Düzce Üniversitesi Bilim ve Teknoloji Dergisi

Araştırma Makalesi

Utilization of FTIR Spectroscopic Method in Classification and Analysis of Mineral Samples Containing Sodium and Potassium

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ABSTRACT

Feldspar is used as an important raw material in the ceramic, porcelain, and glass industries and as a filling material in the welding electrode, rubber, plastic, and paint industries. The ratio of Na_2O (originated from Na-feldspar) and K_2O (originated from K-feldspar) in feldspar plays a decisive role in many issues, from melting points to usage areas. However, since Na-feldspar and K-feldspar have similar physicochemical properties, it is difficult to separate and analyze them from their natural mineral environment by traditional methods. For this reason, it has become necessary to choose a method that can be applied without separating feldspar species from each other and without damaging the sample. The ATR-FTIR method was preferred because of its ease of sample preparation, measurement without damaging the sample, and providing information about the functional groups and other components in the sample. In this study, using ATR-FTIR (attenuated total reflectance-fourier transform infrared) spectroscopy and multivariate statistical techniques, the percentages of Na_2O and K_2O in feldspar samples were analyzed in a natural matrix environment without any pretreatment, and Na-feldspar and K-feldspar samples were grouped.

Keywords: *ATR-FTIR spectroscopy, multivariate analysis, chemometry, feldspar*

Sodyum Ve Potasyum İçeren Maden Numunelerinin Sınıflandırılması ve Analizlerinde FTIR Spektroskopik Yöntemin Kullanılması

ÖZET

Feldispat, seramik, porselen ve cam sanayinde önemli bir hammadde olarak; kaynak elektrodu, kauçuk, plastik ve boya sanayinde dolgu malzemesi olarak kullanılmaktadır. Feldispatın içerdiği Na_2O (Na-feldspat kaynaklı) ve K_2O (K-feldspat kaynaklı) oranı, erime noktasından kullanım alanlarına kadar birçok konuda belirleyici rol oynamaktadır. Fakat Na-feldspat ve K-feldspat benzer fizikokimyasal özelliklere sahip olmaları nedeniyle bulundukları doğal mineral ortamından geleneksel yöntemlerle ayrılıp analiz edilmesi güçtür. Bu nedenle feldispat türlerini birbirinden ayırmadan ve numuneye zarar vermeden uygulanabilecek bir yöntem seçilmesi gerekliliği ortaya çıkmıştır. ATR-FTIR yöntemi örnek hazırlama kolaylığı, numuneye zarar vermeden ölçüm yapılabilmesi ve numunedeki fonsiyonel gruplar ve diğer bileşenler hakkında bilgi vermesi nedeniyle tercih edilmiştir. Bu çalışmada ATR-FTIR (Fourier dönüşümlü kızılötesi-azaltılmış toplam yansıma) spektroskopisi ve çok değişkenli

istatistiksel teknikler kullanılarak feldspat numunelerindeki Na_2O ve K_2O yüzdeleri hiçbir ön işlem uygulamadan, doğal ortamında analiz edilmiştir. Na-feldspat ve K-feldspat numuneleri sınıflandırılmıştır.

Anahtar Kelimeler: *ATR-FTIR spektroskopisi, çok değişkenli analiz, kemometri, feldispat*

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I. INTRODUCTION

Feldspars are defined as alumina silicates, included in the silicates group, and they are rock minerals that make up 60% of the earth's crust [1], [2]. Feldspars are defined as albite ($NaAlSi_3O_8$), orthoclase/microcline ($KAlSi_3O_8$), and anorthite ($CaAl_2Si_2O_8$), depending on the Na, K, or Ca ratios they contain [3], [4].

Table 1. Chemical Composition of Some Pure Feldspar Minerals [1]

	Na_2O	**K_2O**	**CaO**	**Al_2O_3**	**SiO_2**
Albite	11.8	---	---	19.4	68.8
Orthoclase	---	10.9	---	18.4	69.7
Anorthite	---	---	20.1	28.6	43.3

Feldspar, which is an important industrial raw material, is mainly used in the ceramic, porcelain, and glass industries. Moreover, it is used in other sectors, including the paint, plastics, soft abrasives, polish, glaze, and soap industries [5].

The melting temperatures of feldspars are of great importance for the ceramic and glass industries. Although the exact melting points are given in the research, the presence of other feldspar species in the mixtures changes the melting temperatures. The melting temperatures of orthoclase, albite, and anorthite are, respectively, 1200, 1150 and 1500 ^oC [1].

