UV–VIS SPECTROSCOPIC DETECTION COUPLED WITH CHEMOMETRICS FOR THE MEASUREMENT OF MIXED ORGANIC ACIDS IN WATER SAMPLES ENRICHED BY RADIAL ELECTRIC FOCUSING SOLID PHASE EXTRACTION

Yugao Guo[2], Xia Liu[2], Jianyi Liu[2], Xihui Bian[1], Qingyin Zhang[1], Jie Pan[1], Dong Wan[1]

1) *Tianjin Polytechnic University, State Key Laboratory of Separation Membranes and Membrane Processes, Tianjin 300387, China (bianxihui@163.com, zhangqingyin@tjpu.edu.cn, panjie@tjpu.edu.cn, wandong_tjpu@126.com)*

2) *Tianjin Polytechnic University, School of Environmental and Chemical Engineering, Tianjin 300387, China (✉ guoyugao@tjpu.edu.cn, +86 22 8395 5451, 459763286@qq.com, 756628078@qq.com)*

Abstract

Due to the difficulty of detecting traces of organic acid mixture in an aqueous sample and the complexity of resolving UV-Vis spectra effectively, a combinatory method based on a self-made *radical electric focusing solid phase extraction* (REFSPE) device, UV-Vis detection and *partial least squares* (PLS) calculation is proposed here. In this study, REFSPE was used to enhance the extraction process of analytes between the aqueous phase and the membrane phase to enrich the trace of mixed organic acid efficiently. Then, the analytes, which were eluted from the adsorption film by ethanol with the assistance of an ultrasonic cleaning machine, were detected with UV-Vis spectrophotometry. After that, the PLS method was introduced to solve the problem of overlapping peaks in UV-Vis spectra of mixed substances and to quantify each compound. The linearly dependent coefficients between the predicted value of the model and the actual concentration of the sample were all higher than 0.99. The limit values of detection for benzoic acid, phthalic acid and p-toluene sulfonic acid were found at 9.9 µg/L, 12.2 µg/L and 13.8 µg/L with the relative recovery values between 84.8% and 117.9%. The RSD ($n = 20$) values of each component are 1.17%, 1.11% and 0.86%, respectively. Therefore, the proposed combined method can determine traces of complex materials in an aqueous sample efficiently and has wonderful potential applications.

Keywords: chemo-metrics, UV-Vis spectrophotometer, radial electric focusing solid phase extraction, mixed organic acids.

1. Introduction

As for the environmental water analysis, the composition of the compounds is usually complex and the concentration of each component is very low. Even if high-end and expensive analytical instruments (such as atomic absorption spectroscopy, *inductively coupled plasma mass spectrometry* (ICP-MS) [1, 2], ultraviolet and visible spectrophotometry (UV-Vis) [3, 4], stripping voltammetry, liquid chromatography, X-ray fluorescence spectrometry [5, 6] *et al*.) are adopted, only an inconvenient and unsatisfactory solution can be provided in some situations because of

the trace concentration or complicated compositions. Accordingly, a simple, sensitive and economical method for simultaneous detection and analysis of environmental samples is desirable.

In view of the above-mentioned background, although the UV-Vis method is the most widespread and most appealing analytical technique because of its reliability and ease of operation, it is difficult for the traditional UV-Vis approach in two situations of detecting the trace level concentration and simultaneously determining multi-components. In order to quantify different environment components simultaneously, PLS methods can be introduced into the data processing of spectrophotometric analysis [7, 8]. As for the trace level concentration, a proper sample pre-treatment method can enrich the analytes effectively. As a result, various techniques such as adsorption, liquid-liquid extraction, cloud point extraction, *solid phase extraction* (SPE) [9] and co-precipitation [10] were developed. Among them, SPE is the preferred extraction technique except that it is rather time-consuming. Therefore, an electrostatic field, created by a direct-current power supply, was introduced into the SPE system to drive charged ions to migrate directionally and to shorten the operation time [11, 12]. The improved SPE can be named the *radical electric focusing solid phase extraction* (REFSPE).

As for the simultaneous determination of multi-components, chemo-metrics can be introduced as a "mathematical separation" method instead of the conventional "physical separation" to quantify the target component. They have very prominent position in the online analysis and monitoring of complex processes such as petrochemicals [13], agriculture [14], tobacco [15], precious metals [16], food [17] and pharmaceuticals [18]. Among them, the contributions in the biomedicine and environment areas are particularly outstanding. In Maryann Fitzmaurice's group, the diffuse reflectance spectroscopy combined with the support vector machine was used to detect breast lesions with micro-calcifications in 2013 [19]. Recently, the Raman spectroscopy coupled with the chemo-metric method was introduced into monitoring of blood glucose [20] and rapid identification of bio-therapeutic drugs [21] by Ishan Barman's group. Also in 2017, the infrared spectroscopy coupled with chemo-metrics was exploited to classify heavy metal-exposed freshwater bacteria [22].

Amongst these chemo-metric methods, the *partial least squares* (PLS) is one of the most popular multivariate calibration methods for chemo-metrics. The application of UV-Vis combined with PLS in the quantitative analysis of multi-component substances has become the focus of attention of many scholars. In this paper, a combination of REFSPE, UV-Vis detection and improved PLS regression is used to quantify trace of organic acid mixture. The factors that might affect REFSPE are explored, such as elution concentration, elution time, extraction voltage, extraction time, salt effect and so on. The enriched solutions are detected by the UV-Vis analysis. A model of mixed organic acid nonlinear concentration is established and optimized. And the optimal enrichment factors are obtained by using the PLS method to analyse the UV-Vis spectra.

