5—
Liquid Chromatographic Technique in Textile Analysis

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I—
Introduction

Liquid chromatographic (LC) technique has been more and more widely and quickly accepted in the textile industry during recent years. As reported in a survey [1], LC ranked fourth, after ultraviolet-visible (UV-visible) spectrophotometer, optical microscope, and gas chromatograph, as the most widely used instrument in the textile industry. As a matter of fact, the invention of chromatography was due to the separation of normal colorants [2].

The advantages of using LC for textile analyses can be summarized as follows.

1. Strong ability in separation and purification

2. Suitability for molecules that won't evaporate without destroying the structure

3. Sensitivity to small amount of chemicals

4. Simulation of the wet processing environment for the study of textile properties

5. Convenience for analysis

LC analysis related to textiles could be roughly separated into three areas: using conventional stationary phases, such as, C18, for textile analysis; packing textile materials into LC column for textile property and wet processing studies; and using fibrous materials as stationary phases for other operations such as bioseparation and purification.

Conventional LC has been used for dye identification, separation, and purification in textile, food, drug, and cosmetic industries and in forensic examina-

tions [3–10]. It has also been used as a powerful technique for the qualitative and quantitative analysis of textile finishing processes such as the study of flame retardants, stain-resist compounds, durable press (DP) finishes, formaldehyde, DP finishing mechanism, and contaminants on fiber [11–23]. Packing textile material into the column as stationary phase for the investigation of properties such as pore structures and related dyeing and finishing behaviors, dyeability, and dyeing mechanism has been successful [24–36]. Using supercritical fluids as mobile phase, LC also has been reported as an efficient tool for chemical extraction from textile fibers [37] and dye analysis [38].

In addition to the textile analysis, LC using textile materials as stationary phase has also been applied in other areas such as bioseparation and purification. Fibers—natural, synthetic, and hollow—and even a single piece of fabric were all reported as LC stationary phases with advantages of low pressure drop, high chemical and physical stabilities (excellent stability to acid and alkali, high temperature), high liquid flow, and low price [39–45]. This chapter focuses on applications of LC in textile analysis and characterization.

II—
Background

A—
Composition of a Liquid Chromatograph

As shown in Figure 1,a liquid chromatograph is basically composed of a reservoir of liquid (I) that serves as the mobile phase; an LC pump (II) that moves the mobile phase through the system; a pressure gauge (III) indicating the differential pressure between the LC system and its atmosphere; a relief valve (IV) to avoid damage due to unexpected high pressure of the system; an injector (V) that quantitatively controls the sample injection; a sample syringe (VI) that introduces samples for analysis; an LC column (VII) as the key component for the system; a detector (Viii) measuring the concentration of solutes out of the column; a recorder (IX) to record the signals from the detector with calculations such as peak area, slope, and peak location; and an eluate collector (X) to collect the eluate. For dye, finish, and other chemical analysis, samples can be introduced through the injector (V) into the LC system by a sample syringe (VI). The eluent from reservoir (I) could be a single-component solution with a fixed concentration, such as 20 g/L NaC1 aqueous solution, or a gradient that is a multicomponent solution with changing concentrations of some or all of the components, such as an aqueous mobile phase with sodium lauryl sulfate concentration changing linearly from zero to 0.1 *M* in 1 hr. A gradient programmer is Usually used together with LC pumps (II) to control the amount of different components to be mixed at different time. An LC column (VII) used for the analysis of textile chemicals or fibrous materials, such as fibers or fabrics, can be packed with conventional spherical or particulate supports as stationary phases or with the fibers or fabrics being tested. Choosing

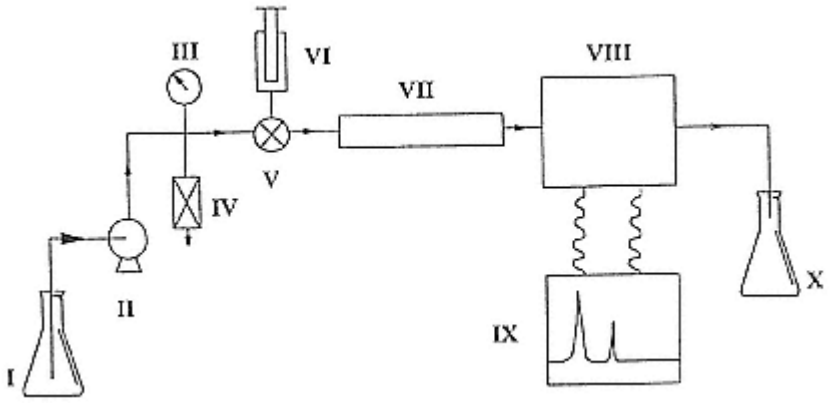

Figure 1
Basic composition of liquid chromatograph: I, a reservoir of eluent served as mobile phase; II, LC pump; III, pressure gauge; IV, relief valve; V, sample injector; VI, sample syringe; VII, LC column; VIII, detector; and X, eluate collector.

the right stationary and mobile phases is most important toward the success of LC analysis. To measure the concentration of solutes elute out of the column, the most commonly used detector is a UV-visible light detector, which can be continuously selected to any wavelength in the ultraviolet and visible light range or be selected within specific wavelengths in the UV-visible range using the right filter. Determination of textile colorants or chemicals with aromatic structures often requires such a detector. For other textile chemicals, such as mineral electrolytes, aliphatic surfactants, or for D_20, sugars, dextrum, polyethylene glycol (PEG) used for pore structure studies, and any other chemicals that do not have strong absorption in the UV-visible range, a differential refractometer is often effective. The differential refractometer is also called an RI detector (RI stands for reflective index). The concentration of chemicals determined by the detector is interpreted and recorded by a chart recorder as a chromatogram or by an integrator as a chromatogram with peak position, peak area, and other calculated parameters.

B—
Basic Concepts

There are some basic terms and concepts of the LC application in textiles that need to be introduced for better understanding of further discussions. Only those mentioned in this chapter are discussed. A thorough discussion of basic LC theory could be obtained from one of the many LC books.

1—
Solute Elution

When a solute is introduced into the LC column, it moves with the mobile phase at the same speed in the spaces between materials of stationary phases. These

spaces are occupied by mobile phase. Solute moves at a slower speed when it contacts the stationary phase if it has some kind of attractive interaction with the stationary phase. The solvent will move the solute out of the column because of the solubility of the solute in the solvent. But due to the dispersion of solute in the voids between solid materials of stationary phase and the different adsorption energies on the surface of stationary phase, the solute does not elute out at the same time. Therefore a peak is observed on chromatogram as shown in Figure 2. The flat portion of a chromatogram where there is no solute being eluted is called the baseline. To describe the position of a peak in the chromatogram, the place that has most of the solute eluted out, that is, the top of the peak, is used.

As shown in Figure 2, time zero is the start of solute movement, that is, the injection time. The term tr is called retention time, which is the time between injection and the peak maximum. The magnitude of t_r depends on the extent of attraction between the solute and the stationary phase; t_r decreases with decreasing attraction. The elution time of a solute that can not penetrate into any of the pores of the stationary phase and has no attraction to the stationary phase only depends on the empty spaces, that is, the magnitude of voids in the stationary phase. The elution time of this excluded component is called the dead time (t_o) (cf. Fig. 2). In addition to the property of mobile and stationary phases, the elution time also de-

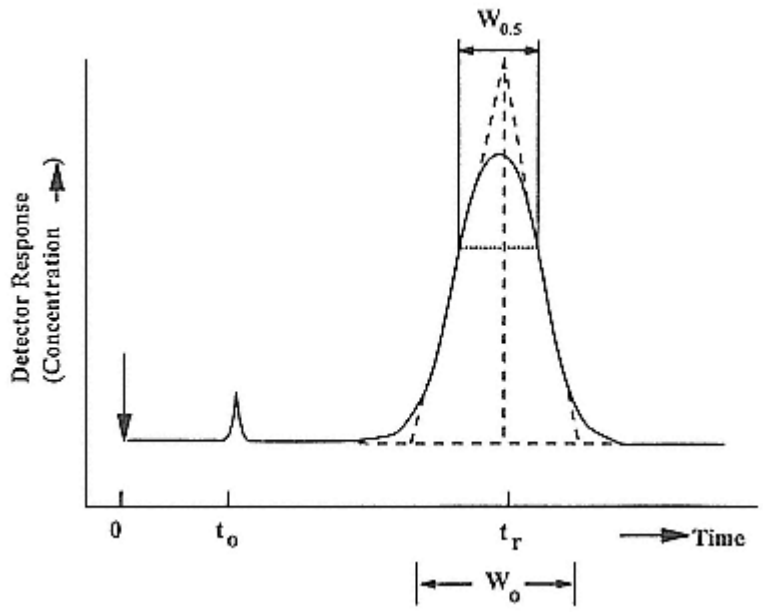

Figure 2
Schematic diagram of a chromatogram.

pends on the flow rate (q) of the mobile phase. Therefore, in addition to dead time and retention time, the terms dead volume (V_o) and retention (V_r) are also used.

$$V_r = qt_r \qquad V_o = qt_o \tag{1}$$

The fundamental equation which relates retention volume to the interaction between solute, solvent and stationary phase is given in Eq. (2),

$$V_r = V_m + KV_s \tag{2}$$

where V_m and V_s are the total volumes of mobile phase and that of stationary phase of the column, respectively; K is the distribution coefficient of the solute between two phases.

2—
Plate Concept

Plate count (N), that is, the number of plates in an LC column, and plate height (H), the size of a single plate, are often used to describe the quality of a column. The terms are borrowed from the distillation theory. Because of the continuous exchange of solute between the mobile phase and stationary phase as the solute moves through the column, equilibrium between the phases is never achieved. Therefore, a column is considered to be divided into a number of theoretical plates. The size of the plate is such that the solute is assumed to have enough time to achieve equilibrium with both mobile and stationary phases. So, if the column performance is good, that is, the sorption and desorption of solute onto stationary phase are fast and efficient, then the size of the plate (H) will be small and there will be a large number of plates (N) in the column. Assuming the peak is Gaussianshaped, plate count is a function of the standard deviation (σ) of the peak and the effective length (L) of the column,

$$N = \frac{L^2}{\sigma^2} \tag{3}$$

where

$$L = \rho \times t_r \tag{4}$$

with p as the linear velocity of mobile phase and t_r the retention volume of the peak. For the Gaussian-shaped peaks, σ: can be derived from the width of the peak at the baseline (W_o), the width of the peak at half-height ($W_{0.50}$) or the width of 0.6065 of the peak height ($W_{0.6065}$) [Eq. (5) and Fig. 2].

$$\sigma = 0.250W_o = 0.426W_{0.50} = 0.500W_{0.6065} \tag{5}$$

Plate height is also used to describe the column efficiency. It is simply calculated by Eq. (6).

$$H = \frac{L}{N} \tag{6}$$

From Eq. (3), (4), and (5), we can also achieve:

$$N = 16(\frac{t_r}{t_{w_0}})2 = 5.51(\frac{t_r}{t_{w_{0.50}}}) = 4.00(\frac{t_r}{t_{w_{0.607}}})^2 \quad (7)$$

where t_w is the peak width in units of time.

3—
Resolution

A good chromatogram for multicomponent analysis requires not only a relatively high plate count but also a good resolution factor (R_s), a measure of how well two bands are resolved [77]. Itis defined as

$$R_s = \frac{t_{r_2} - t_{r_1}}{\frac{1}{2}(t_{w_1} + t_{w_2})} \quad (8)$$

where 1 and 2 represent two peaks.