The chemical compositions of feldspars, especially alkali (K_2O and Na_2O) and alumina contents (AI_2O_3), determine their quality [6]. While alumina increases the strength of glass and ceramic, its alkali content reduces the melting temperature and allows for a shorter firing or melting time. The Na-feldspar mineral (albite) is used as a source of alumina in glass production, while the K-feldspar mineral (microcline or orthoclase) is mostly used in porcelain and ceramic production [4].

Chemical methods such as optical microscopy, electron microscopy, atomic absorption spectroscopy (AAS), x-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR spectroscopy), raman spectroscopy, thermal analysis (DTA/TGA), and bulk chemistry analysis are employed to ascertain the mineral content of rocks [7]-[13].

The ATR-FTIR (attenuated total reflectance-fourier transform infrared) technique is particularly preferred since it solves key issues with infrared analysis like spectrum repeatability and sample preparation [14]. Obtaining fast results without damaging the sample has made the use of ATR-FTIR widespread [15]. On the other hand, Na-feldspar and K-feldspar spectra overlap in the samples examined and cannot be determined by classical methods. Therefore, it is important to determine both minerals together in the same environment. Recently, multivariate calibration techniques have been frequently used in the simultaneous determination of analytes in samples [16]-[21]. The most commonly used multivariate statistical methods are factor analysis (FA), principal component analysis

(PCA), discriminant analysis (DA), principal component regression (PCR), multiple linear regression (MLR), and partial least squares regression (PLS) [14].

In this study, it is aimed to develop a method for the determination of Na_2O and K_2O with the help of multivariate calibration methods by using ATR-FTIR spectra of various feldspar samples whose Na_2O and K_2O contents are known by analyzing them using classical methods.

II. MATERIALS AND METHODS

A. MATERIALS

A. 1. Instrumentation

A Shimadzu IRAffinity-1 FTIR spectrometer equipped with an ATR unit was used for IR spectra.
The IR spectra of each sample were converted into a matrix by applying the code written in Octave 4.2.2, which is largely compatible with MATLAB. Multivariate analysis, calibration, and grouping were performed using the Unscrambler 10.4.1 software (CAMO Software AS, Norway).

A. 2. Reagent

ATR surface was cleaned using acetone to eliminate any contamination from the previous sample. A new background was recorded between each replicate, and the scans were run in triplicate.

A. 3. Samples

The feldspar samples used in this study were kindly obtained from Maden Tetkik Arama Enstitüsü (Mineral Research and Exploration General Directorate) in Türkiye with Na_2O and K_2O contents determined by the atomic spectroscopic method.

B. METHODS

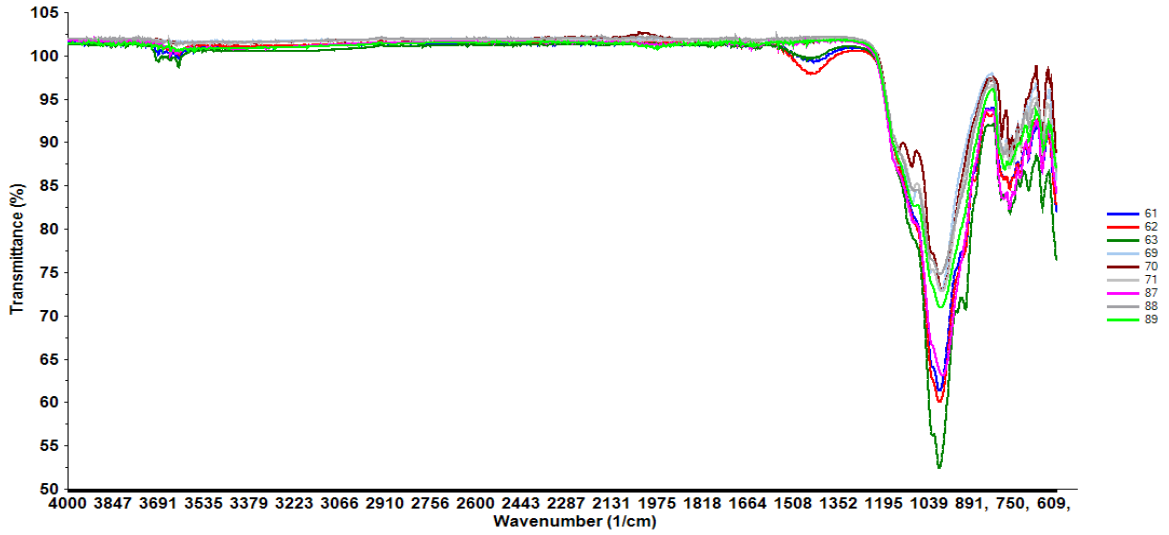
The IR spectra were taken from the feldspar mineral samples without any pretreatment, and the obtained data were converted into a matrix. Quantitative analysis and classification were made using this matrix and multivariate analysis methods in a computer environment.