2. Experimental

2.1. Materials and methods

All chemicals were of analytical reagent grade and were used without further purification. Benzoic acid, phthalic acid and *p*-toluene sulfonic acid, which were replaced by A, B and C in order to facilitate the expression respectively, were purchased from Shanghai Aladdin biochemical technology Co., Ltd., China. Stock solutions of the organic acids were prepared at a concentration of 50 mg/L by dissolving the compounds in ultrapure water and were kept at 4°C.

Standard solutions were prepared by further dilutions of the stock solution with ultrapure water. Anhydrous methanol, anhydrous ethanol and potassium chloride were purchased from Tianjin Kermel Co., Ltd., China. *Polyvinylidene fluoride* (PVDF) membranes were purchased from Tianjin MOTIANMO technology Co., Ltd., China. Ultrapure water was used for all the dissolution and dilution processes in the experiments.

2.2. Instruments

The direct-current power supply of the pre-concentration process was KIKUSUI PMC18-5 (Kikusui Electronics Corporation, Japan), and the 0.5 mm platinum electrode was from the hardware supplies' store. The ultrasonic cleaning machine (Shanghai Crown Ultrasonic Instrument Co., Ltd., China) was used for desorption. The EVOLUTION 300 UV-Vis spectrometer (a range of spectra from 200 to 800 nm) purchased from Thermo Fisher Scientific Co., Ltd., USA, was selected for detection of all the samples.

The REFSPE device, which can enrich charged ions effectively, was carried out on the basis of a home-made instrument. In this device, a radial electric field was applied by the direct-current power supply in an annular region formed by a cylindrical electrode surrounding a single electrode in the central location. In this structure, a stronger and uniform electric field force, which can drive ions to migrate faster and shorten the extraction time significantly without any mixing device, was produced in the extraction system. At the same time, an automatic precise three-dimensional lifting platform was used in the experiments in order to ensure constant operating conditions in each experiment and to reduce the interference of the device's external environment. As a result, the detection accuracy and repeatability were obviously enhanced. The device diagram of REFSPE is shown in Fig. 1.
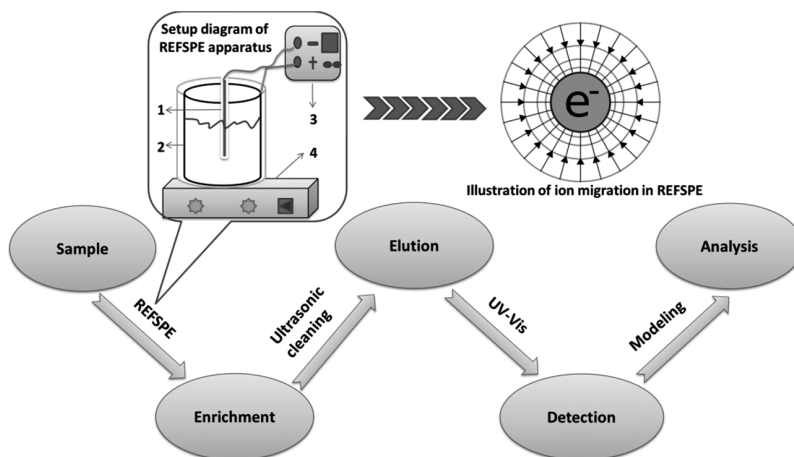

Fig. 1. A flowchart for the experimental operation of organic acid sample enrichment and quantification: 1) a platinum electrode coated with a PVDF hollow fibre membrane; 2) a titanium ruthenium plated cylindrical electrode; 3) a direct-current power supply; 4) an automatic three-dimensional lift platform.

2.3. Operation process

In the proposed experiments, all the experiment preparations were performed in the same way as in our previous work [23]. At the beginning of the extraction experiment, 50 mL sample

www.czasopisma.pan.pl PAN www.journals.pan.pl
Y. Guo, X. Liu, et al.: UV–VIS SPECTROSCOPIC DETECTION COUPLED...
POLSKA AKADEMIA NAUK

solution was enclosed in a home-made titanium plating ruthenium cylindrical container, which served as a cathode pole. Then, the extraction procedure took place in the radial electric field for some time. Charged organic acids were centralized to the membrane, which covered the positive pole of the platinum electrode, placed at the centre of extractor and the pre-concentration process was completed. After that, the mixed organic acids adsorbed on the hollow PVDF membrane were eluted by 2.0 mL of a suitable solvent in the assistance of ultrasonic concussion. After the desorption process, the UV-Vis spectra' data, which were obtained from the EVOLUTION 300 UV-Vis spectrometer, were disintegrated into an individual analyte with the help of chemometrics. Upon the MATLAB® calculation, certain concentrations of each ion were acquired. A simple flowchart of the whole experimental process is shown in Fig. 1.

3. Results and discussion

The conditions of enrichment and quantification such as eluent selection, extraction time, voltage value, elution time, and salt effect were optimized, in order to obtain an effective and sensitive detection of the organic acids' mixture. The *enrichment factor* (EF) values of organic acids were calculated from the specific values of the final concentration of ions in eluent (C_{final}) and the initial concentration of sample solution ($C_{initial}$).

