

IR Spectroscopy as a Quantitative and Predictive Analysis Method of Phenol–Formaldehyde Resol Resins

TIMO HOLOPAINEN,^{1,*} LEILA ALVILA,¹ JOUNI RAINIO,² TUULA T. PAKKANEN¹

¹ University of Joensuu, Department of Chemistry, P.O. Box 111, FIN-80101 Joensuu, Finland

² Dynoresin Oy, FIN-82430 Puhos, Finland

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ABSTRACT: A set of resin samples was characterized by IR and ¹³C-NMR spectroscopy. The suitability of IR spectroscopy for the quantitative analysis of resins was evaluated by statistical methods using the NMR reference data as calibration. The values of interesting properties, for example, the amount of free phenol and the formaldehyde-to-phenol (F/P) molar ratio, of the resins being similar to the calibration resins were predicted from the IR spectra. Also, the predicted results were compared with the ones observed by ¹³C-NMR spectroscopy. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 2175–2185, 1998

Key words: IR spectroscopy; phenol–formaldehyde resin; resol resin; multicomponent spectroscopic analysis

INTRODUCTION

The condensation, modification, and thermal curing of phenol–formaldehyde resol resins can be followed using IR spectroscopy. Valuable qualitative and semiquantitative information, for example, the nature and types of reaction, can be revealed from IR studies. Especially, the appearance of free phenol, methylol groups, and dimethylene ether bridges as well as the formaldehyde-to-phenol (F/P) molar ratio have been studied by IR spectroscopy.^{1–8} In this study, a quick and economic IR spectroscopy was utilized for phenol–formaldehyde resol resins as a predictive and quantitative analysis method. The calibration of the system was done with ¹³C-NMR results and by using multivariate analysis, which has already been used successfully, for example, in FTIR spectroscopy of coals and wood lignins.^{9–12}

*Present address: Dynoresin Oy, FIN-82430 Puhos, Finland.

Correspondence to: L. Alvila.

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EXPERIMENTAL

Resin Preparation

The raw materials, phenol (purchased from J. T. Baker, Deventer, Holland) and formaldehyde (produced by Dynoresin Oy, Puhos, Finland, from methanol), were of high-purity grade. Formaldehyde was used as a formalin solution, which contained 45% formaldehyde, water, and some methanol.

A series of 14 low molecular resins (1–14, Table I) was condensed in two stages, and a series of four high molecular resins in one stage (resins 15 and 16, Table I) or in two stages (resins 17 and 18, Table I) with NaOH as a catalyst (produced by Merck, Darmstadt, Germany). The resins were prepared in a 6-dm³ glass reactor equipped with a stirrer, a condenser, and external cooling and internal heating units. The molar ratio of F/P varied between 1.60 and 2.30, the condensation viscosity between 55 and 800 mPas, and the temperature was 70 or 80°C. The resins were stored frozen at –18°C until analysis.

Table I Condensation Conditions of the Resins

Resin No.	F/P Molar Ratio	Condensation Alkalinity (wt %)	Condensation Viscosity (mPas)	Condensation Temperature (°C)
1	1.60	1.16	60	70
2	1.95	1.25	500	80
3	2.00	1.20	500	80
4	2.08	1.23	500	80
5	2.15	1.25	500	80
6	2.20	1.03	500	80
7	2.20	1.14	500	80
8	2.20	1.20	500	80
9	2.20	1.55	500	80
10	2.30	1.22	500	80
11	1.90	1.25	500	80
12	1.90	1.50	55	70
13	2.08	1.15	350	80
14	2.20	1.13	350	80
15	2.00	1.85	200	80
16	1.99	1.82	800	80
17	1.90	1.42	70	70
18	2.10	6.50	500	80

NMR Experiments

The resins were characterized by NMR spectroscopy to obtain the calibration data set for IR studies. Quantitative ^{13}C -NMR spectra were recorded with a Bruker AMX-400 spectrometer, observing ^{13}C at 100.623 MHz and using an inverse gated ^1H decoupling technique. Typical spectra of the resins were run with a 90° pulse of $11.5\ \mu\text{s}$, a 120-s pulse delay, 600 scans, and a 20-h acquisition time.

DMSO- d_6 , 99 atom % deuterated dimethyl sulf-

oxide (purchased from Aldrich, Steinheim, Germany), was used as a solvent, an agent to obtain a deuterium lock, and an internal chemical shift standard. The ^{13}C signals of the resins were referenced to the central resonance line of DMSO with a δ value of 39.5 ppm.