4—
Capacity Factor

The capacity factor, k, for a solute is defined as:

$$\frac{\text{Moles of the solute in stationary phase}}{\text{Moles of the solute in mobile phase}} = K\frac{V_s}{V_m} = \frac{X_s V_s}{X_m V_m} \quad (9)$$

where X_s and X_m are the concentrations of the solute in the stationary and mobile phases, respectively. From Eq. (2) and (9),

$$k = \frac{V_r - V_m}{V_m} \quad (10)$$

where V_m is equivalent to the column void volume V_o) measured by t_o of an excluded component. Hence, Eq. (10) can be rewritten as

$$k = \frac{t_r - t_o}{t_o} \quad (11)$$

C—
Column Packing

In addition to the selection of the right solvent, choosing the suitable column is the key factor for a successful LC study. For conventional stationary phases, a packed LC column can be bought directly. For other particular stationary phases, the packing techniques can be easily found from many reference books. But the packing of fibrous materials and a whole piece of fabric is worthy of discussion.

1—
Configuration of Fibrous Stationary Phases

The currently available packing technology of fibrous stationary phases could be roughly divided into the five following categories.

1. Yarn or fiber is wound in a spiral manner around a rod and the yarn or fiber wound rod is packed into a column [34,46].

2. Yarn or fiber in a parallel alignment is packed into a column longitudinally [41,42,47].

3. Randomly oriented fiber, yarn, fabric chunk and powder [29,34,43,48].

4. Ordered packing of disks of batting and fabric [29,30,31,34].

5. A piece of fabric rolled tightly and pulled into a column in which the yarns are oriented both parallel and perpendicular to the flow direction [32–36,44,45].

2—
Three Successful Packing Techniques for Textile Studies

Although there are at least five different packing configurations for textile stationary phases, the ones most successfully used in textile studies are methods 3, 4, and 5 discussed in Section II.C. 1. The common problem these textile stationary phases have is the large dead volume (V_o) and channeling due to the high resiliency of textile fibers. Because of that, lower plate count (N) and poor resolution (R_s) are often the disadvantages. Tight and even packing is most frequently used for the improvement of column quality [31,43,45]. Decreasing the size of the column after package [48] and using inactive materials to fill the voids between fiber and yarn [41] also were reported for the improvement of column quality. After packing, the textile column, no matter what packing method is used, needs to be stabilized through swelling and reorganization of the fibrous stationary phase by a continuous flow of the solvent through the column for 12 hr or up to several days [31,34].

a. Randomly Oriented Fiber, Yarn, Fabric Chunk, and Powder Large pieces of textile materials are first cut into small ones using a mill. The size of textiles is suitable for LC column if the material cut could pass through an 80-mesh screen. To decrease the variation of particle size for better N value of the column, the textile material is successively passed through a series of screens with different sizes of holes, from larger to smaller. Screens of 20, 40, 60, and 80 meshes were used by Bertoniere and King [29] for stationary-phase preparation. The prepared material can be packed dry by the tap-and-fill method [49] or, more often, packed wet as an aqueous suspension [29,31].

For the wet packing, the ground textile is suspended in water and the slurry is allowed to settle down into the column by filling the column and an extension with the fiber suspension at the top of the column. A vacuum is applied to the bottom of the column to improve the packing density [43].

b. Disks of Fabric and Batting Stacks of pieces of fabrics [30,31,34], such as four to seven layers [31], are cut into disks with a die. The diameter of the cut fabric disks should match the column's inner diameter exactly. The disks are filled into the column dry by pressing gently into the column with a suitable piston. After closing the column, the mobile phase later required for the analysis is intro-

duced to stabilize the column. More disks can be added into the column after wetting if empty space becomes available during the stabilization process [34]. The advantage of disk packing compared to the ground fabric packing is that the property of the whole fiber can be studied. Some textile properties such as pore volume and its distribution may be affected by cutting the fibers.

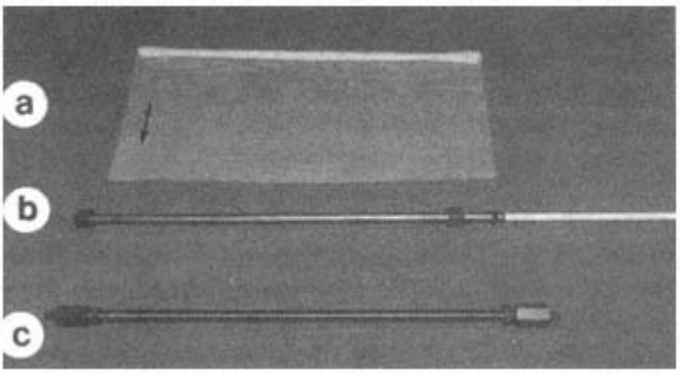

Figure 3
Column packing technique for a whole fabric rolled stationary phase: (a) fabric rolling, (b) rolled fabric partially inserted into metal column, (c) a packed LC column [33].

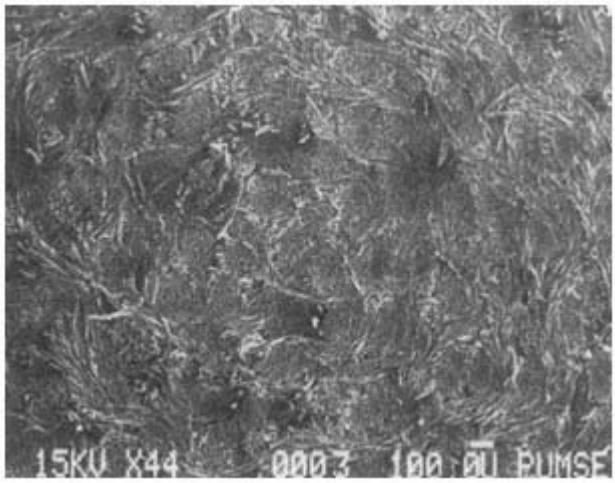

Figure 4
Scanning electron micrograph of the cross section of a cotton fabric roll. The center of the roll is in the middle of the picture [33].

c. Whole Fabric Rolled Stationary Phase The advantages of the whole-fabric stationary phase over the other methods are the retention of the complete structure of a fabric, easy packing as a whole-fiber method compared to the disk method, and the production of a tightly packed column flow.

As indicated in Figure 3, a fabric is rolled tightly along the warp direction (a) and then pulled into an LC column (b). Sometimes wetting helps the tight rolling. Fabric roll can be packed into the column dry or wet. Wetting the fabric roll makes the packing easier, but a dry packed column may have less dead volume due to the successive swelling in the column when water is used to stabilize the column. This packing method gives a column with very tightly rolled fabric as shown by the scanning electron micrograph of the cross section of the rolled fabric (Figure 4). The tight packing ensures the low V_o and good quality of the column.

III—
LC Applications in Textile Anaiysis

LC applications can be classified according to the properties of stationary phases or the application in different textile areas. The LC analyses discussed in this chapter are mainly those related to textile wet processing. They will be analyzed in the order of processing sequence. We first discuss the determination of pore structure (and surface area) and their distribution in textiles, their relation to dyeing and finishing, and then the LC application in dye identification, separation, and purification. Following that, the LC study on dyeing is discussed and finish evaluation also is included.

A—
Pore Structure and Surface Area

The importance of pore structure and surface area to the sorption rate, capacity, and uniformity of chemical reactions involved in dyeing is well known. Wet processing treatments such as scouring, bleaching, and mercerization improve the accessibility of cellulosic fibers. Bertoniere and King [29], Rowland et al. [34], Grunwald et al. [31], and Bredereck and Bluher [30] related this improvement to the fibers' pore volume, which increases upon treatment. Pore volume also affects properties of some synthetic fibers, which become more hydrophilic by increasing the microvids in the fiber [50]. Characterizing the pore structure in textile fibers is also very important when studying dyeing mechanisms [51,52], the dyeability, and the effect of durable press finishing on textile properties [26,27,29,30,31].

The pore structure of fibers can be characterized by mercury intrusion, water adsorption, or size exclusion techniques. Mercury intrusion is limited to determining the pore structure of dried fibers [50], but such a structure changes greatly in water. For example, the surface area determined by vapor sorption of N_2 is only 1.2% of that from water vapor sorption [53]. Since the pore structure of wetted fibers is what really influences properties related to wet processing of textiles, the

water adsorption technique is a more appropriate method to determine this structure. The size exclusion method gives pore volume distribution based on the volume needed for molecular probes of known sizes to enter the accessible pores in a fiber. Again, since water is used as eluent, fibers swell in a manner similar to that observed in textile wet processing. Aggebrandt and Samuelson [54] were the first to use this method for textile fibers. Using size exclusion chromatography (SEC), pore structure, including pore size and surface area distribution, could be obtained from V_r of molecular probes of known sizes. The requirement for the molecular probes is that they have no interactions, either attractive or repulsive, with fibers being studied. The retention of these molecules in the column is only due to the time required for these molecules to travel through all the accessible pores in the column at the same speed as the mobile phase.

Although different models and calculations were reported for the data treatment [30,31,33,34], the basic principle Of obtaining pore structure information through SEC is the same. Using a molecule that is totally excluded from the stationary phase—that is, it is too large to penetrate into any pore of the stationary phase and have no interactions with the surface of that stationary phase—dead volume, V_o, could be obtained from the retention volume of that molecule. Large molecules such as Dextran T-40, average molecular weight (MW) 40,000 [34], or the larger one, Dextran T-2000 (MW = 2,000,000) [30,31], are often used. If the molecule has smaller size, its retention volume (V_r) will increase because it moves into some pores of the stationary phase. The pores that the molecule could move into are called accessible pores. If the total weight of the stationary phase is W, the specific accessible pore volume for i molecule (V_i) is

$$V_i = \frac{V_{r,i} - V_o}{W} \qquad (12)$$

The maximum accessible pore volume is the one that solvent molecules can enter into. For the study of textile behavior during wet processing, the solvent is water. To measure the water-accessible pore volume, molecules with similar size should be used. D_2O seems to be a good candidate because of its similar size to water and sensitivity to detectors such as RI detector. But it was found in many different laboratories while cellulosics were tested that V_{r,D_2O} is much larger than the retention volumes of molecules with similar size [30,31,33,34]. This is probably because of the interaction between D_2O and cellulose, and because of OH/OD interchange reactions [34].

An alternative approach is to calculate the water accessible pore volume from the regression equation

$$V_i = f(MW_i) \qquad (13)$$

by substituting 18 (MW of H_2O) into the equation, or simply from the extrapolation of V_i vs. MW_i or $\log(MW_i)$ plot to $MW_i = 18$. Increasing the size of molecular probe decreases the accessible pore volume. The pore volume difference (ΔV)

between two probes (i - 1 and i, i > i - 1) is the pore volume accessible to molecules with the size smaller than i but larger than i - 1:

$$\Delta V = V_{i-1} - V_i \qquad (14)$$

The commonly used molecular probes are a series of polyethylene glycols (PEG), sugars, and dextrans. Their diameters could be found from papers of Nelson and Oliver [51], Stone and Scallan [56], Ladisch et al. [33], and Bredereck and Bluher [30].

Strictly, ΔV calculated from Eq. (14) is the accessible pore volume for molecular probes larger than i - 1 but smaller than or equal to i. To obtain the real pore structure of the stationary phase, further calculation is necessary. There are basically three different treatment to obtain pore structure from V_1 vs. MW_i data.

