USE OF SPECTROMETRY IN NEAR-INFRARED REGION AND CHEMOMETRICS FOR ORGANIC MATERIAL QUALITY CONTROL

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Introduction

Mass fraction of epoxy groups is one of the basic parameters which specify ability of epoxy resins to enter a polymerization reaction. It designates average molecular weight and is the basic quality measure at the time of incoming control [1-4]. At present, the acid-base titration standardized procedure described in GOST 12497 [5] is used for determination of epoxy group mass fraction. The procedure is quite simple to implement, however, there is a number of difficulties. First, the procedure is generally associated with high labor cost. Secondly, sample preparation involves considerable amount of organic solvents. Thirdly, the procedure is followed by generation of waste subject to recovery. In this context, spectrometry in near-infrared region (NIR) and chemometrics are the alternative procedures which offer several advantages. First, these procedures enable receiving bulk information at short time. Secondly, application of non-destructive method doesn't require sample preparation. Thirdly, processing of spectral data using chemometric approach allows conducting signal-noise discrimination, thus facilitates construction of calibration dependences and optimizes analysis procedure and processing of multidimensional data array [6, 7].

Materials and Equipment

Samples of ED-16, ED-20, DEG-1 epoxy resins of different batches manufactured in 2009 – 2011 were tested. Epoxy group mass fraction for all samples was determined by the standardized procedure of acid-base titration with absolute resultant error ±0.14 %. The results comprise 95 samples of ED-16 epoxy resins with epoxy group mass fraction of ω_{CHEM} within the range from 15.0 % to 18.0 %; 67 samples of ED-20 resins with epoxy group mass fraction ω_{CHEM} within the range from 20.0 % to 23.0 %; 34 samples of DEG-1 resins with epoxy group mass fraction ω_{CHEM} within the range from 21.0 % to 28.0 %. Tests were carried out by using Thermo Fischer Scientific Antaris II near-infrared spectrometer operated by Omnic, TQ Analyst , Result Software. Transmission module was used for sample introduction. The module enables to register IR spectrum of liquid samples in test tubes or cells. Samples of epoxy resins were placed in glass test tubes of 40 mm high and 8 mm in diameter.

Results and discussion

Shown in Fig. 1 and 2 are the IR spectra of ED-16, ED-20, DEG-1 epoxy resin samples. Literature data analysis disclosed that epoxy ring vibrations occur in near-infrared spectrum at 4523 cm^{-1} and 4510 cm^{-1} [8,9], and also at 6060 cm^{-1} [7]. Also, spectrums of DEG-1 resins (Fig. 2) reveal varying bands in the region of 5000 - 6000 cm^{-1} that may prove useful for construction of calibration model.

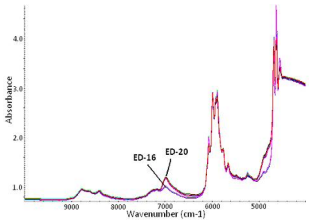

Figure 1 – IR spectrum of ED-16, ED-20 epoxy resins samples

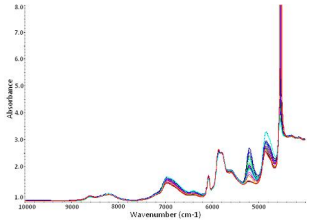

Figure 2 – IR spectrum of DEG-1 epoxy resins samples

To choose the optimum region of IR spectrum of ED-16, ED-20 resins for quantitative determination of epoxy groups, two ranges of 4300-4550 cm^{-1} and 6000-6900 cm^{-1} were conventionally set for DEG-1 resins – four ranges, corresponding to IR spectrum variations, namely: 4500-4600 cm^{-1}, 5049-5326 cm^{-1}, 5350-6017 cm^{-1}, 6013-6098 cm^{-1}. Calibration models were constructed in each spectral range using method of projection on latent structure (PLS) and their quality was estimated by several criterias: RMSEC, RMSEP, R^2 and number of PLS factors. The results are given in Table 1.

Table 1 - Calibration model parameters for determination of epoxy group mass fraction in various wave number ranges.