IR Experiments

All the resins were pretreated under the same conditions. A resin sample of 2.0 g was dissolved

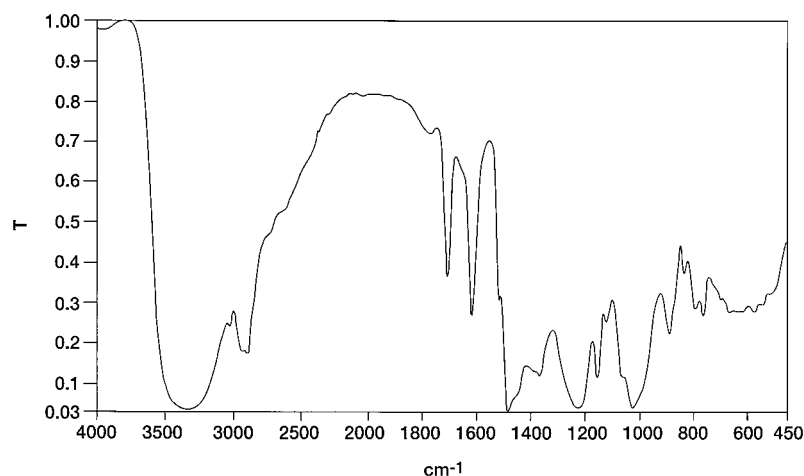


Figure 1 IR spectrum of phenolic resin 10.

in resins (1–14) or mixed with (resins 15–18) 15 mL of acetone (p.a. grade). The mixture was stirred for 1.5 h with 2.5 g of activated molecular sieves of 4 Å to remove water from the resins. Any heat treatment of the resins or resin–solvent systems could not be used due to the rapid curing of the resol resins.

Resins were characterized by a Perkin-Elmer System 2000 FTIR spectrometer equipped with a fast-recovery deuterated triglycine sulfate (FR-DTGS) detector, a single-beam Michelson interferometer with a KBr beamsplitter, a voltage-stabilized air-cooler, and a wire coil as a source. The IR spectra of all the resins were recorded as surface films on the top of KBr tablets after evaporation of the acetone solvent over the drying agent in an exiccator. All spectra were recorded at room temperature, normalized, and baselines were corrected.

IR Software

The IR software^{13,14} consisted of IR Data Manager Release 2 and QUANT+ supplied by Perkin-El-

Table II Assignment of Absorption Bands of the Phenol-Formaldehyde Resin

Wave No. (cm ⁻¹)	Assignment ^a	Nature
3350	$\nu(\text{OH})$	Phenolic and methylol (broad)
3060	$\nu(\text{CH})$	Aromatic
3020	$\nu(\text{CH})$	Aromatic
2930	$\nu_{\text{ip}}(\text{CH}_2)$	Aliphatic
2860	$\nu_{\text{op}}(\text{CH}_2)$	Aliphatic
[1700	$\nu(\text{C}=\text{O})$	Acetone residual]
1610	$\nu(\text{C}=\text{C})$	Benzene ring
1500	$\nu(\text{C}=\text{C})$	Benzene ring
1470	$d(\text{CH}_2)$	Aliphatic
1450	$\nu(\text{C}=\text{C})$	Benzene ring
1370	$d_{\text{ip}}(\text{OH})$	Phenolic
1240	$\nu_{\text{ip}}(\text{C}-\text{O})$	Phenolic
1160	$d_{\text{ip}}(\text{CH})$	Aromatic
1100	$d_{\text{ip}}(\text{CH})$	Aromatic
1010	$\nu(\text{C}-\text{O})$	Methylol
880	$d_{\text{op}}(\text{CH})$	Isolated H
820	$d_{\text{op}}(\text{CH})$	Adjacent 2H, <i>para</i> - substituted
790	$d_{\text{op}}(\text{CH})$	Adjacent 3H
760	$d_{\text{op}}(\text{CH})$	Adjacent 4H, <i>ortho</i> - substituted
690	$d_{\text{op}}(\text{CH})$	Adjacent 5H, phenol

^a ν = stretching, d = deformation, ip = in plane, op = out of plane.

Table III Data of Different Methods

Method	Data Range (cm ⁻¹) ^a		Step ^b (cm ⁻¹)	Baseline Correction of Standard Spectra	No. Properties	No. Factors in Full Regression Model		No. Factors in Final Regression Model		
	Initial	Final				Phenol	Methanol	F/Psyn	F/Pmeas	
A	4000	600	4	No	4	4	1	1	1	1
B	1800	600	1	"	4	4	1	1	1	1
C	1700	700	1	"	4	4	1	1	1	1
D	4000	600	4	Along the strongest signal	10	4	1	1	3	1
E	1800	600	1	"	10	4	1	1	3	1
F	1800	600	1	"	4	4	1	1	3	1
G	1700	700	1	"	4	4	1	1	2	2
H	1800	600	1	At 1240 cm ⁻¹	4	4	1	1	3	1
I	1700	700	1	"	4	4	1	1	3	2

F/Psyn, the P/F molar ratio is synthesis; F/Pmeas, the F/P molar ratio analyzed by NMR.