1. Using ΔV_i directly as the total volume of pores with diameters (D):

$D_{i-1} \leq D \leq D_i$

This approach assumes that molecular probe could penetrate into the pores with same and larger diameters. But because of the uncircular shaped pore openings, the spherical probe could only enter into the pores larger than itself, 2. Using ΔV_i as the volume of pores with diameters (D):

$3D_{1-1} \leq D \leq 3D_1$

This is the commonly used adjustment to calculate the pore structure. The assumption is that molecular probes could penetrate into pores with diameter three times its size or larger. This threefold adjustment was often used for eellulosics [33,55].

3. Instead of using an unchanged threefold adjustment, Knox and Scott [57] developed an equation, Eq. (15), to convert pore volume accessible to molecular probes to pore volume related to the sizes of the pores of the stationary phase.

$$g = K(\ln r) - 1.5\frac{dK}{d(\ln r)} + 0.5\frac{d^2K}{d(\ln r)^2} \qquad (15)$$

where r is the radius of a molecular probe, K is the ratio of accessible pore volume of the molecular probe to the volume of total accessible pores, and g is the ratio of volumes of pores with radii equal to or larger than R to the total pore volumes of the stationary phase. R is the radius of the smallest pores that the molecular probe with the radius of r can reach. As a function of r, K could be Obtained from:

$$K(\ln r) = a \times \exp[b \times (\ln r + c)^2] \qquad (16)$$

where a, b, and c are constants that could be obtained from the regression of experimental K vs. r data by Eq. (16).

If V(R) represents the volume of pores with radii equal to and larger than R, dV/dR vs. R gives a pore volume distribution curve. Furthermore, if the shape of the pores is known, the surface area distribution of the pores can also be calculated. Ladisch et al. [33] gave the detailed calculation with the assumption that the shape of the pores is elliptical.

Bertoniere and colleagues have made important contributions in this area relating pore structure of cellulosics to their preparation, dyeing, and finishing properties. Their research on accessible internal volume of cotton fiber is discussed in another chapter in this volume.

B—
Colorant Identification, Separation, and Purification

To separate a specific dye from other dyes, impurities, and other chemicals in the test system, LC can allow the dye to elute out at specific time and can thus achieve dye identification, separation, and/or purification. The right stationary phase, eluent, and detector are the three key factors to ensure a high-quality LC analysis of dyes.

The commonly used stationary phases are reverse phases of C8, C18, and ODS, silica gel, and polymeric materials such as polystyrene and divinyl benzene beads. Eluents often used are polar solvents such as water, alcohol, and acetonitrile, aqueous solutions of acids and salts, such as citric acid, acetic acid, perchloric acid, sodium sulfate, and ammonium acetate, and solutions of amines such as triethanol amine and *t*-butylammonium hydroxide. Because dyes have large conjugated systems they all have strong absorption in ultraviolet (UV) and visible wavelengths. Thus the most sensitive detectors are UV and/or visible wavelength spectrophotometers. Choosing the specific wavelength with maximum absorbance (λ_{MAX}) due to the maximum sensitivity, the concentration of dye eluted out of the column can be detected and recorded by a chart recorder or an integrator. For a mixture of two or more dyes, which is usually the case for dye analysis, this single-wavelength detector is not enough. The dyes in the mixture usually have different color. Therefore their λ_{MAX} values are different. When these dyes are separated in the column, they come out at slightly different time. If a fixed wavelength is used, it may only be sensitive to one dye. For other dyes, there might be a very small peak or even no peak at all. To overcome this, several detectors set at different wavelengths must be used. However, for the analysis of unknowns, it is impossible to use this preset wavelength method. The development of fast scanning UV/visible light and diode array detectors is an important movement for colorants analysis. Scanning the eluate with the complete UV/visible lights and repeating such scanning quickly can obtain the absorbance for each wavelength. Saving and treating the saved signals can obtain chromatographs in which all peaks are obtained from their λ_{MAX} values. However, no matter how fast the scanning is, the measurement of a specific wavelength by these fast scanning UV/vis-

ible light detectors is discontinuous. This may cause a loss of information, especially for trace and fast LC analyses. A diode array detector [2,4,58,59] measures the entire region light absorbance continuously. The equipment covers the light region up to 600 nm at least. A broad-emission lamp generates light of all wave-lengths passing through the flow cell. The light, after absorption by the colorants in the cell and dispersion by a holographic grating, falls onto an array of diodes. The array contains hundreds of diodes, each for a specific wavelength. The output from the diodes is stored and analyzed by a computer.

Using multiwavelength detectors not only improves the sensitivity of the detector by selecting the signals from λ_{MAX} of a specific colorant, but also allows some unique analysis [2]. An important application is to verify the purity of a solute after separation. Assume there is a dye mixture that has two dyes, a and b, with λ_{MAX} of 430 nm and 575 nm, respectively. For a pure dye (e.g., a), at no matter what concentration, the ratio of absorbance (e.g., A_{430}/A_{575}) should be constant. If the eluate is a mixture, the plot of the absorbance ratio versus retention time will not be a rectangle. An irregular peak top is usually an indication of impurities. This could be easily proved by Lambert-Beer's law:

$$A = kC \tag{17}$$

where A is absorbance, C is concentration, and k is a constant.

When color a elutes out of the column, the concentration changes because of the dispersion. Assuming at time 1, the concentration is $C_1(a)$; at time 2, it is $C_2(a)$. Using λ = 430 nm, it could have

$$A_{430}[C_1(a)] = K_{430}(a) \times C_1(a) \tag{18}$$
$$A_{430}[C_2(a)] = k_{430}(a) \times C_2(a) \tag{19}$$

Using λ = 575 nm, we have

$$A_{575}[C_1(a)] = k_{575}(a) \times C_1(a) \tag{20}$$
$$A_{575}[C_2(a)] = k_{575}(a) \times C_2(a) \tag{21}$$

For color b,

$$A_{430}[C_1(b)] = K_{430}(b) \times C_1(b) \tag{22}$$
$$A_{430}[C_2(b)] = k_{430}(b) \times C_2(b) \tag{23}$$
$$A_{575}[C_1(b)] = K_{575}(b) \times C_1(b) \tag{24}$$
$$A_{575}[C_2(b)] = k_{575}(b) \times C_2(b) \tag{25}$$

Absorbance at a specific wavelength (i) and time is the summation of other Ai values. Using this example of 430 nm and time 1, if the eluate contains both colors,

$$A_{430} = A_{430}[C_1(a)] + A_{430}[C_1(b)] \tag{26}$$

If the eluate has only color a, $A_i[C_i(b)]$ equals to zero. At time 1,

$$A_{430} = A_{430}[C_1(a)] = k_{430}(a) \times C_1(a) \quad (27)$$

$$A_{575} = A_{575}[C_1(a)] = k_{575}(a) \times C_1(a) \quad (28)$$

$$A_{430}/A_{575} = k_{430}/k_{575} \quad (29)$$

The same reasoning can be applied at time 2:

$$A_{430}/A_{575} = k_{430}/k_{575} \quad (30)$$

The ratio is a constant, and it will not change with changing concentrations of the color. If the color is not pure, at time 1 we have

$$A_{430} = A_{430}[C_1(a)] + A_{430}[C_1(b)]$$
$$= K_{430}(a) \times C_1(a) + k_{430}(b) \times C_1(b) \quad (31)$$

$$A_{575} = A_{575}[C_1(a)] + A_{575}[C_1(b)]$$
$$= K_{575}(a) \times C_1(a) + k_{575}(b) \times C_1(b) \quad (32)$$

At time 2,

$$A_{430} = k_{430}(a) \times C_2(a) + k_{430}(b) \times C_2(b) \quad (33)$$

$$A_{575} = k_{575}(a) \times C_2(a) + k_{575}(b) \times C_2(b) \quad (34)$$

Obviously,

$$A_{430}/A_{575}(\text{time 1}) \neq A_{430}/A_{575}(\text{time 2}) \quad (35)$$

The dyes studied by LC method include direct, acid, basic, disperse, vat, and dyes used for cosmetics and food. Table 1 summarizes some of the methods for dye identification, separation, and purification. The detailed techniques can be found from the references in the table.

C—
Dyeing Behavior

Using textile materials as a stationary phase, the dyeing behavior of a specific textile material can be obtained from retention of dye introduced into the column through an injector (VI in Figure 1), and frontal analysis of breakthrough curves can be obtained from running dye solutions with certain concentrations as mobile phases. Dye affinity, dyeing enthalphy, dye compatibility, dye sorption isotherm, and dye-fiber interactions all can be studied through LC.

1—
Dyeing Thermodynamics

If we change the form of Eq. (2), we have

$$K = \frac{V_r - V_m}{V_s} \quad (36)$$

Table 1 LC Method for Dye Analysis

Dye class	Stationary phase	Eluent	Reference
Basic dye	Silica	Methanol/water buffered to pH 9.7 with ammonium acetate	[72]
Disperse dye	ODS	Acetonitrile/water (4/1) buffered to pH 3.2 with citric acid	[9]
	C18	Acetonitrile/water (70/30)	[5]
Direct dye	C18	Methanol/aqueous triethanolamine ion-pairing gradient	[73]
Vat dye	C18	0.05 *M* sodium acetate/0.05 *M* acetic acid in water (19%) and methanol (81%)	[74]
Acid dye	C18	Tetrabutylammonium ion pair	[58]
	Polystyrene/ divinyl benzene	Acetonitrile/water/citric acid/*t*-butylammonium hydroxide, etc.	[59/77]
Cosmetic dye	C8	Acetonitrile/perchloric acid (pH 3) ion pair	[78]
	C18	Methanol/water/acetic acid (89/10/1); methanol/acetic acid/0.01 *M* tetrabutylammonium hydroxide, pH 3.5 with phosphoric acid	[6]
Food dye	ODS	Methanol/aqueous sodium sulfate	[3]
	C18	Isopropanol aqueous solutions	[10]

where $V_m = V_o$, assuming the volume from injection to column inlet is negligible, and $V_s = V_t - V_o$, where V_t is the total solvent volume in the column.

The expression of affinity of a dye is

$$-\Delta\mu^\circ = RT \ln K \qquad (37)$$

where $-\Delta\mu^o$ is the affinity, R is the gas constant, T is absolute temperature, and K is the distribution coefficient. Combining Eqs. (36) and (37), we can write:

$$-\Delta\mu^\circ = RT \ln \frac{V_r - V_m}{V_s} \qquad (38)$$

Thus, the dye affinity can be obtained from elution study by an LC system.
It is well known that

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \qquad (39)$$

where ΔH^o is the heat of dyeing. Substituting $(V_r - V_m)/V_s$ for K,

$$\frac{d \ln [(V_r - V_m)/V_s]}{dT} = \frac{\Delta H^\circ}{RT^2} \qquad (40)$$

From integration we have:

$$\Delta H^\circ = \frac{RT_1T_2}{T_2 - T_1} \ln\left[\frac{(V_{r2} - V_{m2})/V_{s2}}{(V_{r_1} - V_{m_1})/V_{s_1}}\right] \qquad (41)$$

where T_2 and T_1 are two different temperatures and $V_{r_2}, V_{r_1}, V_{s_1}, V_{m_2}$ and V_{m_1} are retention volumes, solvent volumes in the stationary phase(s), and solvent volumes in the mobile phase (m) at temperatures T_2 and T_1, respectively.

Assuming the change of V_m and V_s with temperature is negligible, Eq. (41) could be rewritten as:

$$\Delta H^\circ = \frac{RT_1T_2}{T_2 - T_1} \ln\left(\frac{V_{r_2} - V_m}{V_{r_1} - V_m}\right) \qquad (42)$$

The successful application of textile LC to obtain dyeing thermodynamic parameters is reported by Grunwald et al. [31] and Achwal [24].