3.1. Eluent selection

In these experiments, the organic acids, which were adsorbed on the PVDF membrane by REFSPE, should be desorbed effectively in order to determine the concentrations of each compound. Therefore, an efficient eluent, which has the least effect on the UV-Visible detection and has excellent solubility with analytes, should be screened. According to the similar compatibility principle, alcohol and ether organic solvents are preferred as the eluent. However, the phthalic acid cannot be desorbed efficiently by the ether solvent because it is slightly soluble in ether. Thus, a proper eluent for desorption should be selected from alcoholic organic solvents [24]. At the same time, precipitates are prone to occur when benzoic acid and methanol coexist in the acidic system. Taking the solubility of the three substances presented in the literature into account, ethanol has the largest solubility of these three compounds in all pure alcoholic organic solvents. As a result, the ethanol solvent was selected as the final choice of eluent.

3.2. Effect of applied voltage and absorption time

In REFSPE, the adsorption equilibrium time was shortened by accelerating the mass transfer rate of analytes directionally through the radial electric field force. Not unnaturally, the applied voltage, which has a direct impact on the magnitude of the surrounding electric field force, is bound to affect the effectiveness of REFSPE. Therefore, some experiments were performed at different operation voltages to investigate the time-voltage profiles of REFSPE, which are presented in Fig. 2. It is found from Fig. 2 that the enrichment factors, which have the same tendency as the UV- absorbance, were almost constant when the adsorption equilibrium was achieved. The results in Fig. 2 also show that the adsorption equilibrium time will be much longer when the lower adsorption voltage in a range of 6–8 V is adopted because a weak electric field will result in a relatively slow rate of mass transfer. On the other hand, the directed migration of charged ions in the adsorption process will be disturbed by the escaping bubbles of hydrogen and oxygen gases generated by the water electrolysis process in the solution to be measured when the

adsorption voltage is higher than 8 V. This phenomenon has an obvious effect on the subsequent experiments and the enrichment results. Therefore, 20 min was chosen as the optimal adsorption time when the operation voltage was set to 8 V.
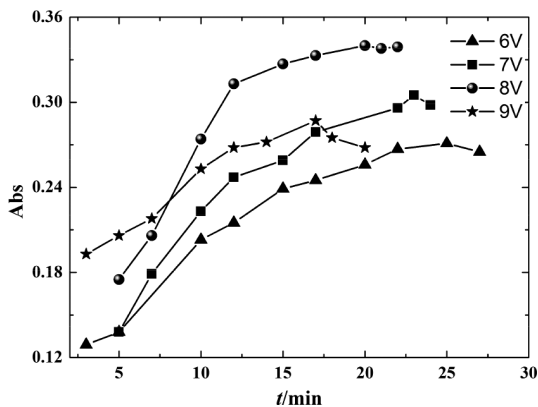

Fig. 2. The influence of adsorption time and voltage on the REFSPE process.

3.3. Effect of elution time

After completion of the enrichment, the organic acids enriched on the extraction membrane need to be eluted and collected for the following UV-Vis detection. In the proposed experiments, the commonly used ultrasonic elution coupled with our optimized eluent of ethanol were selected to desorb the analyte from the PVDF membrane because ultrasound elution is evenly stable with a favourable elution efficiency and safe operation conditions. In the proposed elution process, the adsorption PVDF membrane was put into 2.0 mL ethanol for supersonic elution to accommodate the volume of a regular UV-Vis cuvette. In order to find the appropriate elution time, the desorption operations at different elution times were performed in the same extraction conditions. The relationship between the UV-Vis absorbance data of eluate and the desorption time is shown in Fig. 3. It is clearly seen that the absorbance data tend to increase when the elution time is
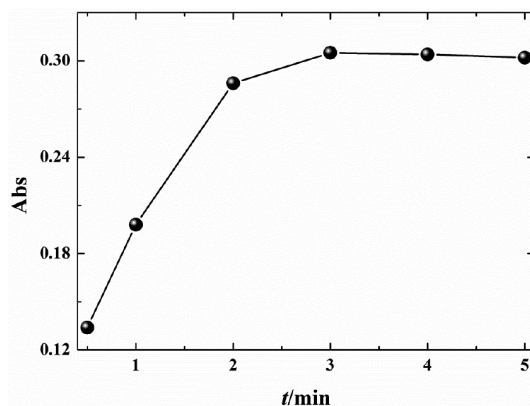

Fig. 3. The influence of elution time on UV-Vis absorbance data.

www.czasopisma.pan.pl   PAN   www.journals.pan.pl
Y. Guo, X. Liu, et al.: UV–VIS SPECTROSCOPIC DETECTION COUPLED…
POLSKA AKADEMIA NAUK

less than 3 min and gradually approach a constant after that threshold value. In other words, the desorption process have reached the elution balance. Therefore, a 3 min period was chosen as the optimal adsorption time in the following experiments.