^a Data with no blank ranges.

^b The step between data points.

Table IV ^{13}C -NMR Results of the Resins 1–10 Used as the IR Calibration Data Set and of the Resins 11–18 Used as Testing Data Set

Resin No.	Free Phenol (%)	Methanol ^a	F/P Molar Ratio		Aromatic Carbons			Methylol Groups ^a		Methylene Bridges ^a	
			In Synthesis	Measured	Phenoxy	Free <i>para</i> ^a	Free <i>ortho</i> ^a	<i>ortho</i>	<i>para</i>	<i>p-p'</i>	<i>o-p'</i>
1	10.45	0.119	1.60	1.58	1.00	0.168	0.748	0.864	0.147	0.166	0.247
2	3.35	0.474	1.95	1.94	1.00	0.062	0.044	0.984	0.108	0.266	0.451
3	2.62	0.440	2.00	2.04	1.00	0.050	0.386	1.005	0.124	0.250	0.405
4	2.73	0.416	2.08	2.03	1.00	0.046	0.361	0.983	0.121	0.214	0.422
5	1.40	0.473	2.15	2.31	1.00	0.034	0.304	1.079	0.123	0.276	0.466
6	1.45	0.359	2.20	2.27	1.00	0.026	0.276	0.973	0.076	0.225	0.338
7	1.14	0.394	2.20	2.44	1.00	0.028	0.263	1.064	0.110	0.248	0.397
8	2.12	0.455	2.20	2.23	1.00	0.037	0.318	1.023	0.124	0.214	0.456
9	1.45	0.462	2.20	2.34	1.00	0.017	0.221	1.098	0.106	0.388	0.364
10	1.18	0.487	2.30	2.34	1.00	0.020	0.218	1.053	0.123	0.314	0.389
11	4.22	0.119	1.90	1.87	1.00	0.066	0.458	0.955	0.127	0.214	0.394
12	1.40	0.186	1.90	1.75	1.00	0.138	0.650	0.929	0.169	0.204	0.226
13	2.04	0.440	2.08	2.00	1.00	0.045	0.351	1.040	0.112	0.265	0.321
14	1.44	0.150	2.20	1.82	1.00	trace	0.054	1.030	0.044	0.151	0.481
15	^b	0.367	2.00	2.13	1.00	0.063	0.216	1.170	0.033	0.201	0.490
16	^b	0.499	1.99	2.00	1.00	0.086	0.171	1.090	trace	0.155	0.577
17	^b	0.160	1.90	1.67	1.00	0.141	0.632	0.948	0.168	0.197	0.265
18	^b	0.455	2.10	2.00	1.00	0.072	0.056	1.050	0.036	0.169	0.557

^a The integral values are related to the value of 1.00 of the phenoxy carbon.

^b Inaccurate integration due to the broad phenolic signals of the spectrum of the high molecular weight resole resin.

mer. IR Data Manager Release 2 is the software package for acquiring, modifying, displaying, and printing IR spectra. QUANT+ is a chemometric quantitative analysis software package for multi-component spectroscopic analysis, which changes the IR spectrum to data points and calculates with statistical methods the correlations between the IR spectrum and the original data set obtained in this study by NMR spectroscopy.

The QUANT+ attempts to establish a relationship for each component of the property of interest between the spectra of a set of calibration standards and the corresponding property values determined by independent means. This relationship is used for subsequent prediction of unknown samples.^{14,15}

The steps of QUANT+ analysis are (1) method building, (2) calibration, (3) prediction, and (4) validation. The method building is a description of the method and all the parameters, such as conditions, processing the spectra, and property values of standards, which are used for calibration and subsequent prediction. QUANT+ calibration builds a regression model for each property in the method based on statistical criteria generated from the data of calibration standards. The calibration spectra are

treated as a matrix and subjected to principal component analysis (PCA), which allows each spectrum to be reduced to a weighted average of the minimum set of factors (principal components) needed to represent all the significant sources of variation, such as chemical, physical, and instrumental in the spectral data. Factors are generated on purely mathematical criteria and each factor describes an individual source of variation. By examining different combinations of factors, the changes occurring in the system can be recognized.^{13,14}

Correlations are established by multiple linear regression (MLR) between the amounts of each factor (the scores) in the spectra of the calibration standards and the corresponding property values from the independent measurement. Only factors that are statistically significant to the regression are retained in the final regression equation. This leads to a simple model.^{13,14}

Prediction of the property values of unknown samples is achieved by determining the scores for the unknown sample spectrum and substituting these into the regression equations. QUANT+ makes use of a matrix manipulating process in order to make a single-step procedure. This approach permits the generation of error and other prediction