2— Dye Sorption Isotherm

Adsorption isotherms of dyes on textiles give thermodynamic parameters from which optimum dyeing conditions can be specified. The primary methods currently used to determine a dye adsorption isotherm [60,61] are based on (a) determining the concentration of the batch solution before and after dyeing equilibrium, (b) extracting and quantifying the adsorbed dye from the fiber after dyeing equilibrium has been established, and (c) immersing the dyed material in a dyebath of zero or small dye concentration, reaching the desorption equilibrium, and then determining the dye adsorbed by method a or b.

During the 1970s, Sharma and Fort [46] introduced the use of LC to study adsorption on fibers; most of the LC work published since that time has not addressed dye adsorption on textiles. Most of the adsorbates studied are much smaller in size than dyes [42,62–67]. The LC method is more accurate and sensitive than the classical batch method of shaking the adsorbent with the solution, measuring the change in solution concentration due to adsorption, and calculating the amount of solute adsorbed by the concentration difference [46,67]. Ladisch and Yang [32] developed a method of using whole fabric as the stationary phase to determine direct dye adsorption isotherms.

Two major approaches for determining adsorption isotherm measurements from liquid chromatography measurements are the minor disturbance method and the frontal analysis method [63].

a. Minor Disturbance Method. DeVault [68] gave the adsorption isotherm f(C) in terms of ideal equilibrium chromatography. The major assumption is that the equilibrium between solution and adsorbent is instantaneously established and that the effect of diffusion is negligible. The equation that gives x, the distance a band of dye has traveled from the column inlet, is

$$x = \frac{V}{V_0 / L + Mf'(C)} \qquad (43)$$

where L is the column length, V is the volume of solution that has passed any given point since the initial time, V_o/L is the effective void volume per unit column length, M is the amount of adsorbent per unit length of the column, and f(C) is the function that gives the amount of solute adsorbed per unit weight of adsorbent, that is, the adsorption isotherm of the solute on the adsorbent; f´(C) is the first-order derivative of f(C).

The linear velocity of the moving concentrated band along the column is given by u, while S is the flow rate of the eluent:

$$u = \frac{S}{V_0/L + Mf'(C)} \qquad (44)$$

For a column of length L, V_0 is the total dead volume.

The retention volume V_r is LS/u, and the total amount of adsorbent in the column W is L × M. Therefore, Eq. (44) can be transformed into Eq. (45):

$$f'(C) = \frac{V_r - V_0}{W} \qquad (45)$$

Integration of Eq. (45) gives

$$f(C_i) = \frac{V_{r,i} - V_0}{W}(C_i - C_{i-1}) + f(C_{i-1}) \qquad (46)$$

where $f(C_i)$ is the amount of adsorbate adsorbed per unit weight of adsorbent at an equilibrium concentration of C_i. In the following discussion, $f(C_i)$ is replaced by the commonly used symbol $Q(C_i)$.

Experiments consist first of equilibrating the column with a solution of concentration C_i. A pulse of a concentration close to C_i is then injected, and the retention time of the pulse is used to obtain $V_{r,i}$ [63]. If $C_i = C_1$, and $C_{i-1} = 0$, Eq. (46) becomes

$$Q(C_1) = f(C_1) = \frac{V_r - V_0}{W}C_1 \qquad (47)$$

For a linear isotherm, or at low dye concentration $(V_r - V_0)/W$ is a constant, which can be obtained by injecting a very dilute solution into the column. This method is applicable only when the assumptions of DeVault's equation are satisfied.

It was reported [32] that the minor disturbance method was unsuitable for studying direct dye sorption on cotton. The sorption data obtained by this method through Eq. (47) was too low compared to what was obtained from conventional batch study. This is probably because of the insufficient time the dyes have in the column for diffusion and obtaining equilibrium sorption.

b. Frontal Analysis Method. Solute will be adsorbed when a solution of concentration C_i passes through a bed equilibrated with the same solution of $C_{i-1}(C_{i-1} < C_i)$. The concentration of the solute C eluting from the column ini-

tially has a lower concentration than C_i and gradually approaches C_i as the new equilibrium is attained. An example is given in Figure 5, which shows a breakthrough curve of CI direct green 26 using the cotton column described by Ladisch et al. [33].

From Figure 5, the total solute coming out of the column (q_0) is

$$q_0 = \int_0^{V_e} g(V)\, dV \qquad (48)$$

where V_e is the elution volume at the point where the outlet concentration is equal to the inlet concentration, and g(V) represents the solute concentration as a function of the volume of eluent. The total solute coming into the column is

$$q_T = C_i V_e \qquad (49)$$

and the solute retained in the column (q_R) is the difference:

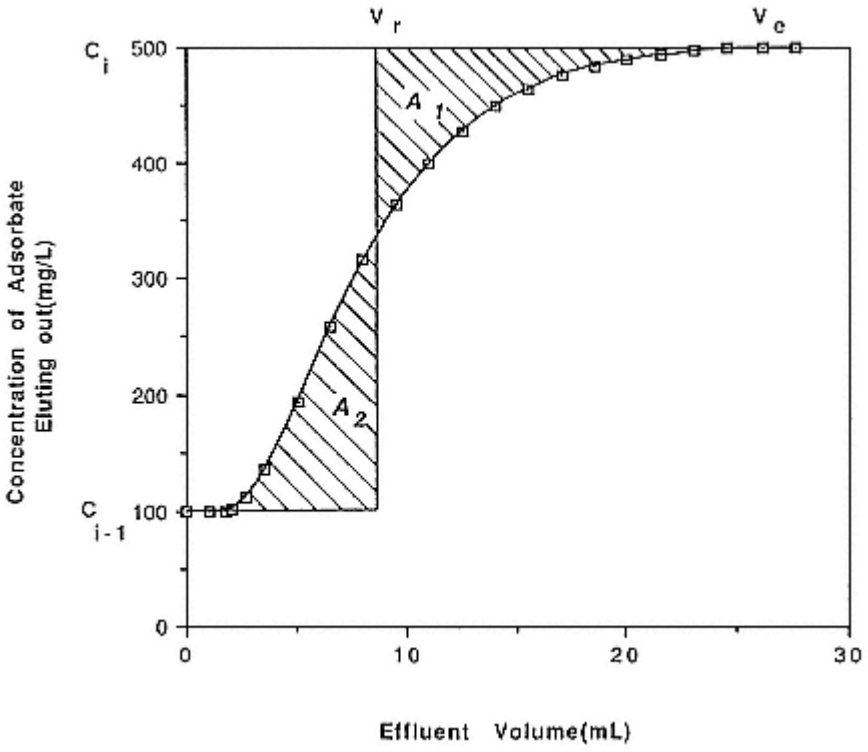

Figure 5
Breakthrough curve of CI direct green 26 with a concentration of 500 mg/L at 30°C. The cotton column was previously equilibrated with a 100 mg/L dye solution. V_r is the eluent volume at which the shadowed area $A_1 = A_2$. [32]

$$q_R = q_T - q_0 = C_i V_e - \int_0^{V_e} g(V)\, dV \qquad (50)$$

The solute adsorbed q is the difference between the total retained solute q_R and the net solute retained in the void volume of the column, q_V:

$$\begin{aligned} q &= q_r - q_V \\ &= C_i V_e - (C_i - C_{i-1})\, V_0 - \int_0^{V_e} g(V)\, dV \end{aligned} \qquad (51)$$

where

$$q_v = (C_1 - C_{i-1})V_0 \qquad (52)$$

$C_{i-1}V_0$ represents the solute retained in the column void volume from the previous run done at an inlet concentration of C_{i-1}. If the total weight of the adsorbent in the bed is equal to W, the solute adsorbed per unit weight of the adsorbent is q/W. If the unit adsorption from the previous study ($C = C_{i-1}$) is Q_{i-1}, then the total adsorption at C_i is

$$\begin{aligned} Q_i &= q/W + Q_{i-1} \\ &= 1/Wt[C_i V_e - (C_i - C_{i-1})V_0 - \int_0^{V_e} g(v)\, dV] + Q_{i-1} \end{aligned} \qquad (53)$$

Assuming at V_e the adsorption in the column was equilibrated at C_i, then Q_i expressed in Eq. (53) gives the equilibrium adsorption of the solute at concentration C_i.

Equilibrium conditions may only be assured if the lowest possible flow rate is used or the eluent flow is periodically stopped once V_e is obtained. Equation (48) would then be rewritten as

$$q_0 = \sum_{j=1}^{n} \int_{V_{ej-1}}^{V_{ej}} g_j(V)\, dV \qquad (54)$$

where N is the number of runs made until true equilibrium is attained. The total amount of dye adsorbed is additive; the volume that elutes for each run is represented by the difference $V_{ej} - V_{ej-1}$, where $V_{e0} = 0$. To calculate q_0 from either Eq. (48) or (54), the area above the breakthrough curve g (V) is usually integrated directly. Alternately, the elution volume V_r, often called the retention volume, is the volume at which the areas A_1 and A_2 are equal and can be used to obtain q_R (see Fig. 5),

$$q_R = \sum_{j=1}^{n} V_{rj}\, \Delta C_j \qquad (55)$$

where

$$\Delta C_j = C_i - C_{ij} = C_i - g_j(V_{ej-1}) \qquad (56)$$

V_{rj} is illustrated in Figure 5. If n = 1 (i.e., only one run is done at a given concentration), then this results in

$$V_{e0} = 0 \qquad g(0) = C_{i-1} \qquad \text{and} \qquad \Delta C = C_i - C_{i-1}$$
$$q_r = V_r(C_i - C_{i-1}) \tag{57}$$

and

$$q = (V_r - V_0)(C_i - C_{i-1}) \tag{58}$$

Thus

$$Q_i = \frac{V_r - V_0}{W}(C_i - C_{i-1}) + Q_{i-1} \tag{59}$$

Using frontal analysis, Ladisch and Yang [32] obtained equilibrium sorption isotherms for direct red 81 and direct green 26 at both 30 and 60°C on cotton. As presented in Figure 6, LC results were very close to that from conventional batch adsorption determination.

3—
Dye Compatibility

Combining several dyes in the same bath for textile dyeing is very common; so knowledge of the behavior, or compatibility, of all the dyes in the mixture is necessary to obtain the expected hue on the fabric. The definition of compatibility is "the propensity of individual dye components in a combination shade to exhaust at similar rates resulting in a buildup of shade that is constant, or nearly constant, in hue throughout the dyeing process" [69].

Compatibility is a problem for almost all dye classes, such as basic, acid, direct, disperse, reactive, and sulfur [70]. This problem is most serious in the basic dyeing of acrylic fibers, since basic dyes show virtually no migration in acrylic fibers under normal dyeing conditions [71]. Therefore, using compatible dyes, especially for the basic dyeing of acrylic, is very important. The most commonly used constant to evaluate dye compatibility is the so-called "compatibility value." In general, there are five compatibility values assigned to dyes, 1 to 5. For a more precise evaluation, the compatibility value of a dye can lie between two adjacent standards, such as 1.5, 2.5, 3.5, or 4.5. The higher the compatibility value of the dye, the lower the affinity of the dye for the fiber. This rating system provides a guideline for selecting dyes to be used in dyebath mixtures. Ideally, dyes used in mixtures should have the same compatibility values.

