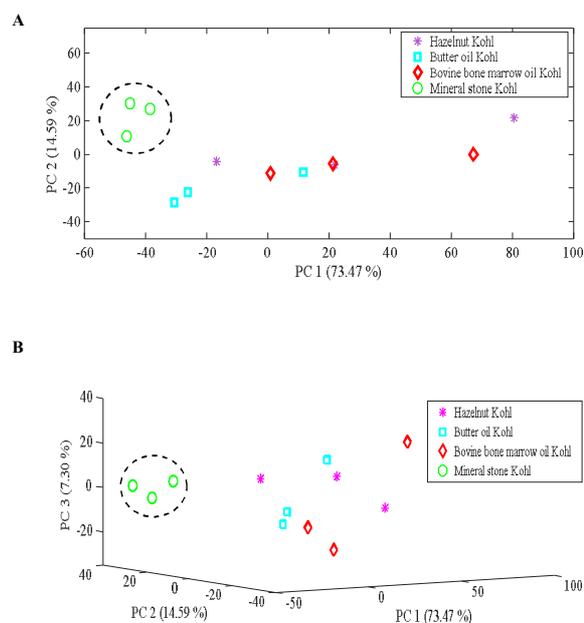


Fig. 4. Distribution pattern of the studied kohl samples in the (A) two-dimensional and (B) three-dimensional, PCA-based factor space of their fluorescence spectra.

Discrimination Using ECVA

Because of the weak results achieved by PCA for discrimination of all kohl samples, we decided to use ECVA that has the advantages of a supervised classification method [28]. Since four classes of kohl samples were investigated in this study, the ECVA solution can be abstracted into a three-dimensional model (one unit less than the number of classes) [30]. The method utilized leave-one-out cross-validation to refine the optimum number of PLS latent variables in the inner part of the ECVA and 4 number of latent variables were chosen as the optimum value. To check the feasibility of the application of ECVA, the values of canonical variates calculated for each sample in three-dimensional space are represented in Fig. 5. There is a clear separation between the 12 kohl samples of various sources in two and three-dimensional space of the canonical variates. However, organic kohl samples from hazelnut and bovine bone marrow oil are located close to each other.

To have quantitative classification performance, the class sensitivity (S_n) and class specificity (S_p) for the model have been calculated [28,31] and the results are given in Table 2. Sensitivity represents the ability of a given classifier to correctly identify the samples of the class, and specificity represents the ability of the classifier to reject samples of other classes [32]. According to the results, the organic kohl samples from butter oil and stone have the best classification parameters while those for the other kohl samples are not so high but are acceptable.

Figure 5 also shows the plot of the external test set samples in the canonical variate space. These samples were prepared according to the same procedure explained for the training samples but a long time later than them (after training the model). So, they did not play any role in the calculation of model coefficient during training of ECVA. Their canonical variates were calculated using the model coefficients calculated in the training step. As observed, all test samples, except 1 sample from stone mineral, could correctly assign to their native class. This confirms the high prediction ability of the model for analysis of future samples.

To show how the canonical variates contribute to the achieved discrimination, they were plotted individually in Fig. 6. The first variates help to discriminate the butter oil and mineral stone kohl samples from hazelnut and bovine

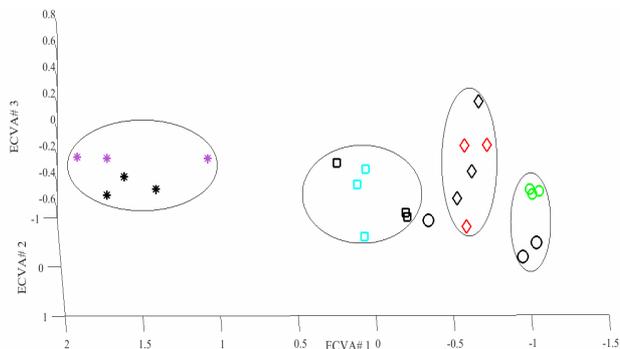


Fig. 5. Distribution pattern of the four different classes of Kohl samples in the three-dimensional plot of extended canonical variates: Hazelnut kohl (star marker), butter oil kohl (square markers), bovine bone marrow oil kohl (diamond markers) and mineral stone kohl (circle markers). The color markers denotes training samples and the black markers denote test samples.

