

Analysis of the Contents of Trace Elements by Inductively Coupled Plasma Atomic Emission Spectroscopy Combined with Chemometric Methods

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ABSTRACT: This study examines the use of inductively coupled plasma atomic emission spectroscopy (ICP-AES) combined with chemometric methods to determine the trace elements such as Al, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Ni, Na, Pb, Sr, Ti and Zn in Kohl samples. The method showed that Kohl exhibited a high lead concentration, indicating that the preparation of Kohl samples is lead sulfide instead of antimony sulfide. Multivariate statistical methods are used to improve our studies. The coefficients calculated for samples exhibited a positive correlation between the trace elements, Sr, Mn, Pb, Na, Fe, Cu, Ti, and Ba indicate a similar behavior of the elements. Also, a negative correlation among Cr, Ca, Ni, K, and Mg was shown. So, no correlation was shown by Zn and Al. In the same way, the principal component analysis shows three groups. The method developed has been successfully applied to the analysis of Kohl samples to give the behavior and relationships between variables.

KEYWORDS: Inductively Coupled plasma atomic emission spectroscopy; Chemometric methods, Kohl samples; Trace elements.

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INTRODUCTION

Moroccan Kohl is a traditional powder-prepared by crushing antimony sulfide, a mineral extracted from the mountainous rocks found in the Atlas, which can mix with other substances. This powder is available from herbalists and is used to treat eye disease and as an eyeliner. Nowadays, many studies have investigated that Kohl can present a health risk due to the presence of a high content of trace elements like lead [1–4].

Therefore, several analytical techniques including Atomic Absorption Spectroscopy (AAS) [5,6], X-ray Diffractometer (XRD) [7], Laser-Induced Breakdown Spectroscopy (LIBS) [8], X-Ray Fluorescence (XRF) Spectrometry and Scanning Electron Microscopy-Energy-Dispersive X-ray Spectroscopy (SEM-EDXS) [9–12], Inductively Coupled Plasma-Optically Emitting Spectra (ICP-OES) [13] and Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES) [14], were developed for the analysis of trace metals in different samples due to their high sensitivity and rapid results.

In the same way, the use of analytical techniques combined with chemometric methods have received increasing attention toward the analysis of trace elements in different matrices such as food [15–19], Cosmetic [20], environment [21–23]. Chemometric methods, such as Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) were used to establish optimal conditions of the analytical methods, to obtain a description of the present data set, its variance, influential variables and to explore similarities between samples.

Nevertheless, the use of analytical techniques combined with chemometric methods have been given less attention for the analysis of cosmetic samples especially Kohl samples. We found only a few works in this context in the last ten years, despite the advantages that can give these methods. The main idea was to use of ATR-FTIR spectroscopy to discriminate and characterize Kohl samples [24] and their varieties as eyeliner [25] and Kajal [26, 27].

In this study, we investigated for the first time the analysis of the trace elements in Moroccan Kohl samples. The method was based on the use of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) for determination of contents of trace element and the chemometric methods were used to study the behavior and the relationship of these elements.

EXPERIMENTAL SECTION

Chemicals and standard solutions

HNO₃ 69% (w/v) and H₂O₂ 35% reagent grade from Scharlau and nanopore water, with a maximum resistivity of 18.2 MΩ cm, obtained from a Milli-Q Millipore system (Bedford, MA, USA) were employed for sample digestion and sample dilution. The stock solution for calibration was prepared by a multi-elemental standard solution of 100 μg mL⁻¹ containing 26 elements (Li, Al, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, K, Se, Na, Sr, Tl, Ti, V, Zn) were dissolved in 5% HNO₃ from Scharlau Chemie (Barcelona, Spain) and a multi-elemental standard solution of 100 μg mL⁻¹ containing 16 lanthanide elements (Dy, Er, Eu, Gd, Ho, Lu, Sm, Sc, Tb, Tm, Yb, Y) were dissolved in 5% HNO₃ from Alfa Aesar (Karlsruhe, Germany). Argon C-45 (purity > 99,995%) was employed as carrier gas and synthetic air was used to dry the hydride formed. The both gas were supplied by Carburos Metálicos (Barcelona, Espagne).