III. RESULTS AND DISCUSSION

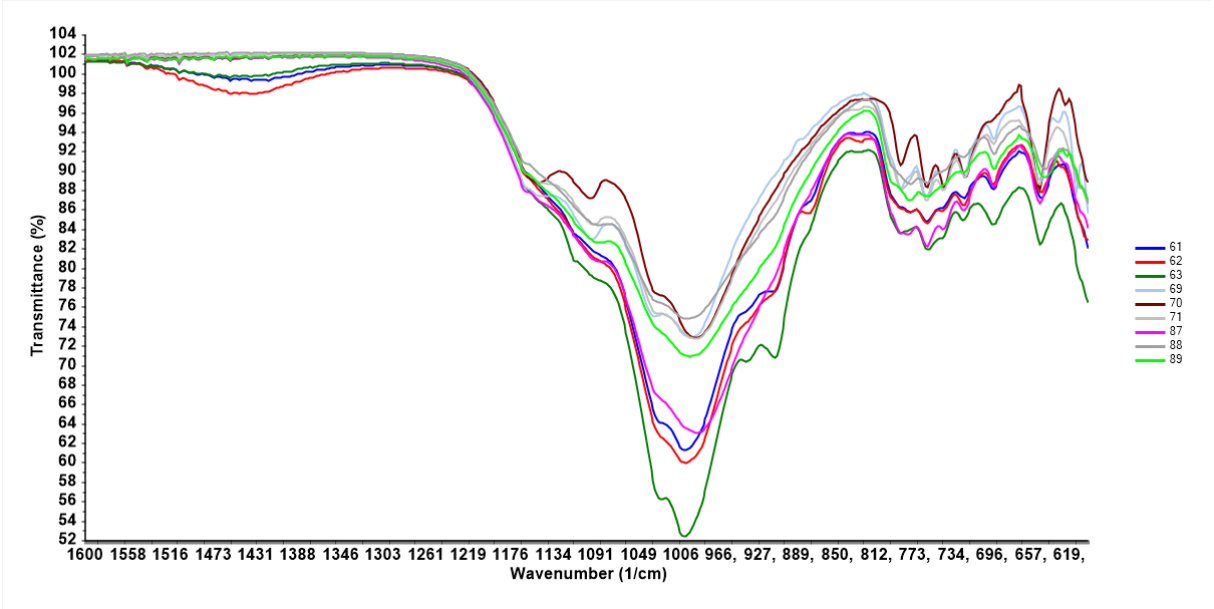
A. EXPERIMENTAL STUDIES

A. 1. Spectroscopic Data

In order to ensure the accuracy and reproducibility of the spectral data, the IR spectra of all mineral samples were taken in triplicate. These data were converted into a matrix using the code written in the Octave 4.2.2 program.



(a)



(b)

Figure 1. (a) *In the wavenumber region of 4000-600* ***(b)*** *In the wavenumber region of 1600-600, the ATR-FTIR spectra of mineral samples used in the calibration set (62, 63, 69, 70, 87, 88) and the estimation set (61, 71, 89)*

Looking at the literature survey [22], [23], and [24], the sharp peak at 1000 cm^{-1}, moderate peaks in the range of 600-650 cm^{-1}, 1100-1200 cm^{-1}, and 700-800 cm^{-1}, and low peaks at 1440cm^{-1}, as shown in Figure 1, are characteristic peaks for feldspars (albite, orthoclase/microcline, and anorthite). However, unlike the other two, the IR spectra of anorthite have fewer peaks that are broader in the literature survey [22], [23], and [24]. The absence of the above-mentioned broader peaks in Figure 1 indicates that anorthite is not present in our samples.

