Analysis of Amino Resins by Carbon/Nitrogen Analyzer. I. Mole Ratios of Components

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Synopsis

Techniques for the determination of the formaldehyde to urea and the formaldehyde to melamine ratios by means of an elemental carbon-nitrogen analyzer are described. Etherified resins require additionally an NMR spectrum of the analyzed sample. Mathematical equations are presented which relate the experimentally determined carbon and nitrogen contents to the compositional characteristics of amino resins. For etherified resins, the ratio of alkoxy groups to the total formaldehyde is also determined. The techniques are assessed by analyzing model samples and by the propagation-of-error treatment of the equations. It is shown that the F/U and F/M ratios can be determined with a good accuracy whether or not the resin is etherified.

INTRODUCTION

The structural analysis of urea–formaldehyde (UF) or melamine–formaldehyde (MF) resins often becomes tedious and time-consuming work. Even such basic information as the formaldehyde to urea ratio (F/U) or the formaldehyde to melamine ratio (F/M) may require a full day's work when the total formaldehyde and the total amine contents are determined by classical methods.[1]

Recent advances in instrumentation allow more elegant and rapid procedures to be employed. Carbon-nitrogen elemental analyzers automatically process the resin sample and supply the carbon and nitrogen contents. From these the structural information can be calculated by means of mathematical equations. As the elements enter the equations in the form of a ratio, the weight of sample is irrelevant to the accuracy of determination and the analysis is very simple, fast, and accurate. Nonmodified resins can be analyzed in the liquid form, if preferred, with no effect of possible water evaporation during sample handling on the F/U or F/M ratio determination.

In the case of etherified amino resins, such as methoxylated, butoxylated, and similar amino resins, some of the total carbon content originates in the alkyl groups. The calculation of F/U or F/M ratios requires knowledge of the ratio of the carbon content originating from formaldehyde to the carbon content originating from both formaldehyde and the alkyl groups. This information can easily be obtained by means of NMR spectroscopy.[2–4]

It should be realized that the presence of components other than urea, melamine, formaldehyde, and alkoxy groups (OR) invalidates the equations for calculations of F/U and F/M ratios as outlined in this work. However, it should not be difficult to derive new equations which would consider the presence of other components such as sugars, polyglycols, dicyanides, etc. This would be practical if such modifiers could be identified and determined. The case of al-

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koxylated resins—which is elaborated upon in this work—can serve as an example.

EXPERIMENTAL

The carbon and nitrogen contents in resins were determined by means of a Perkin-Elmer Elemental Analyzer Model 240. Solid samples were analyzed in a platinum boat. Liquid samples were enclosed in tin capsules. The boat, capsules, and a high-pressure sealing device for enclosing the capsules were obtained from Perkin-Elmer. A blank run for the purpose of rinsing was done before each actual analysis and before the determination of blank values used in the calculations.

The model samples of nonetherified resins were industrial UF resins manufactured by Reichhold plants and laboratory products. Monomethylolurea monomethylether (MMU MME) and dimethylolurea dimethylether (DMU DME) were laboratory products recrystallized no longer than one day prior to analysis.

When required, dry samples were prepared by the vacuum drying of thin films (0.1–0.5 g per 10 cm² of glass plate) at 45–50°C and 0.1–0.2 kPa for the duration of 1 hr.

The NMR spectra of etherified compounds were obtained on a Varian EM-360 spectrometer at 60 MHz. Deuterated chloroform or dimethylsulfoxide were used as solvent.

PROCEDURES

Nonetherified Resins

The nitrogen and carbon contents of a sample are determined by means of a carbon-nitrogen elemental analyzer. An instrument which determines both nitrogen and carbon simultaneously has certain advantages over the separate determinations of the elements. The calculation of F/U or F/M ratios involves a ratio of the carbon content to the nitrogen content, and when one sample is used for both determinations the weight of sample is cancelled in the calculations. This is appreciated particularly when samples analyzed are aqueous solutions since no preliminary drying and/or accurate weighing is necessary. The point becomes obvious from the equations for F/U ratio,

$$F/U = (6.998C/3N) - 1 \qquad (1)$$

and for F/M ratio,

$$F/M = (6.998C/N) - 3 \qquad (2)$$

where F, U, and M are expressed in moles, and C and N represent the contents of carbon and nitrogen, respectively, in weight percent.