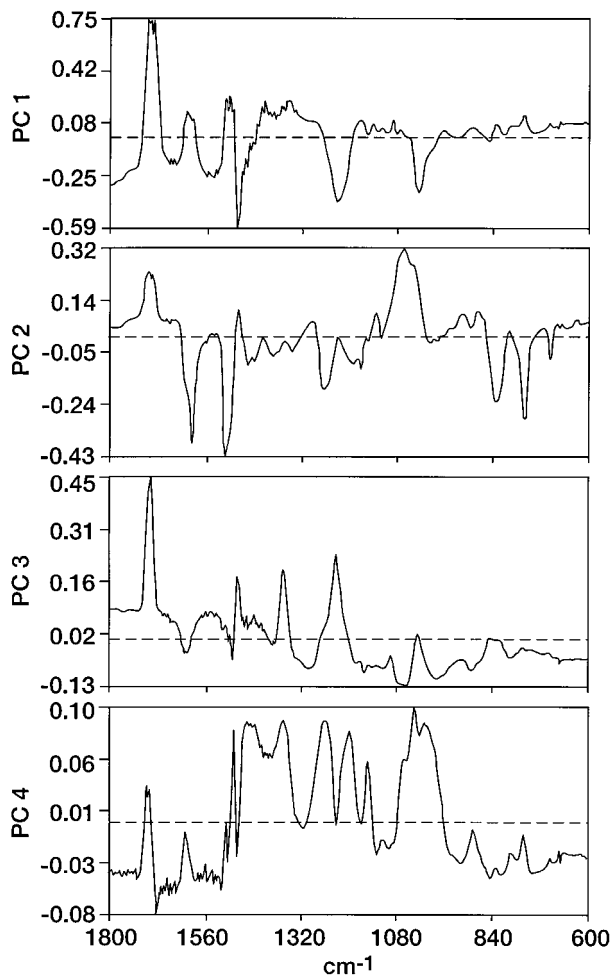


Figure 2 Principal components of method F.

statistics.^{13,14} With validation, QUANT+ tests the prediction of all possible models generated during the calibration.^{13,14}

RESULTS AND DISCUSSION

IR Spectra of Phenolic Resins

Figure 1 represents a typical IR spectrum of a phenolic resin (resin 10, Table I). The signals are assigned in Table II using the literature.¹⁻⁴

Methods

Resins 1–10 were used as standards. Methods A–I (Table III) with different data ranges, steps between different data points, baseline corrections of standard spectra, and number of properties was applied. In principle, method F is included in

Table V Statistical Data of Created Methods

Method	Variance (%)			SEE			SEP			F Value				
	Phenol	Methanol	F/P _{psyn}	Phenol	Methanol	F/P _{psyn}	Phenol	Methanol	F/P _{psyn}	Phenol	Methanol	F/P _{psyn}	F/P _{meas}	
A	98.85	46.95	49.71	0.40	0.084	0.15	0.52	0.145	0.15	0.33	107.5	7.1	7.9	4.6
B	98.78	43.93	42.47	0.41	0.087	0.16	0.53	0.160	0.19	0.30	101.2	6.3	5.9	3.8
C	97.91	42.05	52.42	0.50	0.088	0.15	0.78	0.138	0.20	0.30	93.6	5.8	8.8	5.9
D	84.23	52.27	98.26	1.18	0.080	0.03	1.63	0.134	0.05	0.19	42.7	8.8	112.7	16.2
E/F	95.29	65.13	99.05	0.64	0.068	0.02	1.43	0.124	0.03	0.15	161.9	14.9	207.7	36.2
G	96.38	67.47	99.03	0.60	0.066	0.02	1.49	0.143	0.03	0.15	93.3	16.7	357.8	30.3
H	91.18	61.96	98.78	0.88	0.071	0.03	1.63	0.123	0.04	0.14	82.7	13.0	161.9	29.4
I	84.41	63.98	99.21	1.17	0.070	0.02	2.12	0.121	0.04	0.14	43.3	14.2	250.2	31.2

F/P_{psyn}, the F/P molar ratio in synthesis; F/P_{meas}, the F/P molar ratio analyzed by NMR. In methods A–C, no baseline correction of the standard spectra was done, but in D–G, along the strongest signal and in H–I, at 1240 cm⁻¹.