Sample collection and preparation

Four samples of Kohl, were purchased from different Moroccan herbalists. Samples were stored in plastic flasks. Samples were sieved through a 250 μm mesh before their digestion. For microwave digestion, 0.5 g of each powder sample was weighed inside the digestion reactor. After that 4 mL of concentrated nitric acid (69%), 2 mL of sulfuric acid (98%) and 2 mL hydrogen peroxide (60%) were added to the samples. All samples were digested as follows: 5 min to reach 130°C, 10 min to reach 200°C and 15 min at 200 °C. After cooling to ambient temperature, the reactors were opened and sonicated to eliminate the nitrous oxide vapours. The resultant solutions were transferred to a plastic flask and diluted to 50 mL with ultrapure water. Finally, the solutions were analyzed by ICP-AES.

Determination of elemental content

The element composition of Kohl samples was determined using a Perkin Elmer Model Optima 5300 DV spectrometer (Norwalk, CT, USA) ICP-AES equipped with a Cross Flow nebulizer and an auto sampler AS 93-plus. The ICP-AES operating conditions were: 1.3 kW RF Power, 15 L/min plasma gas flow rate, 2.0 L/min auxiliary gas flow rate, 0.8 L/min nebulizer gas flow rate, 1.1 mL/min sample flow rate. The wavelengths selected are summarized in Table 1. The analytical emission lines

Table 1: Analytical wavelengths of elements

Element	wavelengths (nm)	Element	wavelengths (nm)	Element	wavelengths (nm)
Al	396,153	Fe	238,204	Pr	390,844
As	188,979	Gd	342,247	Sc	361,383
Ba	233,527	Ho	345,600	Se	196,026
Be	313,107	K	766,490	Sm	359,260
Bi	223,061	La	408,672	Sr	407,771
Ca	317,933	Li	670,784	Tb	350,917
Cd	228,616	Lu	261,542	Ti	334,940
Ce	413,764	Mg	285,213	Tl	190,801
Co	228,616	Mn	257,610	Tm	313,126
Cr	267,716	Mo	202,031	V	290,880
Cu	327,393	Na	589,592	Y	371,029
Dy	353,170	Nd	406,109	Yb	328,937
Er	337,271	Ni	231,604	Zn	206,200
Eu	381,967	Pb	220,353	B	249,677

were selected as the most sensitive and selective ones. The calibration standards were prepared by diluting the stock multielemental standard solutions in 5% nitric acid. The calibration range for all the 42 evaluated elements was made from 0.005 to 5 mg/L and it was modified according to the expected concentration range in the samples of the different studied elements.

Chemometric analysis

Multivariate statistical methods were performed using the computer Software SPSS statistics 26 in order to investigate the relationships among the trace elements in Kohl samples.

Pearson's correlations between trace elements are used in almost all related research, as it is simple and clear to optimize the information provided by the correlation matrix.

Principal Component Analysis (PCA) was tested to envisage the distribution and the existence of relationships among the variables in a reduced dimensional space. The number of significant principal components is selected on the basis of the Kaiser criterion of eigenvalues higher than 1 (Kaiser, 1960) and a total explained variance is equal to or higher than 85%. Similarities among different element concentrations in the samples were explored with Factor Analysis (FA). The extraction of factors was done through Principal Component Analysis (PCA) and rotation using unrotated method.

RESULTS AND DISCUSSION

Analytical characteristics and trace element content

The Limit Of Detection (LOD) defined as the ratio between three times the standard deviation of three replicates of the blank signal and the slope of the calibration curve, was calculated in the original samples ($\mu\text{g/g}$) taken into consideration the amount of sample digested and the final dilution employed in the recommended procedure. The LOD of the 42 elements studied varied between 0.05 $\mu\text{g/g}$ for Ti, Ni, and 2 $\mu\text{g/g}$ for K. The Relative Standard Deviations (RSDs) calculated for all samples are less than 9%. The results of LODs and RSDs show that the method is adequate for the determination of trace elements in Kohl samples. Of all the 42 elements studied, 15 elements (Al, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Ni, Na, Pb, Sr, Ti and Zn) were determined in the Kohl samples. The other elements have concentrations below the LOD of the method.