When dried samples are analyzed a platinum boat may be used for handling of samples. For liquid samples, however, closed capsules made of a low-temperature melting material (e.g., tin) must be used.

Etherified Resins

Our experience indicates that etherified resins provide better analytical results when dried. This observation does not arise from the elemental analysis as such but rather from the possibility of the loss of solvents by evaporation during the weighing procedures prior to the elemental analysis. It is also essential that the same sample which has been dried for the C-N analysis is used for the NMR analysis.

The F/U and F/M ratios are calculated by means of the following equations.

$$\frac{F}{U} = \frac{C_F}{C_F + C_A}\left(\frac{6.998C}{3N} - 1\right) \tag{3}$$

$$\frac{F}{M} = \frac{C_F}{C_F + C_A}\left(\frac{6.998C}{N} - 3\right) \tag{4}$$

where C and N are the total carbon and total nitrogen contents, respectively, determined by the elemental analysis, and they are expressed in weight percent. $(C_F/C_F + C_A)$ ratio is calculated by NMR spectroscopy: C_F is the number of carbons originating from formaldehyde (the total formaldehyde peak area divided by a factor of two); C_A is the number of carbons originating from the alkyl groups (e.g., the sum of CH_3 and CH_2 peak area, multiplied by a factor of 4/7 for butoxylated resin).

ASSESSMENT OF THE TECHNIQUES

In order for us to assess the accuracy and reproducibility of the techniques, we repeatedly analyzed several samples of known F/U or F/M ratios from the conditions of their preparation.

Nonetherified Resins

Table I shows results obtained for nonetherified amino resins. The nitrogen and carbon contents—as shown—sometimes deviate appreciably from an average values for a sample, since no attempt was made to weigh the samples accurately. (The readability of the balance used was 0.01 mg.) This fact, however, is not detrimental to the accuracy of determination of F/U and F/M ratios.

Samples UF#1 and UF#2 (supplied as aqueous solutions) were analyzed both without prior drying as well as dried. The first resin demonstrates that relatively stable UF resins can be analyzed in either dried or nondried state with the same results. The small deviation of ±0.05 lies within a range of the maximum error (Table II) calculated by the propagation-of-error treatment. On the other hand, unstable resins that easily loose formaldehyde on drying, such as those with a high F/U ratio, should be analyzed preferably in the original, nondried state. Resin UF#2 with an F/U ratio of 4.5 illustrates this point. Resins UF#3 through UF#6 additionally demonstrate good accuracy of the analytical techniques. These resins were all dried prior to analysis since the high viscosity of nondried samples in these cases made sampling of a few milligrams very difficult. Resin MF was a spray-dried melamine resin. Again, a good accuracy is indicated with the exception of one run which would normally be disregarded.

TABLE I
Analysis of Nonetherified Resins

| Resin | N(%) | C(%) | F/U or F/M | |
			Found	Theoretical
UF#1	17.75	18.68	1.46	1.5
Nondried	17.85	19.44	1.54	
	18.48	19.73	1.49	
UF#1	28.63	31.29	1.55	1.5
Vacuum-dried	28.80	31.60	1.56	
	29.77	32.29	1.53	
	29.41	31.77	1.52	
UF#2	10.76	25.21	4.47	4.5
Nondried	10.81	25.20	4.44	
	10.71	25.01	4.45	
	10.82	25.20	4.43	
UF#2	15.74	34.96	4.18	Less than 4.5
Vacuum-dried	16.02	34.75	4.06	
	15.89	34.75	4.10	
UF#3	31.87	30.94	1.27	1.3
Vacuum-dried	31.82	31.55	1.31	
	31.24	31.58	1.36	
	31.64	31.00	1.29	
UF#4	29.48	31.92	1.53	1.5
Vacuum-dried	29.82	32.09	1.51	
	29.38	31.45	1.50	
	29.62	32.07	1.53	
UF#5	26.96	31.66	1.74	1.7
Vacuum-dried	26.52	30.98	1.72	
	27.02	31.53	1.72	
	27.05	31.48	1.71	
UF#6	27.39	33.02	1.81	1.8
Vacuum-dried	27.10	32.92	1.83	
	27.18	33.09	1.84	
	26.96	32.95	1.85	
MF	40.11	29.91	2.22	2.2
Spray-dried	42.03	32.20	(2.34)	
	42.64	31.69	2.20	
	42.50	31.64	2.21	
	43.40	32.52	2.24	