3.4. Model Eestablishment and optimization

3.4.1. Model establishment

In order to establish an ideal calculation model, appropriate modelling samples and predictive samples should be selected, and then the UV absorption spectra of various samples should be thoroughly collected. The favourable model was screened by optimizing a modelling wavelength point, a suitable spectral pre-processing method and an appropriate number of dependent variables. After that, the model was tested with the prediction samples. The process of calculating the organic acid concentration using PLS is shown in Fig. 4.
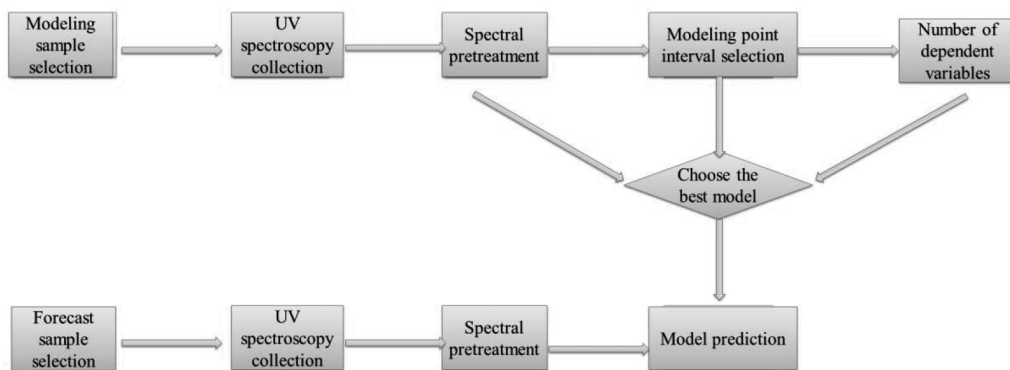

Fig. 4. A flowchart of the PLS modelling of the screening process.

3.4.2. Selection of modelling samples

In the proposed calculation method, the modelling samples were selected according to the actual experimental conditions. The concentration of each substance in these samples was representative and covered most of the samples to be tested. The substances were distributed evenly within the measured concentration and property range. Multivariate models were developed for the concentrations' prediction of organic acids mixture based on 50 random samples containing the active principle in a concentration range of 5–125 mg/L. The calculation errors of these validation samples should be less than 5%.

3.4.3. Collection of UV-Vis spectrum data

In this determination process, the UV-Vis spectrometer was used to acquire UV-Vis spectra at least three times for each sample to ensure accuracy of the spectral data. The UV-Vis absorption spectra of 50 samples are displayed in Fig. 5.

Using this spectral information and its corresponding concentration, the model was initially established with MATLAB. A 50×401 working data matrix, which contained 50 spectral objects and 401 wavenumber variables, was column-centred and block-normalized prior
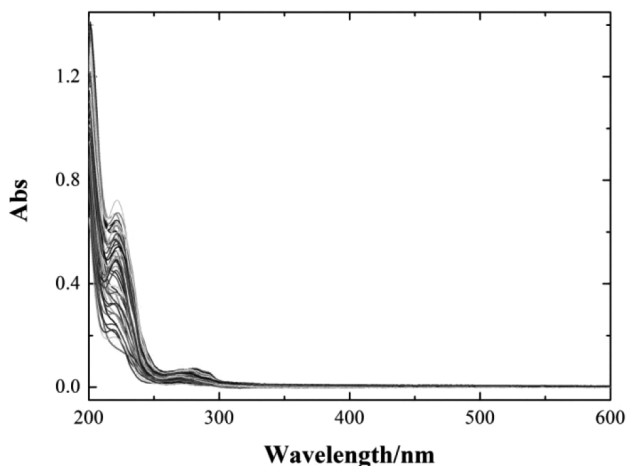
Fig. 5. UV-Vis absorption spectra of 50 validation samples.

to adding a dependent variable. In order to establish a highly stable and accurate calculation model for the quantification of organic acid mixture, these 50 random samples were divided into two groups by selecting every other two samples in the data matrix. The group with 2/3 samples was defined as the calibration set. The remaining 1/3 samples formed the verification data set.

Due to the complex background of the mixed acid samples, as well as the environment and human error, it is difficult to avoid appearing of abnormal spectra in the process of ultraviolet absorption spectrum acquisition. Therefore, it is necessary to effectively remove the abnormal samples during the modelling process in order to establish a representative calibration set for improving applicability and accuracy of the model.

3.4.4. Spectral pre-treatment methods

Preprocessing of the spectral data can reduce the spectral noise, filter the effective information, optimize the spectral measurement wavelength, purify the spectral information, reduce the influence of various non-target factors on the spectrum for a specific sample system, remove abnormal samples, calculate the model and lay the foundation for predicting the concentration or nature of unknown samples. In the proposed spectral pre-treatment method, *multiplicative scatter correction* (MSC), *standard normal variable* (SNV), *Savitzky-Golay smoothing* (S-G), *continuous wavelet transform* (CWT), *first order derivative* (1st Der) and *second order derivative* (2nd Der) were evaluated. The *root mean square error of cross validation* (RMSECV), *root mean square error of prediction* (RMSEP), linear correlation coefficient of $R_{training}$ and $R_{forecast}$ were set as inspection parameters to characterize the advantages and disadvantages of various treatment methods. The pre-treatment method is better when a smaller error value and a greater regression coefficient are obtained. Comparison of different spectral pre-treatment methods, as can be seen in Table 1, indicated that the rejected variable had some difference when the spectral pre-treatment method was used. In the model established after pre-treatment, only the model prediction accuracy of the model based on CWT is slightly higher than that of the original spectral model for all analytes.