The standard method used to evaluate the compatibility of basic dyes entails determining the dyeing behavior of the dye in question when combined with each of five standard dyes having predetermined compatibility values of 1, 2, 3, 4, and 5. The experiment with each standard dye/unknown dye mixture involves dyeing four to six fabrics one after another in the same dyebath at prescribed time intervals. A total of five dye baths, one for each level of compatibility, and 20 to 30 pieces of fabric make up one evaluation for one unknown dye. The compatibility

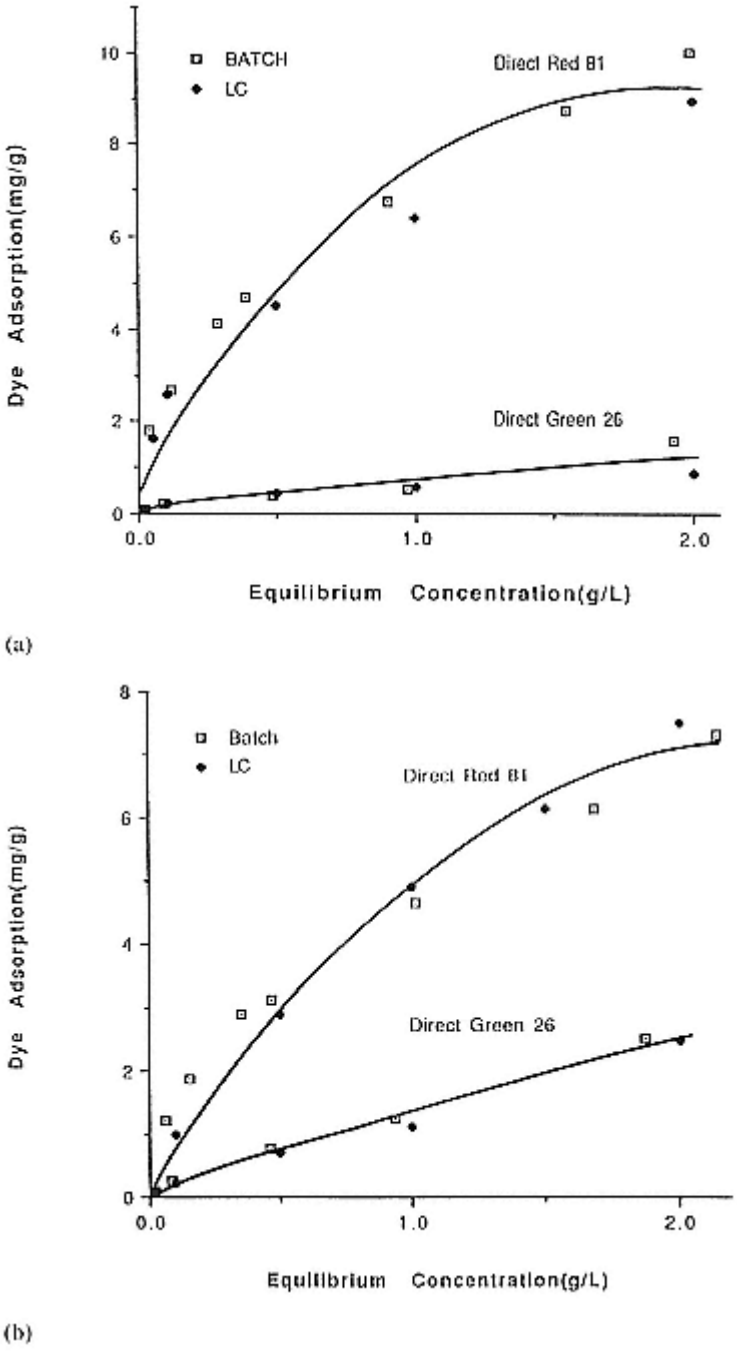

Figure 6
Comparison of adsorption isotherms obtained from LC and batch adsorption methods on cotton fabric at (a) 30°C and (b) 60°C for CI direct red 81 and direct green 26. Curves represent the polynomial regression of both batch and LC data [32].

value of the dye in question is that of the standard dye with which it gives on-tone dyeings throughout the sequence. This method has been adopted by both the American Association of Textile Chemists and Colorists (AATCC) and the Society of Dyers and Colourists (SDC) [69,70] and is used in both laboratories and industries throughout the world.

A method of using fabric LC to determine the compatibility value based on the theory of frontal analysis was developed by Yang and Ladisch [36]. Instead of preparing five dye baths and dyeing 20 to 30 pieces of fabric, one breakthrough study could achieve the compatibility value of a dye.

If two dyes are totally compatible and their initial concentrations are the same, their concentrations in the dye bath will be the same at any time throughout the dyeing. If the same fabric is packed in an LC column and a dye solution is passed through the column, both dyes would again show the same rates of adsorption if they were compatible. The rate of dye sorption would be inversely proportional to the dye eluting from such a column. Thus, the study of compatibility can be related to the frontal analysis of breakthrough curves of LC.

Similar breakthrough curves for two dyes in a mixture indicate compatibility. If the compatibility value C_v of a dye is desired, the breakthrough curve of that dye can be compared with that of each of the five standard dyes described previously. The breakthrough curve of the standard dye that most closely matches the unknown indicates the C_v value of the unknown. This procedure still requires a minimum of five experiments.

The C_v value can also be related to the difference in retention of two dyes in an LC column.

$$R = (V_r^0 - V_r)/\overline{V}_r \quad (60)$$

$$\overline{V}_r = (V_r^0 + V_r)/2 \quad (61)$$

$$\Delta C_v = C_v^0 - C_v \quad (62)$$

R is a factor that reflects the difference in the retention volume of the known and unknown dyes. Since both dyes would be passed through the same column, R is independent of the amount of fabric used for the test, and is also independent of the concentrations of the dyes used if the adsorption isotherms of these two dyes are parallel with each other within the concentration range studied. V_r^0 is the retention volume of the known dye with a compatibility value of C_v^0 V_r is the retention volume of the unknown dye with a compatibility value of C_v, which needs to be determined. Retention volume from a breakthrough curve was calculated the same way as discussed in Section III.C.2.a. (of. Figure 5). V_r is the average retention volume of the known and unknown.

Obviously, ΔC_v is related to R:

$$\Delta C_v = f(R) \quad (63)$$

where f(R) is a function of R.

Equations (62) and (63) give the compatibility value C_v as

$$C_v = C_v^0 - f(R) \quad (64)$$

Using an LC system as shown schematically in Figure 7, two breakthrough curves, one for the standard dye (with known C_v^0 the other for the test dye, could be obtained form one test. If the real expression of f(R) in Eq. (64) is known, the compatibility value of the tested dye could be calculated from Eq. (64). From the work of Yang and Ladisch [36],

$$f(R) = 0.108 - 2.484R \quad (65)$$

Examples of their study on basic dye compatibility are shown in Figure 8. The compatibility values of 10 standard dyes obtained by the LC method were compared with that from AATCC standard values in Table 2. The results of the LC method matched well those of the ATCC Test Method 141–1984 [69].

4— Dye—Fiber Interaction

Textile LC could also be used to study the dye—fiber interactions. The dye to be tested is injected into an LC system using fabric or fiber being studied as stationary phase (cf. Fig. 1). By changing the properties of eluent, and studying the retention volume and shape of the peak of the dye recorded from the outlet of the column, the dye—fiber interactions could be studied.

Yang and Ladisch [35] studied the interactions between cationic dyes and acrylic fiber by this method. Using aqueous solutions of concentrated salt (e.g., 2 *M* NaCl), organic compounds with different sizes of hydrophobic parts, and a combination of both the salt and organic compounds to study the retention of cationic dyes in acrylic column, they found that both ionic and hydrophobic interactions were important for cationic dyeing of acrylic fibers.

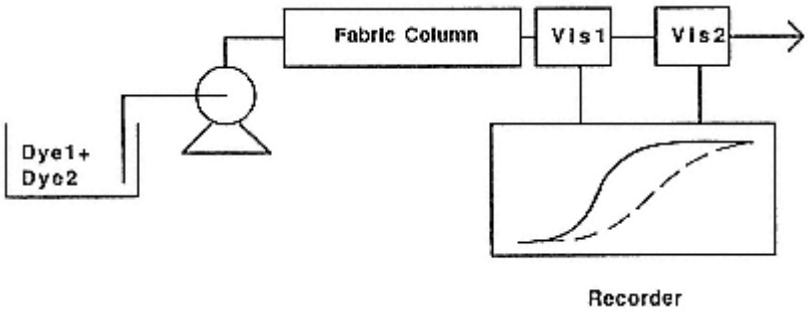

Figure 7
Schematic diagram of LC instrument for the study of basic admixture dyeing, Vis 1, UV-visible light detector with wavelength equal to λ_{max} of dye 1. Vis 2, UV-visible light detector with wavelength equal to λ_{max} of dye 2 [36].

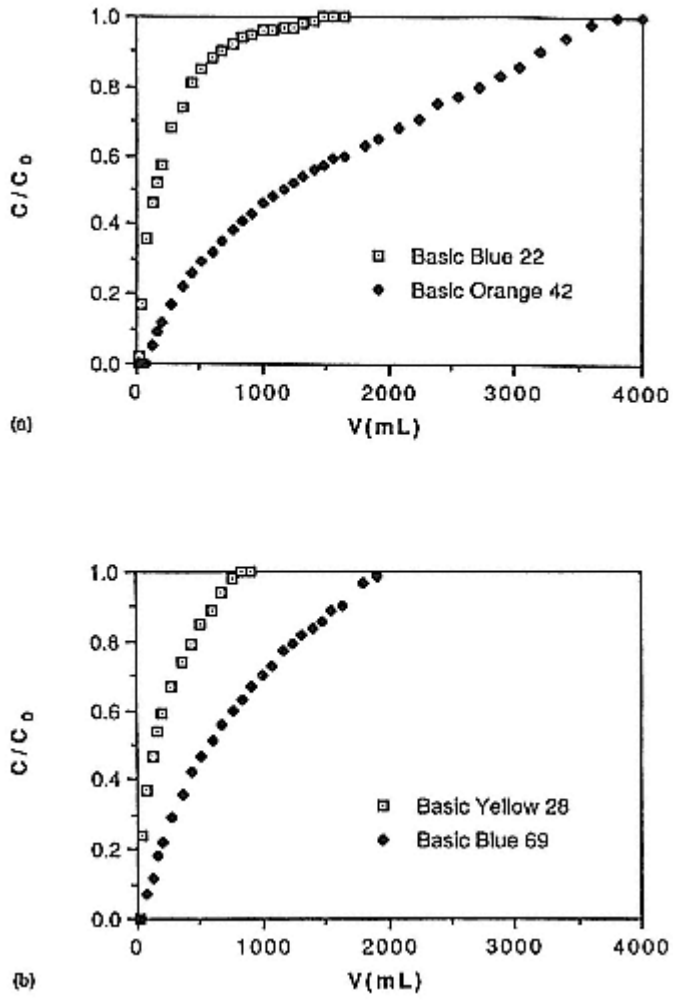

Figure 8
Breakthrough study on basic
dye compatibility [36].

D—
Finish Evaluation

LC has also been used for the study of finishes and finishing processes. It was applied to soil resist finishing [13], flame-resist finishing [23], durable press finishing [11,12,14–18], measurement of low level of formaldehyde [20,21], and low-molecular-weight additives and oligomers in synthetic fiber spinning [22].