Resin Type	ED-16		ED-20		DEG-1			
Region (cm^{-1})	4300 – 4500	6000 – 6900	4300 – 4500	6000 – 6900	4500 – 4600	5049 – 5326	5350 – 6017	6013 – 6098
RMSEC, %	0.149	0.0995	0.172	0.0979	0.460	0.966	0.629	0.438
RMSEP, %	0.191	0.0648	0.253	0.0754	0.520	12.0	0.639	0.373
R^2	0.945	0.941	0.932	0.980	0.930	0.911	0.964	0.983
PLS factors	3	4	4	5	3	3	3	3

It is clear from the results obtained (Table 1) that in wavenumber range of 6000-6900 cm^{-1} the calibration model for ED-20 resins has optimal parameters: less RMSEC and RMSEP values, larger R^2 value. R^2 factor of calibration model constructed for ED-16 resins in wave number range of 4300-4500 cm^{-1} is slightly greater than in the range of 6000-6900 cm^{-1}. However, low value of RMSEC and RMSEP demonstrated that the region of 6000-6900 cm^{-1} is suitable for ED-16 resins. The number of PLS factors for the constructed models differs slightly. For DEG-1 resins the quantity of basic components also is not a determining factor for selection of one wave number range or another, as this quantity is identical to all models. The calibration models constructed in wavenumber ranges of 4500-4600 cm^{-1}, 5049-5326 cm^{-1}, 5350-6017 cm^{-1} have rather low R^2 factor. The model constructed in range of 6013-6098 has the largest R^2 factor value; therefore, it describes to the best advantage the relationship between spectral characteristics and epoxy group concentration in calibration samples. This model has the least RMSEC and RMSEP value and also their optimal agreement. Thus, study of all quality parameters for quantitative determination of epoxy group mass fraction in DEG-1 resins showed that the most useful was the model with wave number range of 6013-6098 cm^{-1} (Table 1).

Calibration models were constructed by using multidimensional techniques, such as principal component regression (PCR) and projection on latent structures (PLS). IR spectra differentiation was also applied for initial spectral data processing (IR spectrum first-order derivative). Sample quantities used in training and test sets when constructing the calibration models are presented in Table 2.

Table 2 – Sample quantities used in training and test sets when constructing the calibration models for determination of epoxy group mass fraction in ED-16, ED-20 and DEG-1 epoxy resins.

Type of epoxy resin	Quantity of samples, pcs	
	Training Set	Test Set
ED-16	77	18
ED-20	53	14
DEG-1	26	8

The accuracy and possibility of practical application of constructed calibration models was estimated according to the following values: RMSEC, RMSEP, R^2, number of PLS factors. Parameters of constructed calibration models are displayed in Tables 3, 4, 5.

Table 3 – Calibration model parameters for determination of epoxy group mass fraction in ED-16 epoxy resins in the range from 15.0% to 18.0% using near-infrared spectrometry.

Parameter	Model		
	a	b	c
Pre-treatment	No processing	No processing	First derivative
Calibration methods	PLC	PCR	PLC
Region, cm^{-1}	6000-6900	6000-6900	6000-6900
R^2	0.945	0.826	0.855
RMSEC, %	0.0995	0.238	0.158
RMSEP, %	0.0648	0.275	0.0997
PLS factors	4	3	1

An analysis of the results obtained (Table 3) showed that for ED-16 epoxy resins the most stable and accurate model is **a** model. In spite of the fact that the model was constructed using the largest value of basic components, it has the least RMSEC and RMSEP values and R^2 correlation factor has the closest approach to unity. Models **b** and **c** have rather low correlation factor; therefore, the agreement between spectral characteristics and known mass fraction of epoxy groups gets worse. Besides, RMSEC and RMSEP parameter increase results in accuracy degradation of calibration models constructed (Table 3). Similar results were obtained for ED-20 epoxy resins (Table 4). Accordingly, PLC technique makes it possible to obtain epoxy group mass fraction values to greater accuracy, than PCR technique. Further data processing doesn't lead to desired improvement in quality of calibration models.