Table 2 summarizes the minimum, maximum, mean, median, standard deviation, and skewness values of the trace element concentration found in the Kohl samples. Large Standard Deviations (SD) were found in the trace element levels in all samples, which indicated a wide variation in the observed data around the mean. From the data in table 2 it can be seen that contents of trace element are classified as follows. The lead (Pb) is the main element at concentration levels from 85000 $\mu\text{g/g}$ till 421000 $\mu\text{g/g}$ indicating that most preparations of Kohl samples were

Table 2: Contents of trace elements ($\mu\text{g/g}$) values in Kohl samples

Element	LD ($\mu\text{g/g}$)	RSD (%)	Maximum	Minimum	Mean	Median	SD	Skewness
Al	0,1	6	92,00	54,00	74,25	75,50	16,01	-0,42
Ba	0,3	5	142,0	32,0	79,3	71,5	48,0	0,76
Ca	1	8	962	151	680	803	363	-1,67
Cr	0,3	8	15,00	5,00	10,75	11,50	4,19	-1,01
Cu	0,5	5	421,0	213,0	351,3	385,5	96,7	-1,51
Fe	0,5	5	952	123	530	523	455	0,01
K	2	5	253,0	124,0	168,5	148,5	58,6	1,59
Mg	1	4	654,0	254,0	451,5	449,0	180,1	0,05
Mn	0,2	6	450,0	120,0	222,3	159,5	153,0	1,90
Na	1	5	897	140	353	188	364	1,96
Ni	0,05	8	54,0	12,0	31,3	29,5	21,4	0,14
Pb	0,8	6	421120	85625	194634	135895	153307	1,82
Sr	0,2	9	23,00	12,00	16,75	16,00	4,65	0,88
Ti	0,05	7	54,00	26,00	42,00	44,00	12,11	-0,81
Zn	0,5	3	652,0	422,0	521,0	505,0	105,7	0,55

lead sulfide, followed by Ca, Cu, Fe, K, Mg, Mn, Na, Zn at the concentration of 100 to 1000 $\mu\text{g/g}$, finally Al, Ba, Cr, Ni, Sr and Ti the concentration less than 100 $\mu\text{g/g}$. In other hand, the highest concentration recorded for Pb in our samples was widely exceeded the value recommended by the United States and other countries.

Multivariate statistical analysis

Correlation analysis

The correlation studies as shown in Table 3 illustrates the behavior and relationship of trace elements in the samples. The coefficients calculated for each element indicated a strong positive correlation among Pb, Mn, Na and Sr. On the other hand, a strong negative correlation between Cr and Ca. These strong correlations between these variables show the similarity of the behavior in Kohl samples. Also, a strong correlation between Pb, Mn, Na and Sr with Cr then Ca, indicates that the existences of Cr and Ca decreases the concentration of Pb, Mn, Na and Sr in the samples. The same result showed by Mg with Fe, Ba and Cu then Ni with Fe and Ti. Similarly, no correlation showed by Al and Zn.

Principal component analysis

The principal component analysis (PCA) is used to reduce the number of dimensions of such datasets, and to

identify the trace elements and their intrinsic relations. Table 4, indicates that three Principal Components (PC) were statistically significant with the eigenvalues higher than 1, contributing 91% of the observed variance. Furthermore, PC1 and PC2 show major contributions, while PC3 has a relatively lower effect.

The factor analysis is used to determine the factor that has the most influence on each variable. Table 5 shows the factor loading, which indicate the variance explained by the variable. The first component (PC1) describe 65,93% of the variance, present a positive factor loading as Sr, Mn, Pb, Na, Fe, Cu, Ti, and a negative factor loading as Cr, Ca, Ni, K, Mg. Hence, we suggested that the behavior of these elements may be relatively independent. PC2 is collected only by Al and Zn, gives 25% of the variance.