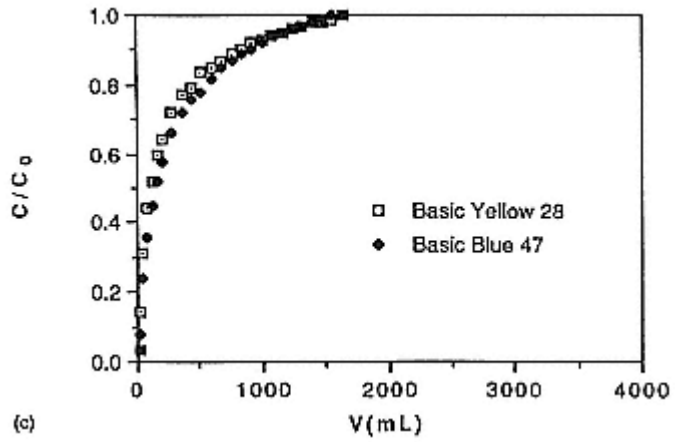

Table 3 summarized some of the LC systems for the analyses of different finishes and finishing processes.

Further information about LC analysis of textile finishes and finishing processes can be found in the chapter in this volume written by K. R. Beck, a pioneer in applying LC to the study of durable-press finishing.

Table 2 Compatibility Values of Standard Basic Dyes Obtained from AATCC Test Method 141–1987 and the Rolled Fabric Liquid Chromatography Column [69]

	Compatibility value, C_v	
CI basic dye	AATCC	LC
Blue 69	1	0.7
Blue 45	2	1.8
Blue 47	3	2.7
Blue 77	4	4.3
Blue 22	5	4.6
Orange 42	1	1.0
Yellow 29	2	1.7
Yellow 28	3	2.7
Yellow 15	4	3.9
Orange 48	5	4.6

Table 3 LC Method for Finish Analysis

Chemical	Stationary phase	Eluent	Detector	Reference
Formaldehyde[a]	C18	Acetonitrile/water (60/40)	UV 340 nm	[20,21]
Sulfonated aromatic compounds finish	C18	Water/acetonitrile (90/10 to 10/90 with linear gradient elution)	UV 254 nm	[13]
Tris(2,3-dibromopropyl) phosphate finish	C18	Methanol/water (70/30)	UV 254 nm	[23]
Poly-*m*-phenylene isophthalamide fiber precipitation and plasticizing baths	C18	Tetrahydrofura/water (53/47)	UV 260 nm	[22]
M-Methylolpyrolidone finish	C18	Water/methanol (70/130)	RI	[17]
DMDHEU finish[b]	Cationic exchange resin	Water	RI	[14,15,19]
	C18	Water	RI	[11,12]
DMEU[c]	C18	Water	RI	[16]

[a]Formaldehyde first reacts with 2,4-dimitrophenyl hydrazine to form the corresponding hydrazone, which is more easily detectable than formaldehyde itself.
[b]DMDHEU, dimethyloldihydroxyethyleneurea.
[c]DMEU, dimethylolethyleneurea.

IV— Conclusions

As an analytical tool, LC has penetrated the textile industry rapidly and is being utilized widely, especially in the chemistry related areas. Although colorant analysis was its original use, it has found many and varied areas of applications from characterization of internal pore structures of fibers to the effects of processing treatments and conditions on fiber/treatment interactions.

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6—
Evaluation of DP Finishes by Chromatographic and Spectroscopic Methods

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I—
Introduction

Chemicals that cross-link cellulose to generate restorative forces for crease retention and smooth drying are called durable press (DP) agents or DP finishes. Analysis of these materials is important for both their production and their application. Chromatography yields both qualitative and quantitative information and provides separation capability for further analyses, such as mass spectrometry. Spectroscopic analysis typically generates information about the nature of the components in the finish. This chapter describes both chromatographic and spectroscopic analyses of DP agents.

II—
Background Information on DP Agents

Modern durable press (DP) treatments of cotton involve the application of crosslinking agents to the cellulosic polymer in order to impart smooth drying, wrinkle resistance, and/or crease retention. The very early durable press finishing agents were urea-formaldehyde (UF) and melamine-formaldehyde (MelF) products. These materials formed three-dimensional polymeric networks inside the fiber and were legitimately called resins. When 1,3-dihydroxymethyl-4,5-dihydroxy-2imidazolidinone (more commonly known as dimethyloldihydroxyethyleneurea or DMDHEU) was introduced in 1964 as a promising new durable-press finish, the term DP resin incorrectly persisted. Unlike the UF and MelF finishes, DMDHEU did not react with itself to form a network polymer, but formed nearly monomeric cross-links between cellulose molecules as shown in Figure 1.

Synthesis of DMDHEU is accomplished [1] by reacting urea, glyoxal, and formaldehyde as shown in Figure 2. Reductions in the amount of formaldehyde

released by fabrics finished with DMDHEU have been accomplished through improved control of curing conditions, better catalysts, and by reacting DMDHEU with alcohols or polyols to convert one or more of the *N*-hemiacetal groups to an acetal. The resulting "capped" finishes are the dominant cross-linking finishes in today's textile market.

Because of the concern over formaldehyde released from DP-finished fabtics, a search for formaldehyde-free cross-linkers has been in progress for several years. One solution to this problem has been to utilize glyoxal-based finishes, such as 1,3-dimethyl-4,5-dihydroxy-2-imidazolidinone (DMDHI), that do not contain formaldehyde. Cross-linking of cellulose by DMDHI is shown in Figure 3.

Polycarboxylic acids, such as 1,2,3,4-butanetetracarboxylic acid (BTCA), have also been shown to be effective nonformaldehyde cross-linking agents. Figure 4 shows the cross-linking of cellulose by BTCA.

Information in this chapter emphasizes analysis of DMDHI, DMDHEU and its derivatives, and polycarboxylic acids. Because of its importance in durable-

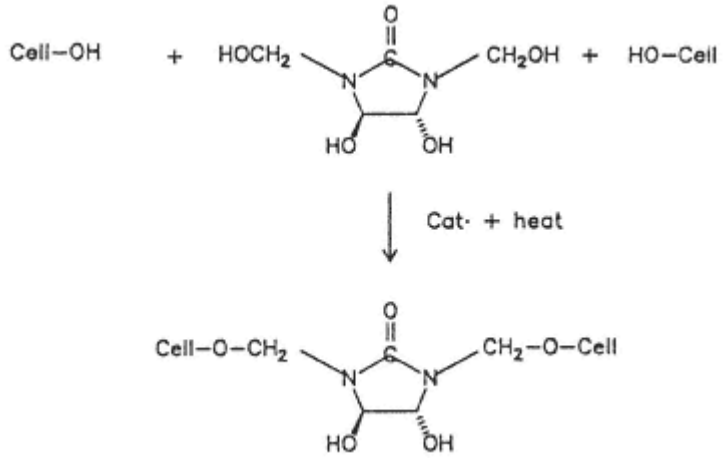

Figure 1
Cross-linking of cellulose with DMDHEU.

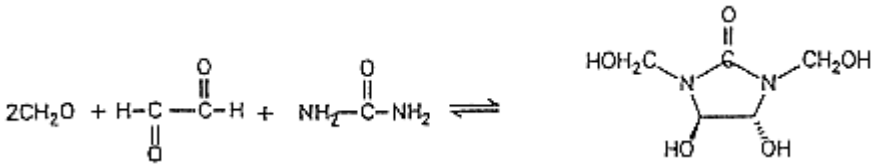

Figure 2
Synthesis of DMDHEU.

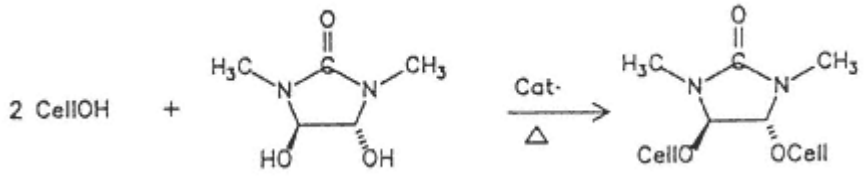

Figure 3
Cross-linking of cellulose by DMDHI

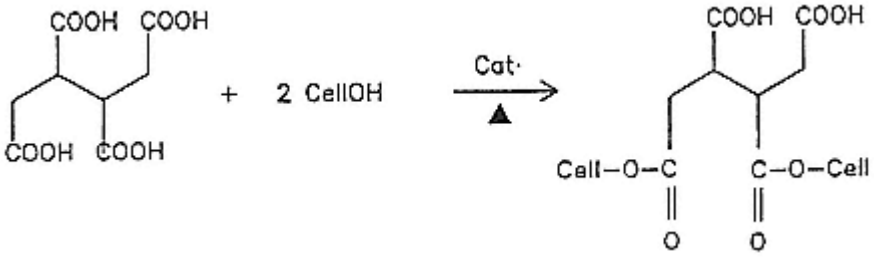

Figure 4
Cross-linking of cellulose by BTCA.

press finishing, appropriate references for formaldehyde analysis are discussed. Analytical techniques include thin-layer chromatography (TLC), gas chromatography (GC), high-performance liquid chromatography (HPLC), ultraviolet-visible spectroscopy (UV-VIS), mid-infrared spectroscopy (IR), near-infrared spectroscopy (NIR), ^{1}H- and ^{13}C-nuclear magnetic resonance spectrometry (NMR), and mass spectrometry (MS).

III—
Chromatographic Analysis of Durable-Press Agents

A—
Thin-Layer Chromatography

Player and Dunn [2] gave a brief introduction to TLC and offer information on several textile applications. More complete descriptions of this technique are available in books, such as those by Fried and Sharma [3] and Touchtone [4]. Because of their relatively high polarity, DP agents are not routinely analyzed by TLC. In an extensive analysis of a variety of DP precursors, Valk and co-workers [5] separated 15 different compounds, such as dihydroxyethyleneurea (DHEU), melamine, and urea, using a chloroform/methanol/water mobile phase and a cellulose stationary phase. Carbamate precursors were separated with carbon tetrachloride/methylene chloride/ethyl acetate/formic acid on silica gel. Moore and Babb [6] used alcohol/water mobile phases and cellulose as a TLC stationary

phase to effect separations of 2-imidazolidinone (EU), 1,3-dihydroxymethyl-2-imidazolidinone (DMEU), 4,5-dihydroxy-2-imidazolidinone (DHEU), DMDHEU, tetramethylated DMDHEU, and 4,5-dimethoxyEU. Because the DP agents were reacted with the stationary phase (cellulose), this method was used to compare reactivity of these materials. Methyl carbamate (MC), *N*-hydroxymethyl methylcarbamate (MMMC), and *N*, *N*-dihydroxymethyl methylcarbamate (DMMC) (Fig. 5) were isolated by thick layer chromatography (chloroform, acetone, 2-propanol on Adsorbosil-1) [7]. In a preliminary portion of this work, Cashen visualized the eluted spots by first hydrolyzing with a sulfuric acid spray followed by acidic chromotropic acid spray.

Rennison [8] identified DMDHI in hydrolysates from fabrics finished with that reagent by eluting the products on silica with 1-propanol/water. Kantschev and Nesnakomova [9] monitored and optimized the synthesis of DHEU from glyoxal and urea with TLC. In an interesting application of TLC for studying DP chemistry, Chen [10] coated an aluminum plate with cellulose to study the interactions between tartaric acid and aluminum sulfate. The tartaric acid alone gave a different retention factor than the aluminum sulfate and mixtures of these two catalyst components. He concluded that there is an interaction between the aluminum ion and the hydroxyl groups of the acid.