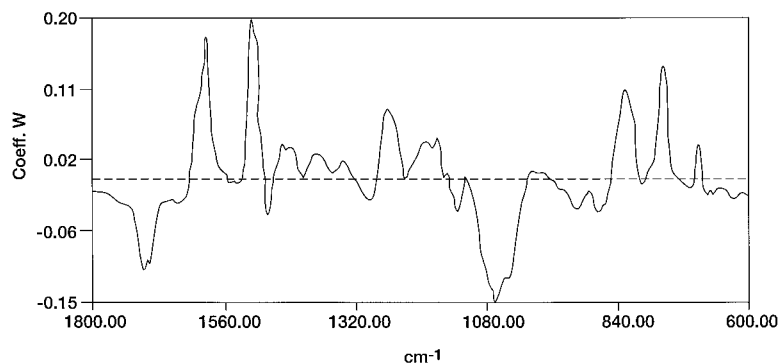


Figure 3 Coefficient weighting of the property phenol in method F.

method E, because data ranges, steps, and baseline corrections are similar, and all the four properties of method F are also included in the properties of method E. In methods A–C and F–I, the properties of interest were the amount of free phenol, the amount of methanol, and the F/P molar ratio, which all were obtained by ^{13}C -NMR spectroscopy,¹⁵ as well as the F/P molar ratio in the resin synthesis (Table IV). In addition to this, in two methods, D and E, the properties used for calibration included also the amount of free *ortho* and *para* carbons, methylol derivatives, and methylene bridges—that is, almost all the structural information acquired with ^{13}C -NMR spectroscopy for resins 1–10.

Principal Components, Coefficient Weightings, and Property Correlations

The principal components, which are the factors generated during the principal component analysis, are represented for method F in Figure 2. The first principal component selected is approximately a weighted average of all the original spec-

tra, and it gives the lowest average residual when subtracted from each spectrum on a least-square basis. The second principal component is the one giving the best overall fit to the residuals. The appearance of the remaining principal components is generally unpredictable as they account successively for the residual variation in the data set. The amount of principal components can be one-half of the number of standards.^{13,14}

Coefficient weightings and property correlations are calculated and displayed for the factors of the methods. Coefficient weightings of the individual variables are those applied by QUANT+ into the modeling of the property value for a given standard and are used for subsequent prediction of unknown samples. Coefficient weightings can determine which features in the data range are related to the property of interest. The intensities of the features in the coefficient weightings are unrelated to the intensities of the features in the spectrum of property of interest.^{13,14} Figure 3 represents the coefficient weighting of the property phenol in method F.

The property correlation spectrum, in Figure 4

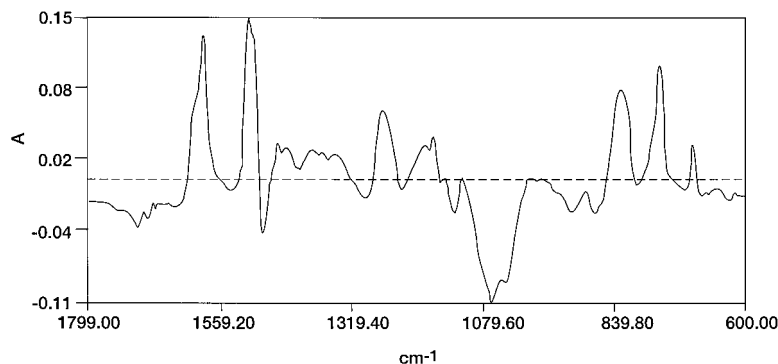


Figure 4 Property correlation spectrum of phenol in method F.

Table VI Additional Statistical Data of Methods D and E

Characteristic Groups	Variance (%)		SEE		SEP		<i>F</i> Value	
	D	E	D	E	D	E	D	E
Free <i>para</i> aromatic	90.12	94.60	0.016	0.011	0.022	0.022	31.9	140.0
Free <i>ortho</i> aromatic	56.02	59.89	0.127	0.121	0.185	0.200	10.2	12.0
<i>ortho</i> -Methylol	72.11	74.79	0.041	0.039	0.056	0.050	9.1	10.4
<i>para</i> -Methylol	57.85	47.28	0.012	0.014	0.016	0.016	11.0	7.2
<i>p-p'</i> -Methylene bridges	40.48	32.21	0.133	0.142	0.200	0.213	5.4	3.8
<i>o-p'</i> -Methylene bridges	26.25	32.53	0.060	0.057	0.114	0.118	2.9	3.9

for phenol in method F, represents the regions of the spectrum that are correlated with the property of interest. For each property defined in a QUANT+ method, the property correlation spectrum is calculated by multiplying the differences between each spectrum and the mean spectrum by the difference between the corresponding property value and mean property value and summing over all samples in the data set. Correlated information is represented as positive bands, while negative bands occur when there exists negative correlation between a given constituent and the total contribution of the remaining constituents.^{13,14} In Figure 4, positive bands are found just in the regions of phenol signals.

Evaluation of Methods

The statistical data of the created methods, by the aid of which the quality of the method can be evaluated, is represented in Table V. The value of variance percent gives the proportion of variability of the property, for example, the contents of phenol, methanol, and F/P values. The variance values of phenol of all the methods are quite high, and most of them are quite close to the optimum of 100%. Also, the property F/P molar ratio in the synthesis has high variance values in the methods (D–I) with baseline corrections of the standard spectra. Some variance values of the property F/P molar ratio analyzed by ¹³C-NMR are quite acceptable.