Table 2. Statistical Parameters (Cross-validation) of the ECVA MModel Constructed for Kohl Samples

Kohl Source	Sensitivity	Specificity
Hazeknut	0.75	0.91
Butter oil	0.75	0.91
Bovin bone marrow	1.00	1.00
Mineral stone	1.00	1.00

bone marrow oil samples. The canonical variates in the second direction show obvious discrimination between kohl samples from butter oil and mineral stone kohl samples. The kohl samples from bovine bone marrow oil possess positive and negative variates in the first and second directions, respectively. On the other hand, discrimination between hazelnut and butter oil kohl samples can be achieved using the second and third canonical variates, where they possess positive and negative variates in the second and third directions, respectively.

CONCLUSIONS

The purpose of this study was the chemical analysis of

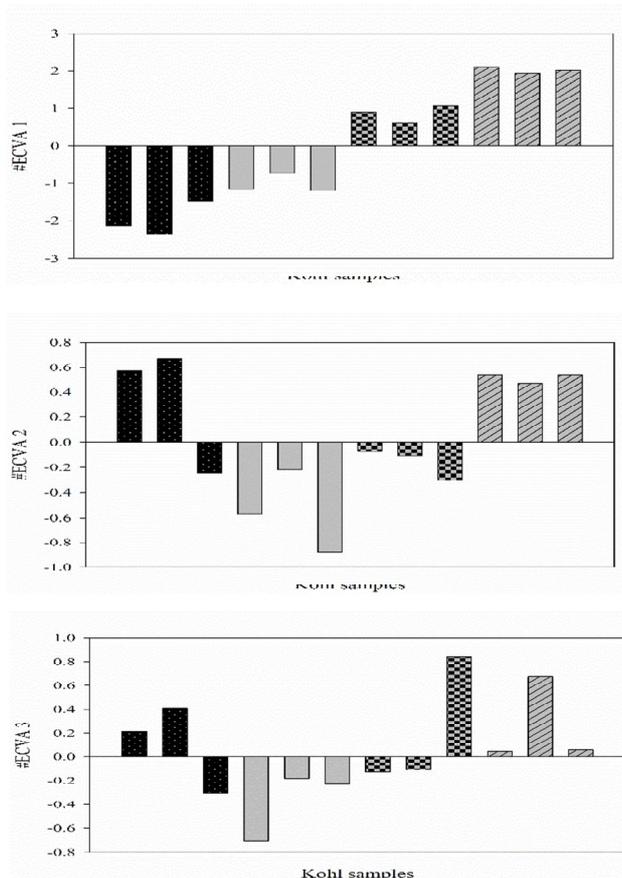


Fig. 6. The values of first, second and third extracted canonical variates for hazelnut kohl, butter oil kohl, Bovine bone marrow oil kohl and mineral stone kohl (from left to right).

four different types of Iranian-made kohl samples. The results show that kohl stone is hazardous to health because of the high levels of lead and other heavy metals. The 3-D fluorescence spectroscopy was studied as a reliable method for the discrimination of various kohl samples. PCA of the fluorescence spectral data does not represent any discrimination between the sources of kohl samples. However, high discrimination was obtained by ECVA. So all kohl samples used in this study have been correctly discriminated against based on their sources. It should be noted that there is insufficient knowledge about the content of kohl in Iran and there is no regulation in contents as cosmetic production. Accordingly, more quality control on commercial kohl is required because of the high levels of

toxic elements and their impact on the health of kohl users. For this goal, spectroscopy methods and chemometrics can be effective methods, and they will be improved public health and prevent possible intoxication of kohl users, so this study can be so effective for kohl consumers.

REFERENCES

- [1] A.D. Hardy, R. Vaishnav, S.S.Z. Alkharusi, H.H. Sutherland, M.A. Worthing, *J. Ethnopharmacol.* 60 (1998) 223.
- [2] V. Sharma, S. Bhardwaj, R. Kumar, *Vib. Spectrosc.* 101 (2019) 81.
- [3] P.H. Ullah, Z.A. Mahmood, M. Sualeh, S.M. Zoha, *Pak. J. Pharm. Sci.* 23 (2010) 48.
- [4] El. Shafey, I. El-Said, B.S. Al-Kitani, *Toxicol Environ. Chem.* 99 (2017) 233.
- [5] J.R. McMichael, B.K. Stoff, *Eur. J. Pediatr.* 177 (2018) 265.
- [6] S. Balarastaghi, Z. Khahaiarmanesh, P. Makhdoumi, H. Alavizadeh, Z. Sameie Mohadam, K. Shirani, Gh. Karimi, *Toxin Rev.* 37 (2018) 117.
- [7] O. Mehrpour, P. Karrari, M. Abdollahi, *DARU J. Pharm. Sci.* 20 (2012) 1.
- [8] A. Pourmand, T.K. Al-Tiae, M. Mazer-Amirshahi, *DARU J. Pharm. Sci.* 20 (2012) 70.
- [9] C. Parry, J. Eaton, *Environ. Health Perspect.* 94 (1991) 121.
- [10] Centers for Disease Control and Prevention (CDC), Infant Lead Poisoning Associated with Use of Tiro, an Eye Cosmetic from Nigeria-Boston, Massachusetts, 2011, *MMWR. Morbidity and Mortality Weekly Report.* 61 (2012) 574.
- [11] Y.H. Hui, *United States Food Laws, Regulations, and Standards*, John Wiley & Sons, California, 1979, pp. 1-168.
- [12] N. Lekouch, A. Sedki, A. Najmeddine, S. Gamon, *Sci. Total Environ.* 280 (2001) 39.
- [13] R.M. Al-Ashban, M. Aslam, A.H. Shah, *Public Health.* 118 (2004) 292.
- [14] A.F.M.Y. Haider, R.S. Lubna, K.M. Abedin, *J. Appl. Spectrosc.* 66 (2012) 420.
- [15] K.N. Jallad, H.G. Hedderich, *J. Hazard. Mater.* 124