Table 1. The effects of different spectral pretreatment methods.

Analytes	Parameter	Spectral pre-treatment method						
		Untreated	S-G	SNV	MSC	1st Der	2nd Der	CWT
A	RMSECV	4.480	4.712	7.035	7.381	5.362	5.520	6.938
	RMSEP	3.672	4.044	7.447	7.981	4.761	3.160	3.274
	$R_{training}$	0.992	0.991	0.982	0.981	0.989	0.989	0.982
	$R_{forecast}$	0.995	0.994	0.981	0.979	0.996	0.996	0.997
B	RMSECV	5.945	6.282	5.451	5.030	5.126	5.673	5.021
	RMSEP	3.939	4.134	11.652	11.323	3.701	4.010	3.882
	$R_{training}$	0.994	0.983	0.988	0.989	0.989	0.986	0.989
	$R_{forecast}$	0.995	0.994	0.981	0.979	0.996	0.996	0.997
C	RMSECV	3.162	3.585	14.996	16.197	5.797	5.077	4.880
	RMSEP	3.909	3.591	13.884	13.920	4.746	4.746	3.769
	$R_{training}$	0.996	0.995	0.938	0.930	0.9889	0.991	0.992
	$R_{forecast}$	0.994	0.994	0.947	0.946	0.992	0.989	0.996

3.4.5. Wavelength selection

Since PLS can effectively separate the overlapping spectra, it can be used in the spectra analysis to achieve a high calculation accuracy. In the prediction process, the wavelength selection can affect the number of independent variables, the volume of calculations, the impact of interference from matter interactions, the influence of the instrument and the environment noise and the redundancy information in the spectrum that is not directly related to the component quantification. The wavelength point was selected using statistics-based methods such as uninformation variable *elimination-PLS* (UVE-PLS), *Monte Carlo uninformation variable elimination-PLS* (MCUVE-PLS) and *random test-PLS* (RT-PLS). The data in Table 2 clearly show that the application of various selected wavelengths almost does not increase the calculation accuracy. That is to say,

Table 2. Influence of wavelength selection on the calculation results.

Analytes	Parameter	Wavelength selection method			
		Untreated	UVE+PLS	MCUVE-PLS	RT-PLS
A	Keep the wavelength point	401.0	85.0	310.0	60.0
	RMSECV	4.941	4.578	4.586	3.407
	RMSEP	3.710	6.324	7.624	6.588
	$R_{training}$	0.991	0.992	0.992	0.996
	$R_{forecast}$	0.995	0.983	0.979	0.983
B	Keep the wavelength point	401.0	230.0	285.0	330.0
	RMSECV	4.669	2.773	3.773	3.903
	RMSEP	3.476	9.839	9.734	9.855
	$R_{training}$	0.982	0.997	0.994	0.994
	$R_{forecast}$	0.996	0.978	0.978	0.978
C	Keep the wavelength point	401.0	360.0	390.0	145.0
	RMSECV	4.521	13.570	14.984	9.908
	RMSEP	3.112	11.650	11.617	10.687
	$R_{training}$	0.993	0.949	0.940	0.972
	$R_{forecast}$	0.996	0.962	0.962	0.965

it is unnecessary for these trace substances to eliminate the multiple scattering effect if an absorption spectrum was obtained. Therefore, full-band modelling was still used in the following computations.

3.4.6. Method evaluation

PLS regression was used for modelling and prediction, evaluating performance in each case in terms of the *root mean square error of prediction* (RMSEP) and the correlation coefficient (R). The number of *latent variables* (LVs) for the PLS model determined the minimum number of loading vectors that provide less than 5% deviation from the absolute minimum RMSECV. As a result, the UV-Vis spectrogram of an organic acid mixture was resolved and quantified by full-band modelling when the CWT method was selected as the one for pre-processing of the spectrum. The optimal model parameters are shown in Fig. 6. It is clearly seen that RMSEP varies
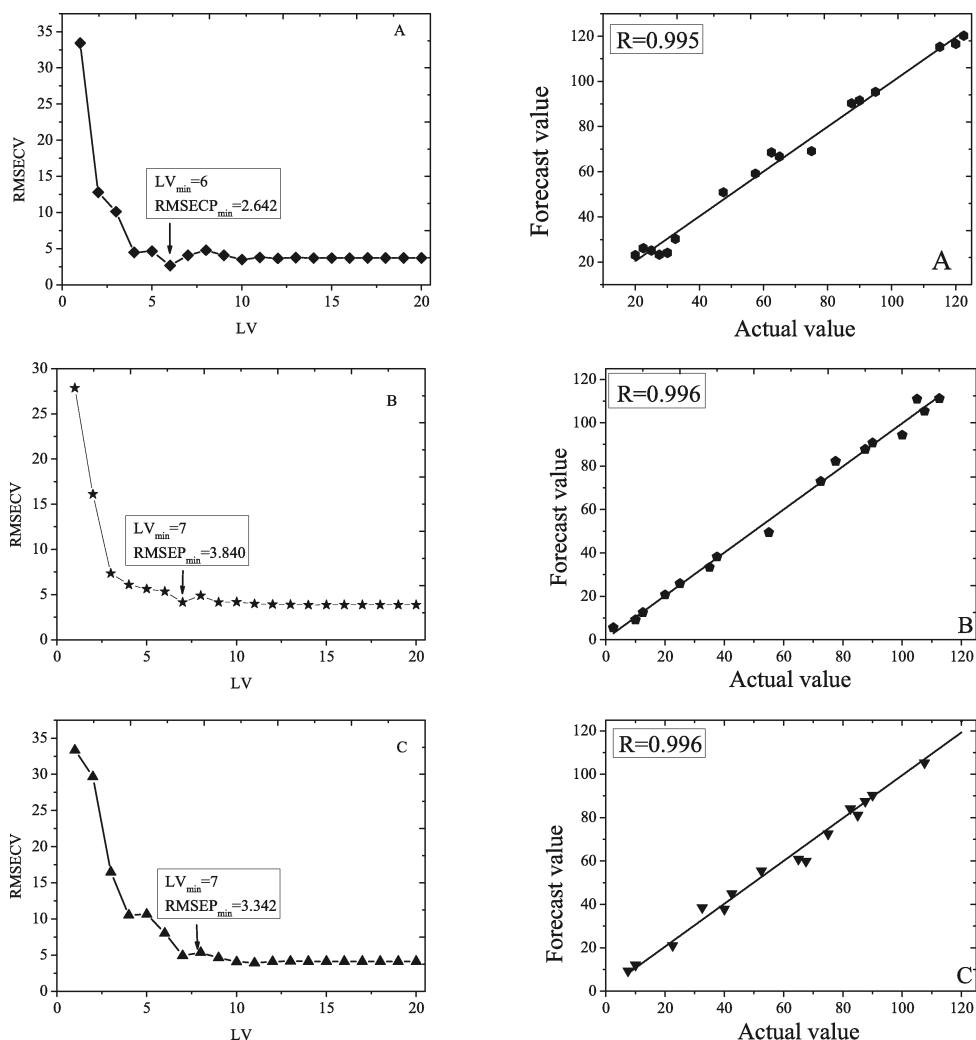