B—
Gas Chromatography

Basic information on gas chromatography and some qualitative and quantitative textile applications are given by Player and Dunn [2]. Instrumental and theoretical details as well as practical information on gas chromatography are presented by Baugh [11]. Because of the presence of hydroxyl and amido NH groups in their structure, DP agents are not sufficiently volatile to be analyzed by gas chromatography. Replacement of hydrogen in the HO and NH groups with trimethylsilyl renders the DP agents sufficiently volatile to be chromatographically separated. Bullock and Rowland [12] separated the *N*-$SiMe_3$, and *N*-CH_2OSiMe_3 derivatives of 1-methyl-2-imidazolidinone on a 2 ft × 0.25 in column packed with GE-XE-60. Divatia et al. [13] added acetone to solutions of DP agents to precipitate the active ingredients. These materials were then silylated in pyridine with *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and analyzed on a 6 ft × 0.25 in column packed with SE-52. In preparation for mass spectrometric analysis of 4,5-dihydroxy-2-imidazolidinone (DHEU), 1-hydroxymethyl-4,5-dihydroxy-2-

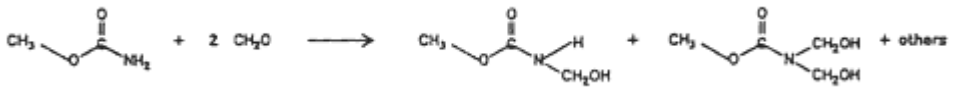

Figure 5
Methylolation of methyl carbamate.

imidazolidinone (MMDHEU), DMDHEU, several methylated derivatives of DMDHEU, and two commercial DP finishing agents, Beck and co-workers [14] dried the DP agents at room temperature and silylated them with *N*-methyl-*N*-trimethylsilyltrifluoroacetamide (MSTFA). MSTFA was selected because it is a stronger silylating agent than BSA and because the by-product, *N*-methyltrifluoroacetamide, is more volatile than acetamide from BSA. Chromatographic separation was effected on a 30-m DB-1701 fused silica column capillary column. A typical chromatogram of a DMDHEU-based commercial DP finish is shown in Figure 6. In this chromatogram, tetrasilylated DMDHEU eluted at 14.41 min. Figure 7 is a chromatogram of silylated glycolated DMDHEU. Compounds eluting from 26.89 to 30.88 are monoglycolated—that is, one DMDHEU -OH has been converted to $-OCH_2CH_2OCH_2CH_2OH$.

In a comparison of the cold sulfite method for determining formaldehyde released from DP-finished fabric with headspace gas chromatography (HGC), Kamath et al. [15] found the two methods to be comparable if the headspace fabric and titration temperature were the same. Low concentrations of formaldehyde in the headspace necessitated the use of a photoionization detector rather than the usual flame ionization detector. The use of HGC was described by these authors in an earlier publication [16].

Vail and Dupuy [17] extracted odor-causing materials from fabrics treated with trimethylolmelamine and analyzed them by GC. They found trimethylamine to be responsible for the fishy smells emanating from the finished fabric.

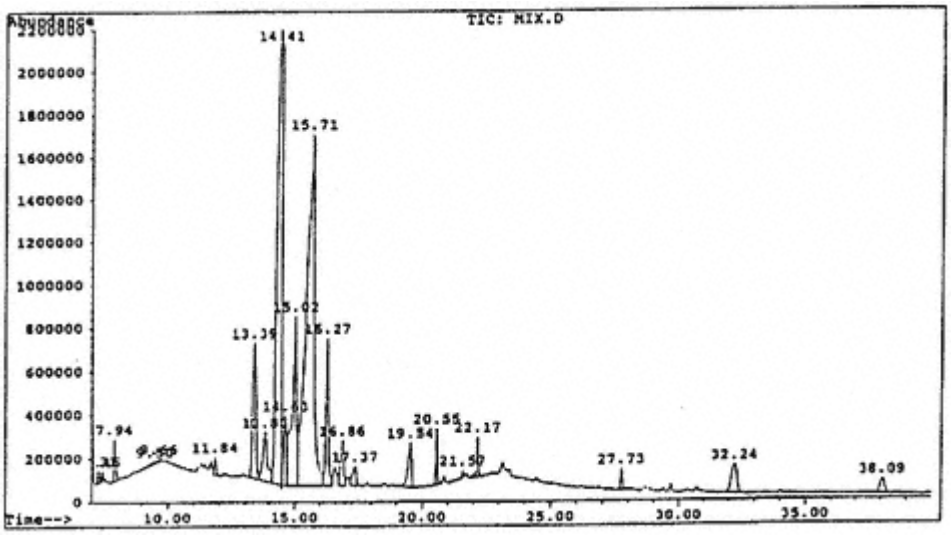

Figure 6
GC chromatogram of trimethylsilylated commercial DMDHEU finish.
(Courtesy S. Yoon, Sequa Chemicals, Inc., Chester, S.C.)

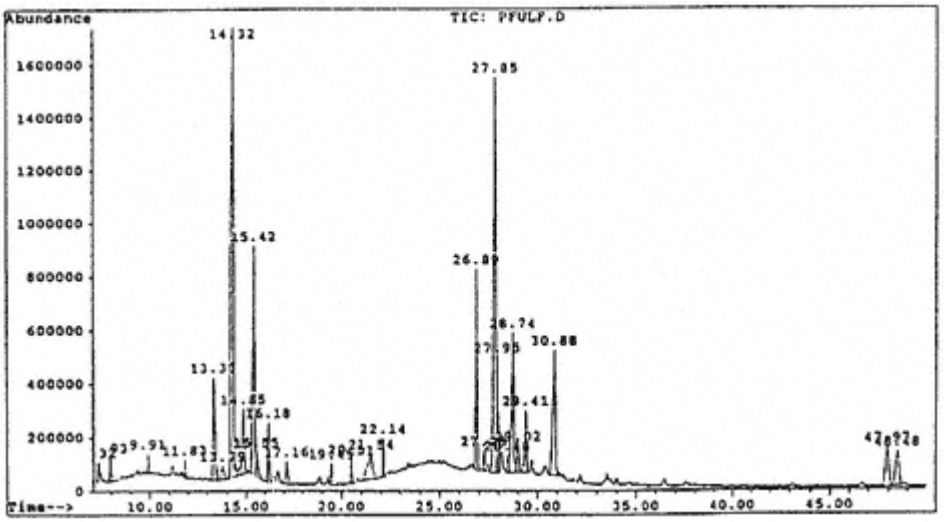

Figure 7
GC chromatogram of trimethysilylated commercial glycolated DMDHEU finish.
(Courtesy S. Yoon, Sequa Chemicals, Inc., Chester, S.C.)

C—
High-Performance Liquid Chromatography

Compounds that are not sufficiently volatile to be separated by gas chromatography may be analyzed by HPLC. Player and Dunn [2] briefly discuss HPLC equipment and some textile applications. Instrumentation, separation mechanisms, and practical tips for use of HPLC may be found in McMaster's book [18] or other similar references. For analysis of DP agents, HPLC has the advantage that no derivatization is necessary as it is in GC. However, resolution in HPLC is not as good as that exhibited by capillary GC.

Early liquid chromatographic analysis of DP agents took advantage of the differences in interactions between mixture components and ion-exchange resins. Kumlin and Simonson [19] developed a liquid chromatographic method for analyzing the components in urea-formaldehyde resins using a mixed anion (DA-X8 as its sulfate salt)—cation (Aminex A-5 as its lithium salt) exchange resin stationary phase and an ethanol—water mobile phase with refractive index detection. With this system the authors were able to separate urea, *N*-hydroxymethylurea (MMU), *N*, *N´*-dihydroxymethylurea (DMU), some methylenediureas, and some oxymethylenediureas. In subsequent Work [20] they used preparative liquid chromatography to separate *N*, *N*-DMU and *N*, *N*, *N*-trihydroxymethylurea (TMU). Structure of these materials was established by 270-MHz ^{1}H-NMR spectra. Symmetrical *N*, *N´*-DMU was formed in much smaller amounts than the unsymmetrical *N*, *N*-DMU. No evidence of tetramethylolurea was found.

Beck et al. [21] used a thermostated column packed with the lithium form of Aminex Q-15S (cation exchange resin) and water as the mobile phase to separate urea, formaldehyde, DHEU, MMDHEU, and DMDHEU. This technique was used to analyze several commercial DP agents. Beck and Pasad [22] used this method to quantitatively determine the amounts of DHEU, MMDHEU, and DMDHEU on fabrics that were partially cured. From these data at 70°C, 90°C, and 110°C, they determined both the rate constants and the energy of activation for the reaction between cellulose and DMDHEU. Beck and Pasad [23] also determined the effect of pad-bath pH and storage period on the hydrolysis of DMDHEU using the same chromatographic method. They concluded that the effect of pad-bath pH is much more important than the storage period on the stability of DMDHEU. DMDHEU was stable up to 55 days, providing the pad-bath pH did not exceed 6.

When reliable reversed-phase HPLC columns became available, they supplanted the ion exchange columns. Octadecylsilyl (C18) phases were most widely used for analysis of DP agents. In most cases, no organic modifier was required as water gave adequate separations. With these columns, plate counts as high as 100,000 plates/m were available and the chromatographer could purchase, rather than pack, a column. Figure 8 shows the structures of two potential cross-linking agents synthesized by Frick and Harper [24]. They followed both the synthesis from glyoxal and the corresponding: diurea and the cis—trans isomerization of the ring hydroxyls by C18 reversed-phase HPLC. Frick and Harper [25] used C18 reversed-phase HPLC to determine the effect of pH on the synthesis of DMDHI from glyoxal and dimethylurea. They concluded that pH 8 was best for this reaction.

Beck and Pasad [26] determined the nature and amounts of reagent residues on fabric padded with 1,3-dihydroxymethyl-2-imidazolidinone (DMEU) using reversed-phase C18 HPLC. They found, as expected, that DMEU is much less stable than DMDHEU on fabric. Because DMEU reacts with itself, condensation products as well as 1-hydroxymethyl-2-imidazolidinone (MMEU) and EU were

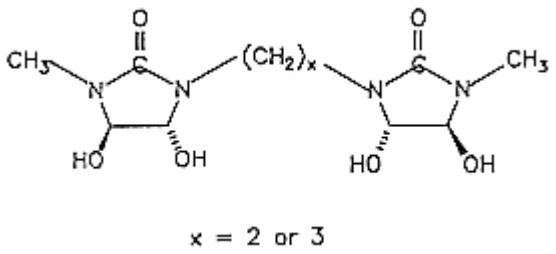

Figure 8
Multifunctional dihydroxyimidazolidinone cross-linking agents.

observed in the chromatograms. In a related study of reagent residues on fabrics treated with *N*-hydroxymethylpyrrolidone (NMP), a monofunctional model compound for DP finishing, Beck and co-workers [27] used C18 HPLC to determine the amounts of those residues. Pasad et al. [28] used preparative HPLC to isolate a component from a commercial DMDHEU finish. ^{13}C-NMR supported a structure consistent with a dimer of DMDHEU.

In an effort to better understand the role of formaldehyde scavengers in DP finishing, Vail and Beck [29] used reversed-phase HPLC and ^{1}H-NMR to study the effect of EU and urea on formaldehyde released by DMMC-treated fabrics. The scavengers altered the equilibrium between DMMC and formaldehyde in the pad baths and diminished cross-linking in the fabric finished with those baths.

Two papers, each of which summarized the status of HPLC analysis of DP agents, were published in 1984. Beck and co-workers [30] compared results of cation-exchange columns and reversed-phase columns for analysis of DP agents. They also included reversed-phase chromatograms of partially and fully methylated DMDHEU finishes. In these chromatograms, the presence of both trans- and cisisomers of 1,3-dimethoxymethyl-4,5-dihydroxy-2-imidazolidinone (DMMDHEU) was indicated. Retention times of the *cis*-isomers of DMDHI and DMMDHEU were about 3 min longer than those of the trans-isomers. Stronger interaction between the cis-hydroxyls and the stationary phase, possibly exposed silanol groups, is the most likely explanation for this elution behavior. Andrews [31] studied urea formaldehyde condensation products, DMDHEU, methylatd DMDHEU, and some other DP agents by reversed-phase HPLC to determine the effect of catalyst on hydrolysis of the finishes. It was also determined that the concentration of monomethylolated species decreases as formaldehyde concentration increases in these finish mixtures.