Table 4 – Calibration model parameters for determination of epoxy group mass fraction in ED-20 epoxy resins in the range from 20.0% to 23.0% using near-infrared spectrometry

Parameter	Model		
	a	b	c
Pre-treatment	No processing	No processing	First derivative
Calibration methods	PLS	PCR	PLS
Region, cm^{-1}	6000-6900	6000-6900	6000-6900
R^2	0.963	0.924	0.932
RMSEC, %	0.128	0.181	0.172
RMSEP, %	0.169	0.164	0.253
PLS factors	4	2	4

The parameters of calibration models constructed for DEG-1 resins are reproduced in Table 5. Model **c** has high correlation factor, however RMSEC and RMSEP values do not agree perfectly well amongst themselves. Models **a** and **b** have similar quality parameters and differ only in basic components quantity. Model **a** is more accurate because it was constructed using fewer basic components.

Table 5 – Calibration model parameters for determination of epoxy group mass fraction in DEG-1 epoxy resins using near-infrared spectrometry.

Parameter	Model		
	a	b	c
Pre-treatment	No processing	No processing	First derivative
Calibration methods	PLS	PCR	PLS
Region, cm^{-1}	6013-6098	6013-6098	6013-6098
R^2	0.991	0.991	0.999
RMSEC, %	0.290	0.285	0.072
RMSEP, %	0.355	0.349	0.793
PLS factors	4	7	7

Figures 3, 4 and 5 display correlation dependences of epoxy group mass fraction determination results obtained using two procedures (i.e. acid-base titration ω_{CHEM} and near-infrared spectrometry ω_{NIR}). Ideally, correlation dependences should represent straight lines located at an angle 45° to axes of coordinates; however, practically it is not always possible to obtain the same result.

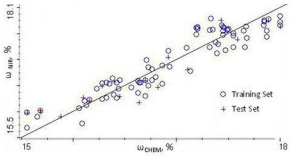

Figure 3 - Correlation dependences of epoxy group mass fraction determination results obtained by using acid-base titration (ω_{CHEM}) and near-infrared spectrometry (ω_{NIR}) for ED-16 epoxy resins

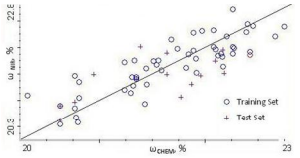

Figure 4 - Correlation dependences of epoxy group mass fraction determination results obtained by using acid-base titration (ω_{CHEM}) and near-infrared spectrometry (ω_{NIR}) for ED-20 epoxy resins

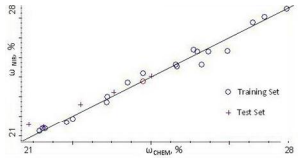

Figure 5 - Correlation dependences of epoxy group mass fraction determination results obtained by using acid-base titration (ω_{CHEM}) and near-infrared spectrometry (ω_{NIR}) for DEG-1 epoxy resins

Thus, by using PLC technique and by means of near-infrared spectrometry the calibration models for determination of epoxy group mass fraction for ED-16, ED-20 and DEG-1 epoxy resins were constructed. Metrological characteristics of error in epoxy group mass fraction determination are given in Table 6.

Table 6 - Characteristics of relative accuracy in measurement of epoxy group mass fraction in ED-16, ED-20 and DEG-1 epoxy resins using confidence factor P=0,95 and two parallel determinations (n=2).

Type of epoxy resin	Measuring range for epoxy group mass fraction, %	Convergence characteristics $\pm\varepsilon$, in parts	Residual bias characteristics, $\pm\theta$, in parts	Confidence resultant error $\pm\theta$, in parts
ED-16	from 15.0 to 18.0 incl.	0.015	0.019	0.033
ED-20	from 20.0 to 23.0 incl.	0.010	0.011	0.020
DEG-1	from 21.0 to 28.0 incl.	0.010	0.013	0.020

The estimate of correctness of epoxy group mass fraction determination using near-infrared spectrometry shows insignificance of bias in the whole measuring range for each type of epoxy resin.

Conclusions

The possibility of using near-infrared spectrometry technique and chemometrics for an analysis of ED-16, ED-20 and DEG-1 epoxy resins were illustrated. The express procedures for epoxy group mass fraction determination of ED-16, ED-20 and DEG-1 resins were developed. The use of developed express procedures instead of the existing standardized procedure makes it possible to reduce considerably the labor cost and analysis time for organic material quality control.

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