In this figure, it is seen that the most important peak is in the 880-1300 cm^{-1} wavelength range. The peaks observed around 1000 cm^{-1} are due to the interaction of Si-O-Si and Si-O-Al [25]. The peak at 1002 cm^{-1} shows asymmetric stretching vibrations of Si-O-Si bands. The symmetrical stresses of these bands are observed at 795 cm^{-1}. The absorption bands at 1435 cm^{-1} and 780 cm^{-1} indicate, respectively,

the presence of calcite, and quartz [26], [27]. When we examined the IR spectra of the samples, we determined that they were albite and microcline/orthoclase.

In order to evaluate the differences in mineral content of feldspar samples as a whole, the PCA method was used for qualitative analysis and classification, which is one of the multivariate calibration methods, and the PLS method was used for quantitative analysis. For this purpose, the Unscramler program was used.

A. 2. Grouping Samples

The classification of groups belonging to albite and orthoclase samples was carried out by the PCA method. For samples containing albite and albite+orthoclase, the grouping process was successful in the wave number range of 1420-1470 cm^{-1}.

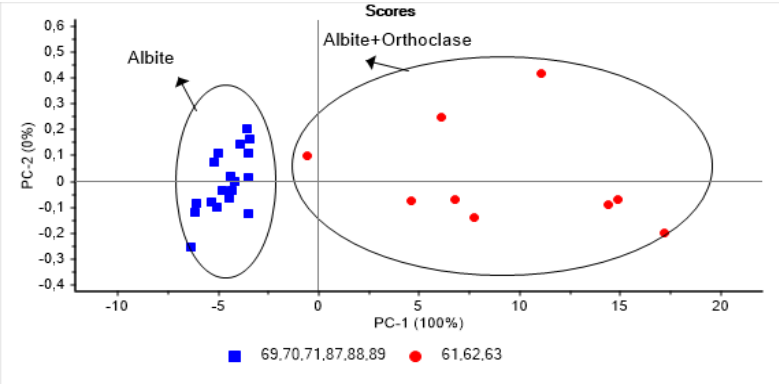


Figure 2. *PCA score (1420-1470 cm^{-1}) plot of albite and albite+orthoclase mineral samples*

Figure 2 shows the score plot of the PCA model. PC1 (99,99%) and PC2 (0,01%) explain one hundred percent of the total variance.

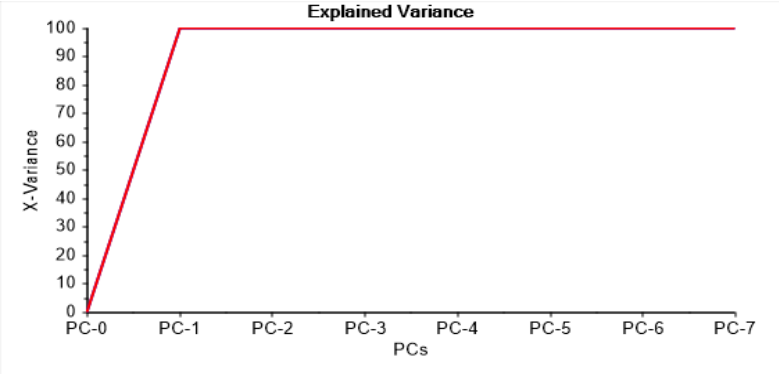


Figure 3. *PCA (1420-1470 cm^{-1}) explained variance plot*

In Figure 3, it is seen that the calibration and validation values in the first principal component are close to 100% and parallel to each other. The first principal component (PC1) explains about one hundred percent of the variance.

A. 3. Quantitative determination of Na_2O and K_2O with spectroscopic methods and PLS modeling

The data collected from the FTIR spectra were randomly divided into two sets: a calibration set and a prediction set to be used in the development of calibration and prediction models. Six of the samples

(62, 63, 69, 70, 87, and 88) were used for the calibration set, and the calibration graph was drawn. Three of the samples (61, 71, and 89) were used as the estimation set, and quantitative analysis was performed. The cross-validation method was applied to the calibration set.