Fig. 6. Optimal model parameters for different materials.

www.czasopisma.pan.pl　　PAN　　www.journals.pan.pl
Y. Guo, X. Liu, et al.: UV–VIS SPECTROSCOPIC DETECTION COUPLED…
POLSKA AKADEMIA NAUK

with LVs and the smallest RMSEPs are 2.642, 3.840, and 3.342 corresponding to materials A, B and C, respectively. The linearly dependent coefficients, which were obtained through correlation between the predicted value of the model and the actual concentration of the sample, were all higher than 0.990. The *limit of detection* (LOD) was also computed based on the definition of the triple standard deviation of the blank. The determination values of LOD for A, B, and C were found to be 9.9 μg/L, 12.2 μg/L and 13.8 μg/L, respectively. The mean value of carryover for PVDF fibre was 3.24%.
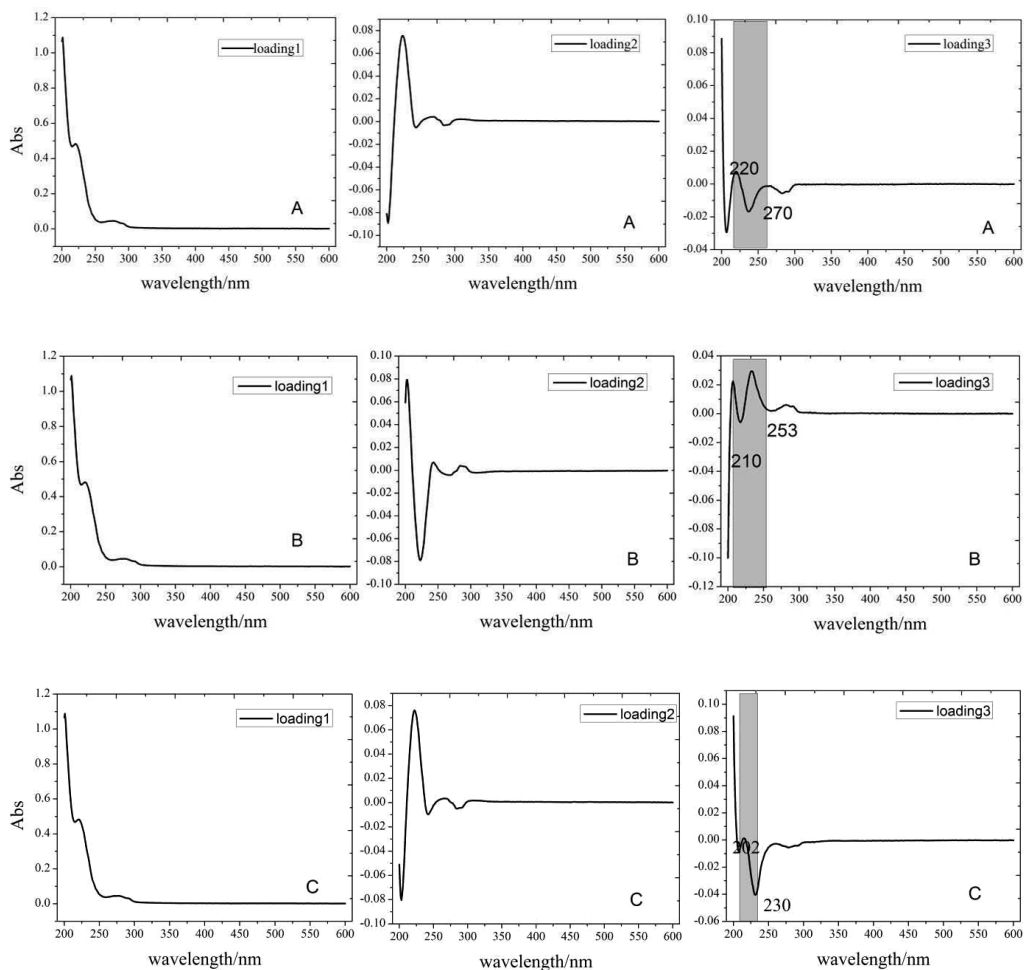

Fig. 7. Illustration of principal components for the UV-Vis measurements.