- (2005) 236.
- [16] J.P. Jani, C.V. Raiyani, N.M. Desai, S.K. Kahyap, *Hum. Toxicol.* 7 (1988) 195.
- [17] Q. Zhuang, W. Cao, Y. Ni, Y. Wang, *Talanta* 185 (2018) 491.
- [18] J. SádeČká, J. TóThoVá, *Czech J. Food Sci.* 25 (2007) 159.
- [19] S. Heidari, B. Hemmateenejad, S. Yousefinejad, *J. Lumin.* 203 (2018) 90.
- [20] M. Casale, B. Basquini, M. Hooshiyari, S. Orlandini, E. Mustorgi, C. Malegori, F. Turrini, M. Cruz Ortiz, L.A. Sarabia, S. Furlanetto, *J. Pharm. Biomed. Anal.* 159 (2018) 311.
- [21] K. Javidnia, M. Parish, S. Karimi, B. Hemmateenejad, *SAA* 104 (2013) 175.
- [22] O.N. Tiwari, C. Devadoss, M. Pradhan, T. Nandy, *Int. J. Environ. Sci. Technol. (IJEST)* 14 (2017) 49.
- [23] B. Hemmateenejad, J. Tashkhourian, M.M. Bordbar, N. Mobaraki, *JICS* 14 (2017) 595.
- [24] M.M. Bordbar, J. Tashkhourian, B. Hemmateenejad, *Sens. Actuators B Chem.* 257 (2018) 783.
- [25] Y. Ma, D.Q. Huo, H. Qin, C.H. Shen, P. Yang, C.J. Hou, *J. Appl. Spectrosc.* 84 (2017) 361.
- [26] M. Mahboubifar, B. Hemmateenejad, S. Yousefinejad, *J. AOAC Int.* 100 (2017) 351.
- [27] B. Hemmateenejad, S. Dorostkar, *Energy & Fuels* 28 (2014) 761.
- [28] S. Yousefinejad, M. Bahram, T. Baheri, *JICS* 15 (2018) 163.
- [29] S. Yousefinejad, L. Aalizadeh, F. Honarasa, *Anal. Methods* 8 (2016) 4640.
- [30] L. Nørgaard, R. Bro, F. Westad, S.B. Sngelsen, *J. Chemom.* 20 (2006) 425.
- [31] A. Ikegami, M. Takagi, Z. Fatmi, Y. Kobayashi, M. Ohtsu, X. Cui, N. Mise, A. Mizuno, A. Sahito, A. Khoso, F. Kayama, *Environ. Pollut.* 218 (2016) 723.
- [32] F.A.O Joint, WHO Expert Committee on Food Additives, Additives, Safety Evaluation of Certain Food Additives and Contaminants, World Health Organization, Geneva, 2006.
- [33] WHO, International Travel and Health: Situation as on 1 January 2010. 2010: World Health Organization.
- [34] N. Chavoshi, B. Hemmateenejad, *J. Fluoresc.* 31 (2021) 455.
- [35] B.V.L Bund, *JCF.* 12 (2017) 51.
- [36] L. Nørgaard, G. Soletormos, N. Harrit, M. Albrechtsen, O. Olsen, D. Nielsen, K. Kampmann, R. Bro, *J. Chemom.* 21 (2007) 451.
- [37] A.C. Olivieri, *Principal Component Analysis, in Introduction to Multivariate Calibration*, Springer, 2018, pp. 57-71.
- [38] D.W. Sun, *Infrared Spectroscopy for Food Quality Analysis and Control*, Academic Press, 2009.