In addition, the Fig. 1 shows the graphical projection of the PCA. The first component (PC1) regroups the elements as Sr, Mn, Pb, Na, Fe, Cu, Ti and Ba, which exhibited a strong positive correlation between Sr, Mn, Pb, Na and less between, Fe, Cu, Ti, Ba. In the same way, The PC1 regroups the elements as Cr, Ca, Ni, K and Mg, which exhibited a strong negative correlation between Cr, Ca and less between, K, Ni, Mg. The second component (PC2), has loading on Al and Zn.

Table 3: Correlation matrix for trace elements in the samples

	Al	Ba	Ca	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Sr	Ti	Zn
Al	1														
Ba	0,401	1													
Ca	0,691	-0,355	1												
Cr	0,567	-0,452	0,981	1											
Cu	0,091	0,820	-0,636	-0,765	1										
Fe	-0,046	0,890	-0,690	-0,719	0,782	1									
K	-0,002	-0,755	0,689	0,813	-0,994	-0,749	1								
Mg	-0,198	-0,971	0,559	0,650	-0,908	-0,943	0,866	1							
Mn	-0,774	0,235	-0,992	-0,958	0,548	0,601	-0,611	-0,451	1						
Na	-0,811	0,202	-0,980	-0,924	0,471	0,597	-0,531	-0,412	0,993	1					
Ni	0,091	-0,844	0,671	0,673	-0,682	-0,989	0,645	0,890	-0,589	-0,602	1				
Pb	-0,782	0,257	-0,975	-0,913	0,472	0,651	-0,523	-0,454	0,981	0,995	-0,665	1			
Sr	-0,523	0,516	-0,976	-0,997	0,789	0,773	-0,829	-0,704	0,944	0,913	-0,730	0,910	1		
Ti	-0,382	0,569	-0,705	-0,630	0,394	0,858	-0,376	-0,639	0,663	0,715	-0,918	0,780	0,675	1	
Zn	0,748	0,474	0,522	0,511	-0,095	0,230	0,203	-0,262	-0,601	-0,562	-0,279	-0,480	-0,439	0,171	1

Table 4: Total variance of trace elements in Kohl samples by PCA

	Eigenvalue	Percentage of variance %	Cumulative %
PC1	9,889	65,930	65,930
PC2	3,760	25,069	90,999
PC3	1,350	9,001	100,000

Table 5: Factor loadings of trace elements in Kohl samples

	Factor 1	Factor 2	Factor 3
Sr	0,982	-0,132	-0,136
Cr	-0,964	0,202	0,173
Ca	-0,951	0,309	0,009
Mn	0,905	-0,425	0,005
Pb	0,902	-0,386	0,195
Na	0,886	-0,447	0,121
Fe	0,874	0,449	0,187
Ni	-0,846	-0,419	-0,330
K	-0,814	-0,292	0,502
Cu	0,793	0,394	-0,465
Ti	0,788	0,125	0,603
Mg	-0,786	-0,611	0,094
Al	-0,448	0,865	-0,227
Zn	-0,270	0,846	0,460
Ba	0,626	0,779	-0,036