In order to determine the analytic degree of the PLS model for the mixed components, the loading test was carried out to analyse the absorption peaks of the components of the mixed substances and compare them with the peak positions of the real samples. The results show that the loading1 and loading 2 basically contain the mixed substances. The peak profiles obtained in loading 3 are consistent with the actual peak profiles of a single substance sample lying in the ranges of 220–270, 210–253, 202–230 nm, respectively.

3.5. Determination of real sample

In the previous experiments, the optimal conditions were obtained from a standard solution. In this context, unknown real samples with traces of organic acid compounds were quantified by the PLS method as a prediction set after the enrichment by REFSPE, elution by ethanol and detection by the UV-Vis spectrophotometer. The predicted concentration and the *enrichment factor* (EF) values are shown in Table 3. It can be clearly seen from the results of 20 repeated trials that the enrichment factors of the three species reach 17, 19 and 20 times, respectively. The RSD ($n = 20$) values of each component are 1.17%, 1.11% and 0.86% with the relative recovery of 84.8–117.9. Therefore, the proposed method can be used to determine traces of charged substances effectively.

Table 3. The final predicted concentration and enrichment factor values.

Sample	$C_{P,A}$ (mg/L)	EF_A	$C_{P,B}$ (mg/L)	EF_B	$C_{P,C}$ (mg/L)	EF_C
1	85.137	17.027	97.516	19.503	101.729	20.346
2	85.331	17.066	96.501	19.300	103.436	20.687
3	86.102	17.220	95.528	19.106	102.820	20.564
4	87.352	17.470	96.594	19.319	101.761	20.352
5	86.465	17.293	98.644	19.729	102.721	20.544
6	88.107	17.621	97.670	19.534	102.163	20.433
7	86.550	17.310	98.827	19.765	102.340	20.468
8	87.312	17.462	96.579	19.316	102.644	20.529
9	85.524	17.104	97.536	19.507	101.088	20.218
10	86.061	17.212	97.194	19.439	103.199	20.640
11	85.342	17.068	95.218	19.044	100.526	20.105
12	87.563	17.512	96.954	19.391	101.355	20.271
13	86.213	17.242	96.105	19.221	103.335	20.667
14	87.361	17.472	95.755	19.151	104.155	20.831
15	86.012	17.202	96.753	19.351	101.759	20.352
16	85.135	17.027	97.654	19.531	101.814	20.363
17	87.221	17.444	97.405	19.481	103.085	20.617
18	85.207	17.041	97.685	19.537	102.255	20.451
19	88.219	17.643	99.005	19.801	101.683	20.337
20	85.231	17.046	97.418	19.484	102.528	20.506

4. Conclusion

In this paper, the feasibility of a combined method using REFSPE enrichment, ultrasonic eluting, UV-Vis detection and PLS calculation was tested for the determination of organic acids in water samples. All the factors influencing the experiments were optimized based on the established flowchart of the determination. The forecast analysis method, which coupled UV-Vis spectra with the PLS model, was optimized by selecting an appropriate spectral pre-processing method, optimizing the modelling wavelength interval and adjusting the number of dependent variables. The optimized model was used to quantify unknown real samples and proved to be successful. The proposed tentative method provides a simple and effective solution for the de-

termination of traces of mixed organic acids in aqueous solutions. The chemo-metric analysis which can serve as a supplementary means in the experiments, will offer a great help to the sophisticated scientific research.

Acknowledgments

References

[1] Mendiguchia, C., Garcia-Vargas, M., Moreno, C. (2008). Screening of dissolved heavy metals (Cu, Zn, Mn, Al, Cd, Ni, Pb) in seawater by a liquid-membrane-ICP-MS approach. *Anal. Bioanal. Chem.*, 391, 773–778.

[2] Salama, A.K. (2015). Assessment of metals in cosmetics commonly used in saudi arabia. *Environ. Monit. Assess.*, 188, 553.

[3] Nakajima, H., Hara, K., Yamamoto, Y., Itoh, K. (2015). Effects of Cu on the content of chlorophylls and secondary metabolites in the Cu-hyperaccumulator lichen Stereocaulon japonicum. *Ecotoxicol. Environ. Saf.*, 113, 477–482.

[4] Jia, J., Wu, A., Luan, S. (2014). Spectrometry recognition of polyethyleneimine towards heavy metal ions. *Colloids Surf., A*, 449, 1–7.

[5] Weindorf, D.C., Zhu, Y., Chakraborty, S., Bakr, N., Huang, B. (2012). Use of portable X-ray fluorescence spectrometry for environmental quality assessment of peri-urban agriculture. *Environ. Monit. Assess.*, 184, 217–227.