The tabulated results demonstrate the error of F/U and F/M determination as found by actual experiments. For the complete assessment of the accuracy of the determination, two kinds of errors were calculated: (a) the limit of error[5] by the propagation-of-error treatment, which determines a maximum possible error in a quantity; (b) the probable error[5] which is 3.8 times smaller than the limit of error, and which is defined as a quantity with such a value that the probability that the magnitude of an error will be less than the probable error is equal to the probability that it will exceed the probable error.

$$\text{Maximum error in } \frac{F}{U} = \frac{7C}{3N}\left(\frac{dC}{C} + \frac{dN}{N}\right) \tag{5}$$

$$\text{Maximum error in } \frac{F}{M} = \frac{7C}{N}\left(\frac{dC}{C} + \frac{dN}{N}\right) \tag{6}$$

where dC and dN are absolute errors in the determination of carbon and nitrogen, respectively.

TABLE II
Calculated Errors in Analysis of Nonmodified Resins[a]

Assumed error in C N (absolute %)		Concentration of sample, %	Limit of error in		Probable error in	
C	N		F/U	F/M	F/U	F/M
0.2	0.2	50	0.07	0.12	0.02	0.03
0.3	0.3	50	0.11	0.18	0.03	0.05
0.2	0.2	100	0.04	0.06	0.01	0.02
0.3	0.3	100	0.06	0.09	0.02	0.03

[a] Calculated for resins with F/U and F/M ratios equal to 1.5 and 2.5, respectively.

$$\text{Probable error} = (\text{maximum error})/3.8 \tag{7}$$

Equations (5) and (6) illustrate that an error in the F/U or F/M determination decreases proportionally with increasing concentration of a sample and slightly with decreasing F/U or F/M ratio. Typical errors for some common resins are presented in Table II.

Etherified Resins

The analytical techniques for etherified amino resins were assessed by the analysis of MMU MME, DMU DME, and commercial etherified amino resins. Table III summarizes the results. In these cases, a microbalance was used with a readability of 0.001 mg. A very good agreement of the found values with the expected ones was obtained for the model compounds.

When etherified resins are analyzed, the accuracy of the F/U and F/M ratio determinations is given not only by the elemental analysis, but also by the accuracy of the NMR analysis which provides a $C_F/(C_F + C_A)$ ratio. For the model

TABLE III
Analysis of Etherified Resins

Resin	N(%)	C(%)	$C_F/(C_F + C_A)$	F/U or F/M Found	F/U or F/M Theoretical	OR/F[c] Found	OR/F[c] Theoretical
MMU MME[a]	27.00	34.00	0.506	1.01	1.00	0.98	1.00
Vacuum-dried	26.55	34.28		1.02			
	27.06	34.58		1.00			
DMU DME[b]	18.74	40.28	0.500	2.01	2.00	1.00	1.00
Vacuum-dried	18.82	40.59		2.02			
	18.79	40.35		2.00			
UF-isobutylated	19.26	48.51	0.378	1.84		0.41	
Vacuum-dried	19.35	48.53		1.83			
	19.00	48.83		1.89			
	19.37	49.07		1.86			
	19.20	48.80		1.86			
MF-butylated	20.44	53.48	0.273	4.18		0.66	
Vacuum-dried	20.05	52.41		4.17			
	20.46	52.99		4.13			
	20.56	53.14		4.12			
	20.61	53.95		4.18			

[a] Monomethylolurea monomethylether.
[b] Dimethylolurea dimethylether.
[c] Alkoxy groups/formaldehyde (by moles).

compounds, the agreement between the experimental and theoretical values was due to the fact that both the C-N and NMR analyses provided excellent accuracy. The NMR spectra showed a very good resolution which enabled us to determine the $C_F/(C_F + C_A)$ ratio accurately. This may not be always the case. In order for an analyst to be able to estimate an error under his particular conditions, Table IV lists the limit of error and the probable error for different inaccuracies in the nitrogen and carbon contents and $C_F/(C_F + C_A)$ ratio determinations. In any case, errors can be estimated by means of the following equations.