The standard error of estimate (SEE) describes the model error, which represents the lower limit of the prediction error. It gives an indication of the quality of fit of the regression. The standard error of prediction (SEP) is the magnitude of the error expected when independent samples are predicted using the model.^{13,14} Naturally, the minor standard errors are preferable. All the F/P

errors are low, especially in the methods (D–I) with baseline corrections of the standard spectra. Most of the phenol errors are valid, but all the methanol errors can be estimated to be too high compared to the real values of methanol.

Also, the *F* value is a good indication of the performance of the method, because it can be regarded as a measure of the signal to noise. Ideally, this value should be as high as possible for a good model, and the poorest regressions give lower values than 3.0 for the *F* value.^{13,14} The *F* values of phenol of all the methods are especially valid as well as are the values of the F/P molar ratio in the synthesis of the methods D–I, where the baselines of the standard spectra were corrected. Again, the lower *F* values of methanol than those of phenol and of the F/P ratios indicate the invalidity of the methanol determination. The analysis of a methanol amount cannot be done by these methods, because during the IR sample preparation, some methanol may have evaporated.

As a conclusion, methods D–I with baseline corrections of standard spectra seemed to be valid. The effect of the spectral data range on the results is not found in this study. Methods E (or F, which differs from E only in the number of properties) and G could be evaluated as the best ones on the basis of high variances, low standard errors, and high *F* values.

The complementary statistical data of methods D and E, where the more complete ¹³C-NMR analysis of resins 1–10 is used in the calibration, are represented in Table VI. Statistical values, variance %, standard errors, and especially the *F* values higher than 3.0 indicate that methods D and E are best suited for the determination of free aromatic and methylol groups. However, the final estimation of the validity of the method can be done after studying the prediction results.

Table VII Analysis of Resin 11 by Selected Methods

Method	Baseline Correction of the Spectrum	Total Analysis				Phenol %				F/P Molar Ratio in Synthesis			
		RMS Error	Peak to Peak	M Distance	F Ratio	NMR Analysis	Predicted	R Error	M Distance	In Synthesis	Predicted	R Error	M Distance
A	No	0.012	0.080	0.06	4.7	4.22	4.22	0.43	0.15	1.90	2.00	0.16	0.35
B	"	0.013	0.078	0.06	6.0	4.22	4.22	0.44	0.15	1.90	2.07	0.17	0.26
C	"	0.013	0.073	0.07	6.0	4.22	4.22	0.53	0.19	1.90	2.06	0.16	0.26
D	"	0.055	0.356	3.11	44.4	4.22	4.22	1.24	0.27	1.90	2.08	0.03	0.17
E/F	"	0.037	0.294	1.80	20.2	4.22	4.22	0.68	0.33	1.90	1.98	0.03	0.17
G	"	0.034	0.255	1.52	17.8	4.22	4.22	0.65	0.25	1.90	1.96	0.02	0.25
H	"	0.063	0.440	3.12	48.8	4.22	4.22	0.97	0.52	1.90	1.87	0.03	0.30
I	"	0.053	0.364	2.59	35.9	4.22	4.22	1.27	0.43	1.90	1.94	0.04	2.72
A	Along the strongest signal	0.016	0.124	0.69	8.8	4.22	4.22	0.52	0.65	1.90	1.82	0.18	1.21
B	"	0.019	0.098	0.61	11.9	4.22	4.22	0.52	0.59	1.90	2.08	0.17	0.25
C	"	0.018	0.096	0.64	11.2	4.22	4.22	0.63	0.74	1.90	2.10	0.15	0.25
D	"	0.013	0.101	0.35	2.6	4.22	4.22	1.28	0.47	1.90	1.90	0.04	0.27
E/F	"	0.018	0.098	0.25	4.5	4.22	4.22	0.71	0.50	1.90	1.91	0.03	0.26
G	"	0.017	0.093	0.27	4.6	4.22	4.22	0.66	0.34	1.90	1.91	0.02	0.34
H	"	0.018	0.101	0.13	3.9	4.22	4.22	0.96	0.49	1.90	1.91	0.03	0.25
I	"	0.017	0.099	0.13	3.6	4.22	4.22	1.28	0.48	1.90	1.91	0.02	0.25
A	At 1240 cm ⁻¹	0.017	0.134	0.89	10.0	4.22	4.22	0.54	0.81	1.90	1.79	0.19	1.45
B	"	0.020	0.103	0.79	13.5	4.22	4.22	0.55	0.73	1.90	2.08	0.17	0.25
C	"	0.019	0.101	0.81	12.5	4.22	4.22	0.65	0.91	1.90	2.11	0.15	0.26
D	"	0.018	0.122	0.90	4.8	4.22	4.22	1.30	0.54	1.90	1.87	0.04	0.31
E/F	"	0.021	0.119	0.55	6.7	4.22	4.22	0.71	0.54	1.90	1.90	0.03	0.28
G	"	0.020	0.105	0.57	6.5	4.22	4.22	0.67	0.36	1.90	1.91	0.02	0.36
H	"	0.018	0.103	0.20	3.9	4.22	4.22	0.96	0.49	1.90	1.91	0.03	0.25
I	"	0.017	0.095	0.23	3.8	4.22	4.22	1.28	0.49	1.90	1.90	0.02	0.35

In methods A–C, no baseline correction of standard spectra was done, but in D–G, along the strongest signal, and in H–I, at 1240 cm⁻¹.