Table 2. *Samples used for the calibration set*

Sample Number	Percentage of Na_2O in the sample (taken from MTA)	Percentage of K_2O in the sample (taken from MTA)
62	2.60	3.50
63	2.90	3.60
69	5.60	0.15
70	8.50	0.33
87	4.40	0.55
88	4.80	0.25

Table 3. *PLS Model Performance using ATR-FTIR*

	Spectral Region	Spectrum Derivative	Calibration				Validation			
			RMSEC	Slope	Offset	R-square	RMSEV	Slope	Offset	R-square
ATR - FTIR	All *(600-4000 cm^{-1})*	Normal Faktor 4	0.2526	0.9833	0.0801	0.9833	0.5622	0.9217	0.3200	0.9262
	(880-1300 cm^{-1})	Normal Faktor 5	0.1733	0.9921	0.0377	0.9921	0.3263	1.0051	0.0452	0.9751
	(600-880 cm^{-1})	Normal Faktor 6	0.1939	0.9901	0.0472	0.9901	0.4383	0.9396	0.2855	0.9551

RMSEC: Root mean square error of calibration
RMSEV: Root mean square error of cross-validation
ATR-FTIR: Attenuated total reflectance-Fourier transform infrared

In order to determine the Na_2O and K_2O ratios in the feldspar content, three calibration models were developed with the PLS algorithm using the normal ATR-FTIR technique and different spectral regions. To see if the model performed better and if any appreciable reductions in errors could be obtained, various spectral regions were used. The importance of choosing the optimum wavelength range in the relevant literature It is emphasized in terms of important points such as eliminating non-correlated components and improving the predictive ability of the established models [28]. The statistical results for three PLS calibration models based on different spectral regions are shown in Table 3. Considering the spectral regions, it was shown that the PLS model using the spectral range (880-1300cm^{-1}) has the best results, with the highest R-square of 0.9921, the lowest REMSEC of 0.1733, and the lowest REMSEV of 0.3263. R^2 values close to 1 and error values as small as possible were taken into account to select the best calibration model and strong prediction [29].

The predicted residual error sum of squares (PRESS) and factor number of each model were determined by the software.

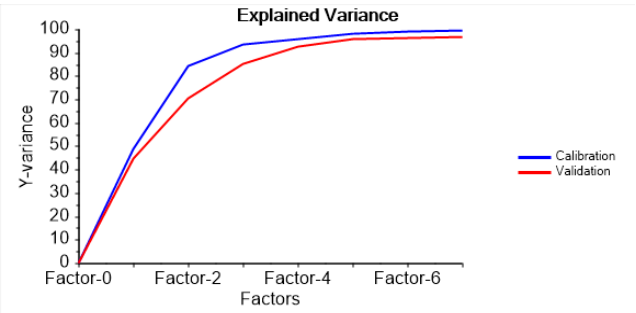


Figure 4. *PLS (880-1300cm^{-1}) explained variance plot*

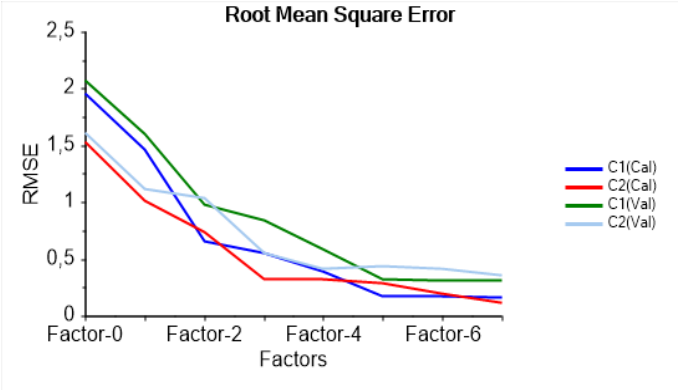


Figure 5. *PLS (880-1300cm^{-1}) root mean square error plot*

The aim was to determine the factor value where the calibration and validation plots of the developed pls model were closest to each other and to the 100% value in Figure 4. It was necessary to determine the factor value where the root mean square error of calibration and validation in the pls model developed were closest to each other and to the 0% value in Figure 5. It was seen that REMSEC and REMSEV values continue to near 0% in Factor 5.

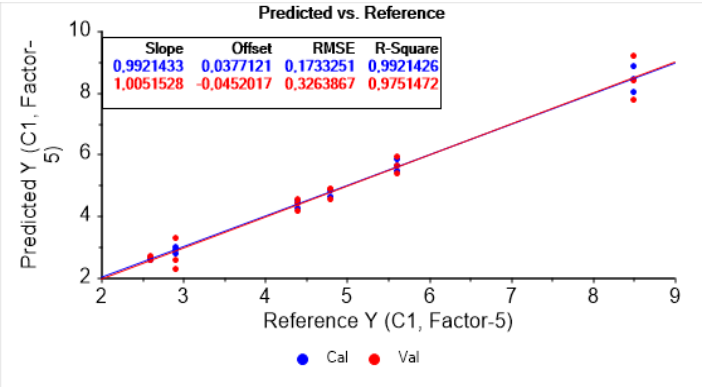


Figure 6. *Calibration and validation plot for Na_2O (R^2 0,9921)*

Figure 6 shows the plot of predicted and reference values for the best PLS model for Na_2O.