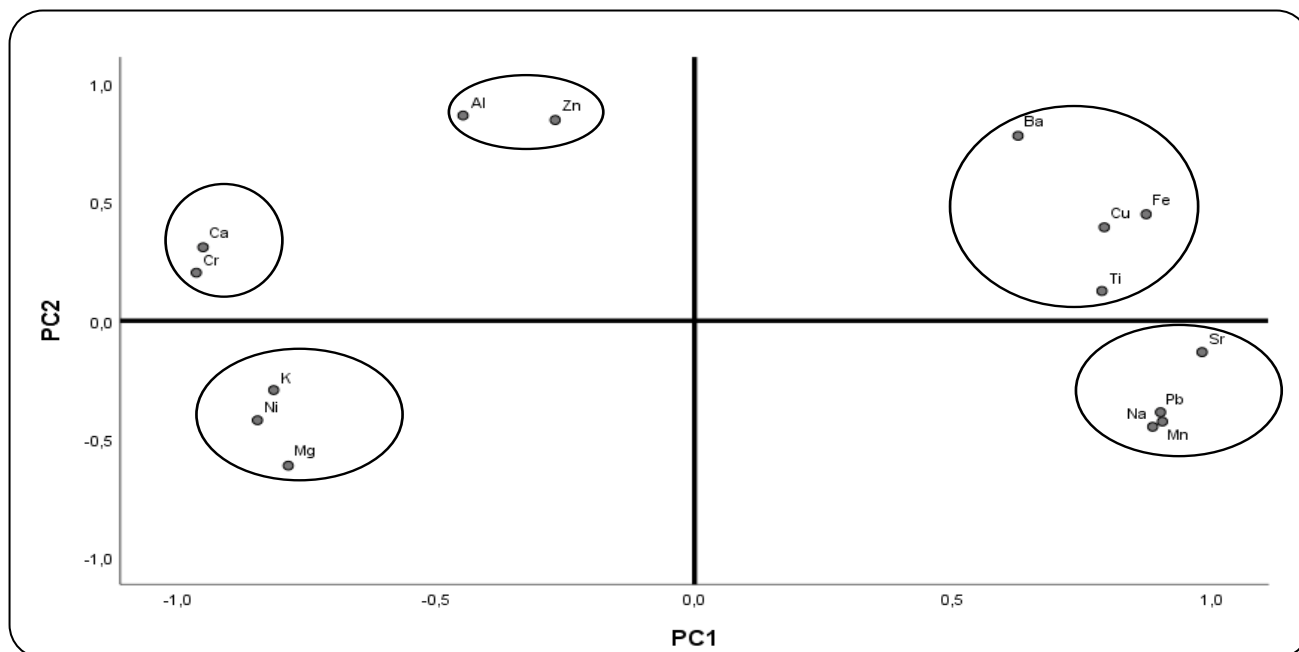


Fig. 1 : Loading plots of trace elements in the space defined by two components

CONCLUSION

In this study, we proposed a method based on Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) for the determination of trace elements such as Al, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Ni, Na, Pb, Sr, Ti and Zn in Kohl samples as part to evaluate the quality of these samples. The method showed that, the Kohl contains a high lead content from 85000 $\mu\text{g/g}$ till 421000 $\mu\text{g/g}$ indicating that most preparations are lead sulfide instead of antimony sulfide, followed by Ca, Cu, Fe, K, Mg, Mn, Na, Zn at the concentration of 100 to 1000 $\mu\text{g/g}$, finally Al, Ba, Cr, Ni, Sr and Ti the concentration less than 100 $\mu\text{g/g}$.

The multivariate statistical analysis was used to study the behavior and the relationship of these trace elements in the samples. The correlation and principal component extracted indicate the existence of a correlation relationship between the elements which have a high concentration onto the elements which have a low concentration. The distribution of trace elements was organized in three groups. The first component (PC1) regroups the elements as Sr, Mn, Pb, Na, Fe, Cu, Ti and Ba, exhibited a positive correlation. The second group contains the elements Cr, Ca, Ni, K and Mg, exhibited a negative correlation. The second component (PC2), assemble the third group as Al and Zn. Finally, we observed that work should be done to improve this study based on the comparison of samples of commercial Kohl available from herbalist and Kohl traditionally prepared by women.

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REFERENCES

- [1] Navarro-Tapia E., Serra-Delgado M., Fernández-López L., Meseguer-Gilabert M., Falcón M., Sebastiani G., Sailer S., Garcia-Algar O., Andreu-Fernández V., [Toxic Elements in Traditional Kohl-Based Eye Cosmetics in Spanish and German Markets](#), *International Journal of Environmental Research and Public Health*, **18** (11): 1–16 (2021).
- [2] Amry M. A., Al-Saikhan F., Ayoubi A., [Toxic Effect of Cadmium Found in Eyeliner to the Eye of a 21 Year Old Saudi Woman: A Case Report](#), *Saudi Pharmaceutical Journal*, **19** (4): 269–272 (2011).
- [3] Aguiní S., Mansouri E.H., Azzouz M., Abtroun R., Alamir B., Reggabi M., [Khôl: Source Dg Exposition Au Plomb - Détermination Du Taux de Plomb Dans 45 Échantillons Par SAAE](#), *Toxicologie Analytique et Clinique*, **27** (2): 59–65 (2015).