Table VIII Analysis of Structural Groups of Resin 11 by Method E

Baseline Correction of the Spectrum of Resin 11	Characteristic Groups	NMR Analysis	Predicted	<i>R</i> Error	<i>M</i> Distance
No	Free <i>para</i> aromatic	0.066	0.072	0.012	0.328
"	Free <i>ortho</i> aromatic	0.458	0.388	0.128	0.328
"	<i>ortho</i> -Methylol	0.955	0.981	0.041	0.222
"	<i>para</i> -Methylol	0.127	0.123	0.015	0.328
"	<i>p-p'</i> -Methylene bridges	0.214	0.277	0.151	0.328
"	<i>o-p'</i> -Methylene bridges	0.394	0.374	0.061	0.328
Along the strongest signal	Free <i>para</i> Aromatic	0.066	0.090	0.012	0.499
"	Free <i>ortho</i> Aromatic	0.458	0.446	0.132	0.499
"	<i>ortho</i> -Methylol	0.955	0.957	0.042	0.342
"	<i>para</i> -Methylol	0.127	0.128	0.015	0.499
"	<i>p-p'</i> -Methylene bridges	0.214	0.239	0.156	0.499
"	<i>o-p'</i> -Methylene bridges	0.394	0.358	0.063	0.499
At 1240 cm ⁻¹	Free <i>para</i> Aromatic	0.066	0.093	0.012	0.539
"	Free <i>ortho</i> Aromatic	0.458	0.456	0.133	0.539
"	<i>ortho</i> -Methylol	0.955	0.953	0.043	0.369
"	<i>para</i> -Methylol	0.127	0.129	0.015	0.539
"	<i>p-p'</i> -Methylene bridges	0.214	0.232	0.157	0.539
"	<i>o-p'</i> -Methylene bridges	0.394	0.355	0.063	0.539

In method E, baseline correction of standard spectra along the strongest signal was done.

Analysis of the Resins with the Created Methods

Methods A–I are evaluated with the spectrum of resin 11 (Table VII). The baselines of the IR spectra of the concerned sample resins were not corrected or the correction was done along the strongest signal or at the frequency of 1240 cm⁻¹, where the strong signal of the stretching of phenolic C—O appears.

The results are the predicted properties as well as the root mean-square of error, peak-to-peak error, Mahalanobis ratio (*M* distance ratio), and *F* ratio for total analysis, as well as the *R* error and *M* distance ratio for each property.

The root mean-square of an error (RMS error) gives an overall indication of the quality of reproduction of the observed spectrum. It should be of the order of the standard deviation of the noise in the spectrum. With a good estimate, it is below 0.08, and with a poor one, over 0.1.^{13,14} All the tested methods and all the correction procedures for resin 11 fulfill this requirement of a valid estimate.

The peak-to-peak error gives an indication of localized anomalies in the observed spectrum. It should be no more than about five times the RMS error if the residuals consist only of random noise. Larger values indicate features in the predicted sample not present in the calibration set.^{13,14} Most

of the peak-to-peak error values for resin 11 are only slightly over five times the RMS error.

The total *M* distance ratio is calculated using all the principal components in the calibration model. If the *M* distance ratio is greater than 1.0, it indicates features in the unknown sample spectrum that are not reflected in the calibration set. This indicates the incompatibility of the sample and calibration set. The property *M* distance ratio based only on the principal components in the reduced regression model is calculated for each property. Both the total and the property *M* distance ratios must be less than 1.0 if total confidence is to be attached to the predicted value.^{13,14} Most of the obtained *M* distance ratios for resin 11 are below the value of 1.0. The best results, the lowest *M* distances, are found in the cases when the baseline correction methods of the spectrum of resin 11 are similar to the baseline corrections of the standard spectra.