[6] Shan, Q., Zhang, X.L., Zhang, Y., Jia, W.B., Ling, Y.S., Hei, D.Q., Chu, S.N. (2015). Development of an online X-ray fluorescence analysis system for heavy metals measurement in cement raw meal. *Spectrosc. Lett.*, 49, 188–193.

[7] El, H.J., De, M.F., Bou, S.J., Canioni, L., Mounaix, P., Bousquet, B. (2014). Chemometrics applied to quantitative analysis of ternary mixtures by terahertz spectroscopy. *Anal. Chem.*, 86, 4927–4933.

[8] Nishikiori, R., Yamaguchi, M., Takano, K., Enatsu, T., Tani, M., de Silva, U.C., Kawashita, N., Takagi, T., Morimoto, S., Hangyo, M. (2008). Application of partial least square on quantitative analysis of L-, D-, and DL-tartaric acid by terahertz absorption spectra. *Chem. Pharm. Bull.*, 56, 305–307.

[9] Dogan, C.E., Akcin, G. (2007). Solid phase extraction and determination of lead in water samples using silica gel homogeneously modified by thiosalicylic acid. *Anal. Lett.*, 40, 2524–2543.

[10] Feist, B., Mikula, B. (2014). Preconcentration of some metal ions with lanthanum-8-hydroxyquinoline co-precipitation system. *Food Chem.*, 147, 225–229.

[11] Mehdinia, A., Aziz-Zanjani, M.O. (2013). Advances for sensitive, rapid and selective extraction in different configurations of solid-phase microextraction. *TrAC, Trends Anal. Chem.*, 51, 13–22.

[12] Montesdeoca-Esponda, S., Vega-Morales, T., Sosa-Ferrera, Z., Santana-Rodríguez, J.J. (2013). Extraction and determination methodologies for benzotriazole UV stabilizers in personal-care products in environmental and biological samples. *TrAC, Trends Anal. Chem.*, 51, 23–32.

[13] Olawoyin, R., Heidrich, B., Oyewole, S., Okareh, O.T., Mcglothlin, C.W. (2014). Chemometric analysis of ecological toxicants in petrochemical and industrial environments. *Chemosphere*, 112, 114–119.

[14] Purcell, D.E., O'Shea, M.G., Kokot, S. (2007). Role of chemometrics for at-field application of NIR spectroscopy to predict sugarcane clonal performance. *Chemom. Intell. Lab. Syst.*, 87, 113–124.

[15] Chen, W.R., Bin, J., Lu, H.M., Zhang, Z.M., Liang, Y.Z. (2016). Calibration transfer via an extreme learning machine auto-encoder. *Analyst*, 141, 1973.

[16] Ni, Y., Huang, C., Kokot, S. (2007). Simultaneous determination of iron and aluminium by differential kinetic spectrophotometric method and chemometrics. *Anal. Chim. Acta*, 599, 209–218.

[17] Rios-Reina, R., Elcoroaristizabal, S., Ocana-Gonzalez, J.A., Garcia-Gonzalez, D.L., Amigo, J.M., Callejon, R.M. (2017). Characterization and authentication of Spanish PDO wine vinegars using multidimensional fluorescence and chemometrics. *Food chem.*, 230, 108–116.

[18] Baptistao, M., Rocha, W.F.d.C., Poppi, R.J. (2011). Quality control of the paracetamol drug by chemometrics and imaging spectroscopy in the near infrared region. *J. Mol. Struct.*, 1002, 167–171.

[19] Soares, J.S., Barman, I., Dingari, N.C., Volynskaya, Z., Liu, W., Klein, N., Plecha, D., Dasari, R.R., Fitzmaurice, M. (2013). Diagnostic power of diffuse reflectance spectroscopy for targeted detection of breast lesions with microcalcifications. *P. Natl. Acad. Sci. USA*, 110, 471–476.

[20] Pandey, R., Paidi, S.K., Valdez, T.A., Zhang, C., Spegazzini, N., Dasari, R.R., Barman, I. (2017). Noninvasive Monitoring of Blood Glucose with Raman Spectroscopy. *Accounts Chem. Res.*, 20150, 264–272.

[21] Paidi, S.K., Siddhanta, S., Strouse, R., McGivney, J.B., Larkin, C., Barman, I. (2016). Rapid identification of biotherapeutics with label-free Raman spectroscopy. *Anal. Chem.*, 88, 4361–4368.

[22] Gurbanov, R., Gozen, A.G., Severcan, F. (2017). Rapid classification of heavy metal-exposed freshwater bacteria by infrared spectroscopy coupled with chemometrics using supervised method. *Spectrochim. Acta A*, 189, 282–290.

[23] Guo, Y., Liu, X., Han, Y., Bian, X., Zhang, Q. (2017). Effective enrichment and simultaneous quantitative analysis of trace heavy metal ions mixture in aqueous samples by the combination of radial electric focusing solid phase extraction, UV-Vis spectrophotometric determination and partial least squares regression. *Water, Air, Soil Pollut.*, 228, 317.

[24] Humayun, H.Y., Shaarani, M.N.N.M., Warrior, A., Abdullah, B., Salam, M.A. (2016). The effect of co-solvent on the solubility of a sparingly soluble crystal of benzoic acid. *Procedia Eng.*, 148, 1320–1325.