$$\text{Maximum error in } \frac{F}{U} = \frac{F}{U} \frac{d[C_F/(C_F + C_A)]}{C_F/(C_F + C_A)} + \frac{C_F}{C_F + C_A} \frac{7C}{3N}\left(\frac{dC}{C} + \frac{dN}{N}\right) \quad (8)$$

$$\text{Maximum error in } \frac{F}{M} = \frac{F}{M} \frac{d[C_F/(C_F + C_A)]}{C_F/(C_F + C_A)} + \frac{C_F}{C_F/(C_F + C_A)} \frac{7C}{N}\left(\frac{dC}{C} + \frac{dN}{N}\right)$$

$$(9)$$

where dC, dN, and $d[C_F/(C_F + C_A)]$ are absolute errors in the determination of C, N, and $C_F/(C_F + C_A)$, respectively.

Commercial etherified amino resins were analyzed by the aforementioned techniques to establish reproducibility of results. The F/U and F/M ratios of the commercial resins cannot be accurately calculated from the condition of their preparation. Consequently, the theoretical values of such resins were not displayed. However, a very good reproducibility of results was obtained which supported the applicability of the analytical techniques discussed herein.

CONCLUSIONS AND DISCUSSION

The F/U and F/M ratios of amino resins can easily be determined by means of an elemental carbon/nitrogen analyzer. In general, the techniques of analysis can be applied to aqueous solutions as well as dried samples, and both nonetherified and etherified amino resins can be analyzed. Aqueous solutions of nonetherified resins provide a reasonable accuracy of the F/U and F/M determination, such as ±0.02 to ±0.05 in terms of the probable error. If required, the error can be decreased by drying the sample prior to analysis; the error decreases proportionally with increasing the concentration of resin in the sample. Maximum accuracy is achieved when a dried resin is analyzed. Serious consideration,

TABLE IV
Calculated Errors in Analysis of Etherified Resins[a]

| C | N | $C_F/(C_F + C_A)$ | Concentration of | Limit of error in | | Probable error in | |
(absolute %)		(rel. %)	sample, %	F/U	F/M	F/U	F/M
0.2	0.2	2	50	0.11	0.16	0.03	0.04
0.3	0.3	2	50	0.15	0.21	0.04	0.06
0.2	0.2	4	50	0.15	0.22	0.04	0.06
0.3	0.3	4	50	0.19	0.27	0.05	0.07
0.2	0.2	2	100	0.08	0.11	0.02	0.03
0.3	0.3	2	100	0.10	0.14	0.03	0.04
0.2	0.2	4	100	0.12	0.17	0.03	0.04
0.3	0.3	4	100	0.14	0.20	0.04	0.05

The first two columns are grouped under "Assumed error in".

[a] Calculated for dimethylolurea dimethylether and trimethylolmelamine trimethylether.

however, should be given to the stability of the sample under the conditions of drying.   Urea–formaldehyde condensates with F/U ratio of 3 and higher, for example, should be analyzed as supplied in solution.

Etherified resins should be analyzed always after the solvent removal, since there is a possibility of solvent loss during the weighing and sampling procedures. As opposed to aqueous solutions of nonetherified resins where the loss of water plays no role in the F/U and F/M determination, the loss of organic solvent from the sample of etherified resin to be analyzed would affect the accuracy of analysis. The reason is the necessity to supplement the elemental analysis by the NMR analysis of the *same* sample.   In most cases, however, dried samples should be preferred to nondried ones for the simple reason of difficulties encountered when a viscous liquid is to be sampled.

The error of determination of F/U and F/M ratios is larger for etherified resins than for nonetherified ones.   The NMR determination of the relative amount of formaldehyde carbon in etherified resins can probably be done with a relative error between 2% and 4%.   This would provide typically F/U and F/M ratios for dried samples with the probable error between 0.02 and 0.05, i.e., a half of errors in the final results should be within the range of 0.02–0.05.

Note that the analytical techniques described herein allow us also to determine the ratio of alkoxy groups (OR) to the total formaldehyde content in a sample, OR/F.   These ratios were obtained during the analysis of the model compounds and commercial etherified resins, and they are displayed in Table III.

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