- [4] Gondal M.A., Dastageer M.A., Al-Adel F.F., Naqvi A.A., Habibullah Y.B., [Detection of Highly Toxic Elements \(Lead and Chromium\) in Commercially Available Eyeliner \(Kohl\) Using Laser Induced Break down Spectroscopy](#), *Optics and Laser Technology*, **75**: 99–104 (2015).
- [5] Jamali S., Khoso M.A., Zaman M.H., Jamil Y., Bhutto W.A., Abbas A., Mari R.H., Kalhor M.S., Shaikh N.M., [Elemental Analysis of Kohl Using Laser Ablation and Atomic Absorption Spectroscopy \(AAS\) Techniques](#), *Physica B: Condensed Matter*, **620**: 413278 (2021).
- [6] Massadeh A.M., El-khateeb M.Y., Ibrahim S.M., [Evaluation of Cd, Cr, Cu, Ni, and Pb in Selected Cosmetic Products from Jordanian, Sudanese, and Syrian Markets](#), *Public Health*, **149**: 130–137 (2017).
- [7] Ullah P.H., Mahmood Z.A., Sualeh M., Zoha S.M.S., [Studies on the Chemical Composition of Kohl Stone by X-Ray Diffractometer](#), *Pakistan Journal of Pharmaceutical Sciences*, **23** (1): 48–52 (2010).
- [8] Haider A.F.M.Y., Lubna R.S., Abedin K.M., [Elemental Analyses and Determination of Lead Content in Kohl \(Stone\) by Laser-Induced Breakdown Spectroscopy](#), *Applied Spectroscopy*, **66** (4): 420–425 (2012).
- [9] Filella M., Martignier A., Turner A., [Kohl Containing Lead \(and Other Toxic Elements\) Is Widely Available in Europe](#), *Environmental Research*, **187**: 109658 (2020).
- [10] Daar E., Alsubaie A., Almgren K.S., Barnes S., Alanazi A., Alyahyawi A., Alomairy S., Al-Sulaiti H., Bradley D.A., [X-Ray Fluorescence Analysis of Pb, Fe and Zn in Kohl](#), *Results in Physics*, **7**: 3590–3595 (2017).
- [11] Riesmeier M., Keute J., Veall M.A., Borschneck D., Stevenson A., Garnett A., Williams A., Ragan M., Devière T., [Recipes of Ancient Egyptian Kohls More Diverse than Previously Thought](#), *Scientific Reports*, **12** (1): 1–11 (2022).
- [12] Bassal N., Mahmoud H., Fayez-Hassan M., [Elemental Composition Study of Kohl Samples](#), *Arab Journal of Nuclear Sciences and Applications*, **46** (3): 133–140 (2013).
- [13] Gulnaziya I., Nicholas Y.J., Mohammad A.A., Farihausnah H., Mohamed K.A., [Removal of Zinc from Wastewater through the Reduction Potential Determination and Electrodeposition Using Adsorption-Desorption Solutions](#), *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **39** (6): 121–130 (2020).
- [14] Shojaei Z., Iravani E., Moosavian M.A., Torab Mostaeedi M., [Lead Adsorption onto Surface Modified Nano Titania: Kinetic and Thermodynamic Studies](#), *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **39** (6): 105–119 (2020).
- [15] Hassan M.M., Ahmad W., Zareef M., Rong Y., Xu Y., Jiao T., He P., Li H., Chen Q., [Rapid Detection of Mercury in Food via Rhodamine 6G Signal Using Surface-Enhanced Raman Scattering Coupled Multivariate Calibration](#), *Food Chemistry*, **358**: (2021).
- [16] Varga T., Sajtos Z., Gajdos Z., Jull A.J.T., Molnár M., Baranyai E., [Honey as an Indicator of Long-Term Environmental Changes: MP-AES Analysis Coupled with ¹⁴C-Based Age Determination of Hungarian Honey Samples](#), *Science of the Total Environment*, **736**: (2020).
- [17] Song O.Y., Islam M.A., Son J.H., Jeong J.Y., Kim H.E., Yeon L.S., Khan N., Jamila N., Kim K.S., [Elemental Composition of Pork Meat from Conventional and Animal Welfare Farms by Inductively Coupled Plasma-Optical Emission Spectrometry \(ICP-OES\) and ICP-Mass Spectrometry \(ICP-MS\) and Their Authentication via Multivariate Chemometric Analysis](#), *Meat Science*, **172**: 108344 (2021).
- [18] Pérez-Rodríguez M., Dirchwolf P.M., Rodríguez-Negrín Z., Pellerano R.G., [Assessing Mineral Profiles for Rice Flour Fraud Detection by Principal Component Analysis Based Data Fusion](#), *Food Chemistry*, **339**: 128125 (2021).
- [19] Fernandes Serra Moura H., de Souza Dias F., Beatriz Souza e Souza L., Magalhães B.E.A. de, de Aragão Tannus C., Correia de Carvalho W., Cardoso Brandão G., dos Santos W.N.L., Graças Andrade Korn M., Cristina Muniz Batista dos Santos D., Vieira Lopes M., de Andrade Santana D., de Freitas Santos Júnior A., [Evaluation of Multielement/Proximate Composition and Bioactive Phenolics Contents of Unconventional Edible Plants from Brazil Using Multivariate Analysis Techniques](#), *Elsevier Ltd*, **363**.
- [20] Angrish A., Kumar R., Chauhan R., Sharma V., [On the IR Spectroscopy and Chemometric Based Rapid and Non-Destructive Method for the Investigation of Sunscreen Stains: Application in Forensic Science](#), *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, **242**: 118708 (2020).