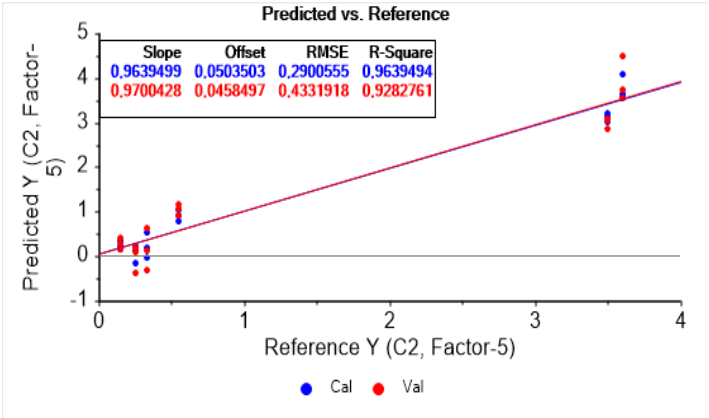


Figure 7. *Calibration and validation plot for K_2O (R^2 0,9639)*

Figure 7 shows the plot of predicted and reference values for the best PLS model for K_2O.

Table 4. *Samples used for the test set*

Faktor 5	Results obtained by PLS (*880-1300cm^{-1}*) Method		Results taken from MTA	
Sample Number	**Na_2O percentage**	**K_2O percentage**	**Na_2O percentage**	**K_2O percentage**
61	3.077	2.934	2.60	4.00
61	2.901	3.077	2.60	4.00
61	2.734	3.004	2.60	4.00
71	5.359	0.720	5.00	0.42
71	5.650	0.273	5.00	0.42
71	5.590	0.422	5.00	0.42
89	4.831	0.038	4.80	0.25
89	4.799	0.053	4.80	0.25
89	4.844	0.090	4.80	0.25

Table 5. *Paired sample t-test for difference in concentration between sample parameters*

Parameter	**Mean±Std. Error**	**N**	**Standard Deviation**	**d.f.**	**$t_{calculated}$**	**$t_{critical}$ (p=0.05)**	**Rmks**
Na_2O %	0.287±0.147	3	0.254	2	1.96	4.30	NS
K_2O %	0.378±0.316	3	0.548	2	1.19	4.30	NS
N: Number of sample d.f.: degrees of freedom p: probability level Rmks: Remarks S: Significant NS: Not Significant t: test statistic							

Samples numbered 61, 71, and 89 were used for the calculations in Table 5. The results of the analysis show that the parameters have a low standard deviation. They show no significant variation from the results of the paired sample student t-test for the samples shown in Table 5. These parameters have their calculated values ($t_{calculated}$) lower than the table values at $P \leq 0.05$. For this reason, there is no significant difference between the results at the 95% confidence interval, according to the null hypothesis.

IV. CONCLUSION

In this study, feldspar minerals were grouped using the ATR-FTIR spectroscopic method together with the chemometric method, and the percentages of Na_2O and K_2O were determined quantitatively. The PCA multivariate analysis technique used for grouping was successful with the normal ATR-FTIR spectrum in the spectral range of 1420-1470 cm^{-1}. For quantitative analysis, samples were randomly divided into two sets. Six of the samples (62, 63, 69, 70, 87, and 88) were used for the calibration set, and the calibration graph was drawn. Three of the samples (61, 71, and 89) were used as the test set, and quantitative analysis was performed. The cross-validation method was applied to the calibration set by the software. Moreover, the PLS multivariate regression technique was applied to the normal ATR-FTIR spectrums at different wavelengths, for example, 4000-600, 1300-880, and 880-600 cm^{-1}, and the result with the highest R square value (close to 1) and minimum error values was found at the 880-1300 wavelength in Table 3. When the PLS (880-1300 cm^{-1}) explained variance plot and PLS (880-1300 cm^{-1}) root mean square error plot were evaluated, factor 5 was reached. The results obtained were quite close to the values previously determined by the atomic spectroscopic method in Table 4. When they were compared with the paired sample t-test, there was no significant difference. In this way, the predictive capacity of the calibration was checked with the analysis of the test set.
The developed method can be used as an alternative to standard methods because it is fast, low-cost, and prevents time loss.

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