The spectral residual *F* ratio is the ratio of variance of the errors between the original and the calculated spectra and the average variance of factors not used in the multiple linear regression stage. An *F* ratio greater than 3.00 for an unknown sample should indicate an outlier.^{13,14} All the *F* ratios in the analysis of resin 11 are high, but, again, the lowest values are found if the spec-

Table IX Predicted Results Obtained by Method E/F

Resin	Phenol %			F/P Molar Ratio in Synthesis			F/P Molar Ratio Analyzed by NMR			
	NMR Analysis	Predicted	R Error	In Synthesis	Predicted	R Error	Measured	Predicted	R Error	M Distance
11	4.22	4.23	0.68	1.90	1.98	0.03	1.87	2.03	0.12	0.33
12	2.20	5.33	0.70	1.90	1.95	0.03	1.75	1.94	0.13	0.49
13	2.03	1.86	0.68	2.08	2.17	0.03	2.00	2.23	0.12	0.28
14	1.44	1.95	0.68	2.20	2.15	0.03	1.82	2.22	0.12	0.28
15	^a	^a	^a	2.00	2.16	0.03	2.13	2.30	0.12	0.37
16	^a	^a	^a	1.99	2.19	0.03	2.00	2.32	0.12	0.40
17	^a	^a	^a	1.90	2.02	0.03	1.67	2.03	0.12	0.33
18	^a	^a	^a	2.10	2.17	0.03	2.00	2.32	0.12	0.40

Baseline correction of spectra of standards in method E/F along the strongest signal and no baseline correction of spectra of resins 11–18 were done.

^a Not presented because of inaccurate NMR integration due to the broad phenolic signals of the spectrum of the high-molecular weight resole resins.

Table X Predicted Results Obtained by Method G

Resin	Phenol %			F/P Molar Ratio in Synthesis			F/P Molar Ratio Analyzed by NMR			
	NMR Analysis	Predicted	R Error	In Synthesis	Predicted	R Error	Measured	Predicted	R Error	M Distance
11	4.22	4.55	0.65	1.90	1.96	0.02	1.87	1.99	0.10	0.25
12	1.40	5.69	0.67	1.90	1.89	0.03	1.75	1.90	0.11	0.40
13	2.04	2.73	0.64	2.08	2.08	0.02	2.00	2.15	0.10	0.22
14	1.44	2.95	0.65	2.20	2.05	0.02	1.82	2.13	0.10	0.25
15	^a	^a	^a	2.00	2.04	0.03	2.13	2.13	0.11	0.47
16	^a	^a	^a	1.99	2.07	0.03	2.00	2.16	0.11	0.51
17	^a	^a	^a	1.90	1.95	0.02	1.67	1.98	0.10	0.26
18	^a	^a	^a	2.10	2.05	0.03	2.00	2.14	0.11	0.48

Baseline correction of spectra of standards in method G along the strongest signal and no baseline correction of spectra of resins 11–18 were done.

^a Not presented because of inaccurate NMR integration due to the broad phenolic signals of the spectrum of the high molecular weight resole resins.

trum of resin 11 is exposed to the similar baseline correction as the standard spectra.

The R error for the property gives a 95% confidence interval for the accuracy of the prediction result, provided that the sample is spanned by the calibration set.^{13,14} As a result, half of the phenol values of resin 11 are valid, taking into account the confidence interval of the R error. The best prediction for the phenol content is reached when the baseline of the spectrum of resin 11 was not corrected. The correction seems to have a strong effect on the phenol signal as well as on the results containing phenol. All the methods give reasonable predicted values for the F/P molar ratio of resin 11.

The structural data analyzed with method E for resin 11 is collected in Table VIII. The prediction of the structural groups of resin 11 seems to be quite acceptable. All the M distance values are valid. The whole prediction of structural groups was best when the baseline of the spectrum of resin 11 was corrected as well as the baselines of the standard spectra.

The results of methods E (or F) and G were chosen for the further studies. The phenol contents of low molecular weight resins 11–14 and the F/P molar ratios of resins 11–18 were predicted by these methods. The results are displayed in Tables IX and X. The ¹³C-NMR analysis of the phenol contents of high molecular weight resins was not accurate enough for the further studies due to the broad signals of the phenolic region. In method E (or F), the NMR-analyzed phenol contents are included in the predicted phenol contents in the limits of R error, except the phenol of resin 12. In method G, the prediction results of the phenol content are not as valid as in method E (or F). The predicted F/P molar ratio values are close to the ones calculated from the initial materials, but not just within the low R error values. Instead, the predicted F/P values deviate more from the NMR-analyzed ones, although no extremely invalid results are found. The baseline correction of the resin spectra along the strongest signal as done in the standard spectra was found to improve the prediction of the F/P values.

CONCLUSIONS

The quantitative results obtained with FTIR spectroscopy using multicomponent spectroscopic analysis of a software package QUANT+ were quite reliable for detecting the amount of free phenol and the F/P molar ratio. Chemometric programs can be used quite effectively in this type of analysis of resins. The structural data of phenol-formaldehyde resol resins predicted with IR spectroscopy is quite congruent with the information obtained by ¹³C-NMR spectroscopy.

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