- [21] Lawley C.J.M., Somers A.M., Kjarsgaard B.A., [Rapid Geochemical Imaging of Rocks and Minerals with Handheld Laser Induced Breakdown Spectroscopy \(LIBS\)](#), *Journal of Geochemical Exploration*, **222**: 106694 (2021).
- [22] Aslam S.N., Huber C., Asimakopoulos A.G., Steinnes E., Mikkelsen Ø., [Trace Elements and Polychlorinated Biphenyls \(PCBs\) in Terrestrial Compartments of Svalbard, Norwegian Arctic](#), *Science of the Total Environment*, **685**: 1127–1138 (2019).
- [23] Wang T., He M., Shen T., Liu F., He Y., Liu X., Qiu Z., [Multi-Element Analysis of Heavy Metal Content in Soils Using Laser-Induced Breakdown Spectroscopy: A Case Study in Eastern China](#), *Spectrochimica Acta - Part B Atomic Spectroscopy*, **149**: 300–312 (2018).
- [24] Sharma V., Bhardwaj S., Kumar R., [On the Spectroscopic Investigation of Kohl Stains via ATR-FTIR and Multivariate Analysis: Application in Forensic Trace Evidence](#), *Vibrational Spectroscopy*, **101**: 81–91 (2019).
- [25] Arora T., Verma R., Kumar R., Chauhan R., Kumar B., Sharma V., [Chemometrics Based ATR-FTIR Spectroscopy Method for Rapid and Non-Destructive Discrimination between Eyeliner and Mascara Traces](#), *Microchemical Journal*, **164**: 106080 (2021).
- [26] Asri M.N.M., Verma R., Ibrahim M.H., Sharma V., Nor N.A.M., [Rapid Non-Destructive Techniques to Identify the Traces of Kajal Using Chemometrics; A Comparison of ATR-FTIR and Raman Spectroscopy](#), *Microchemical Journal*, **169**: 106556 (2021).
- [27] Sharma S., Chopi R., Kumar R., Sharma V., Singh R., [Differentiation of Locally Manufactured Kajal by Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy Supported by Chemometric Analysis](#), *Forensic Science International*, **303**: 109930 (2019).