Ernes [32] developed an HPLC method for determination of formaldehyde in aqueous solutions generated in American Association of Textile Chemists and Colorants (AATCC) Test Method 112 [33]. Conversion to its 2,4-dinitrophenylhydrazone (2,4-DNP) allowed reversed-phase chromatographic analysis of formaldehyde from 2 to 10,000 µg/g of fabric. Results were comparable with those obtained using the Nash reagent specified in Method 112. The advantage of a chromatographic method such as this one is that the separation removes any interfering substances since their 2,4-DNP derivatives would have different retention times. Yoon [34] describes both normal and reversed-phase methods for analyzing the 2,4-DNP of formaldehyde. In that same reference, Yoon also describes the preparation and HPLC analysis of the dimedon derivative of formaldehyde.

Two recent developments in HPLC detectors are worthy of special note. The first, called LC Transform (by Lab Connections), is a simple interface that allows the eluent from an HPLC to be deposited on a small circular disk. The mobilephase solvent is evaporated as the disk rotates, leaving the eluted analytes in a circular track. The disk is then placed in a device in the beam of an FTIR spectro-

meter. IR spectra are obtained as the disk rotates. Figure 9 shows the chromatogram of a commercial glycolated DMDHEU finish using this detector. Examples of spectral information from this technique are presented in the Section IV.C. This appears to be a powerful tool for monitoring analytes eluted from an HPLC column, regardless of the mechanism of separation.

A versatile, universal evaporative light scattering detector (ELSD) has been developed by Varex and is available through Alltech. Column eluent is nebulized with nitrogen gas to form a uniform dispersion of droplets. As the droplets pass through a heated tube, the solvent evaporates, leaving very fine particles of dried analyte in solvent vapor. As the particles pass through a flow cell, they scatter light from a laser diode. The scattered light is detected by a silicon diode, generating, after amplification, a chromatogram. Since solvent is evaporated, ELSD can be used with gradient elution and its response is not affected by changes in column or laboratory temperatures. It is more sensitive than refractive index (RI). A schematic diagram of the ELSD is shown in Figure 10. For comparison with the

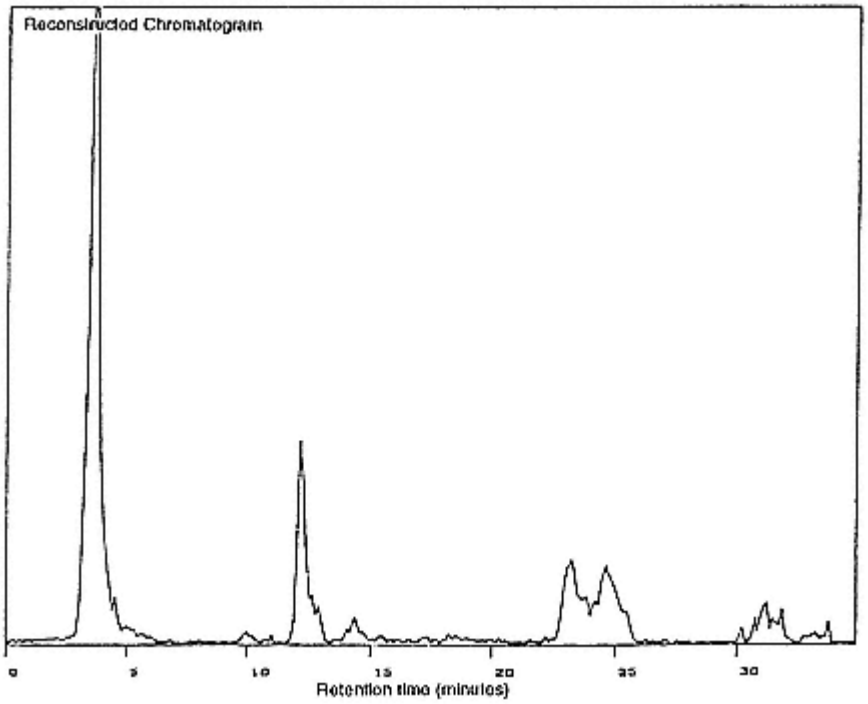

Figure 9
HPL Chromatogram of glycolated finish using LC Transform detector.
(Courtesy S. Yoon, Sequa Chemicals, Inc., Chester, S.C.)

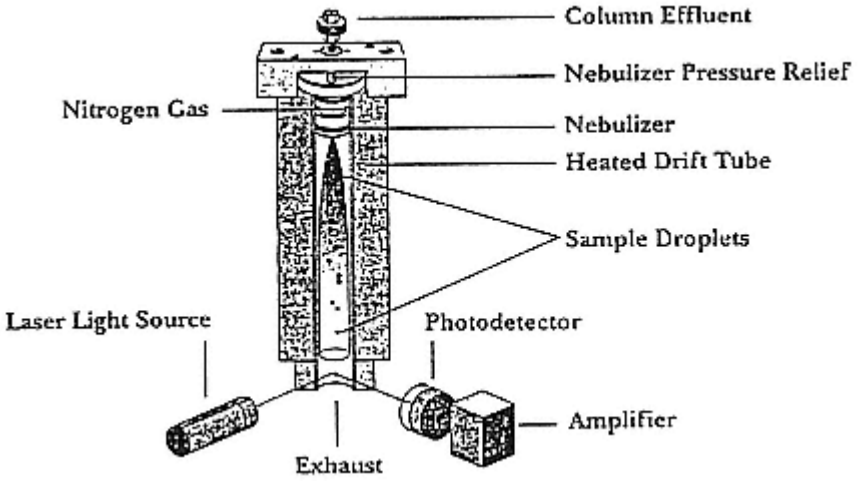

Figure 10
Schematic diagram of ELSD:
(Diagram furnished by Alltech.)

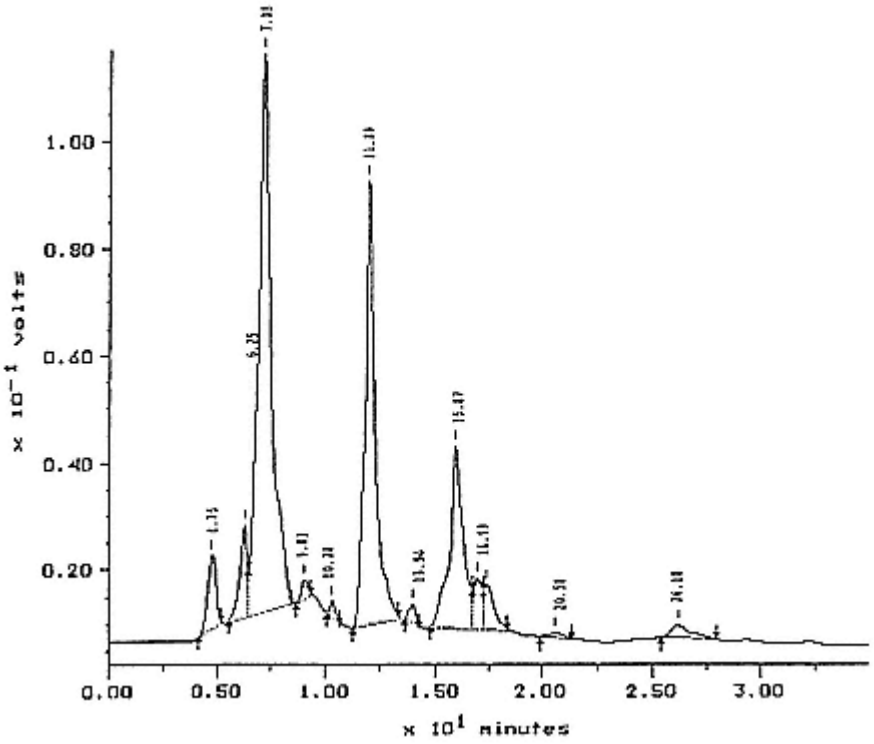

Figure 11
Refractive index chromatogram of glycolated DMDHEU.
(Courtesy S. Yoon, Sequa Chemicals, Inc., Chester, S.C.)

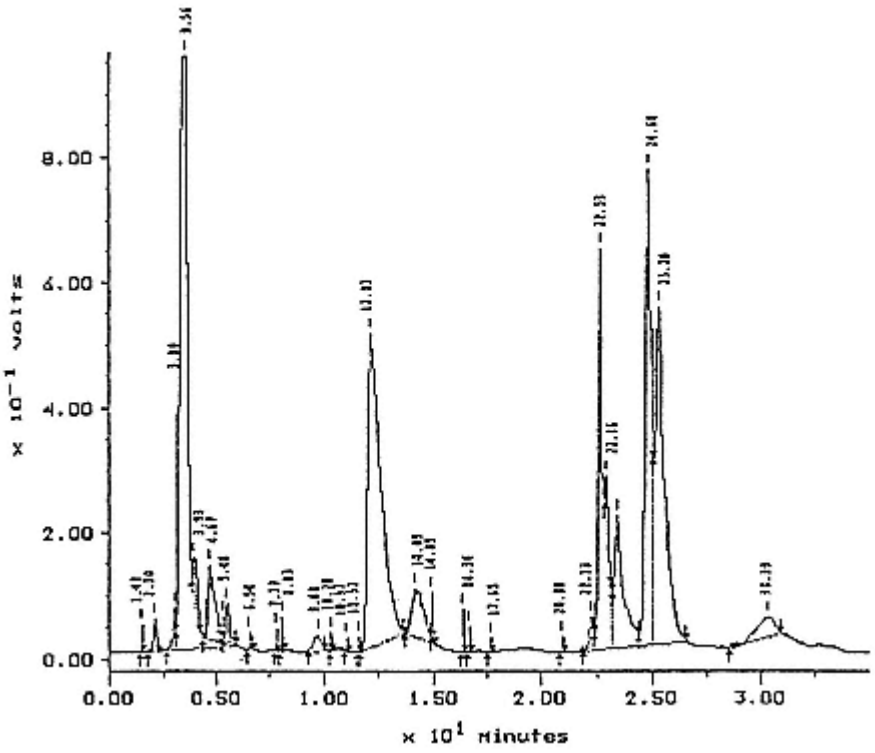

Figure 12
ELSD chromatogram of glycolated DMDHEU.
(Courtesy S. Yoon, Sequa Chemicals, Inc., Chester, S.C.)

RI chromatogram (Fig. 11) and LC Transform responses (Fig. 9), Fig. 12 shows an ELSD chromatogram of the same sample.

IV—
Spectroscopic Analysis of Durable-Press Agents

A—
Ultraviolet-Visible Spectroscopy

General background information on UV-VIS spectroscopy can be found in any modern instrument analysis text book or in specific references, such as Perkampus [35].

Since the carbonyl group in most DP agents absorbs energy in the short wavelength ultraviolet region (~210 nm), UV-VIS spectroscopy is not particularly useful for their analysis. On the other hand, formaldehyde absorbs radiation at 397 nm, which should make its concentration measurable with visible radiation.

Unfortunately, the molar absorbtivity for this $n \rightarrow \pi^*$ is so small that this is not possible. To compensate for this weak absorption, formaldehyde is typically converted to a derivative which absorbs strongly in either the UV or VIS region. The use of several reagents, including acetylacetone (Nash reagent), chromotropic acid, 3-methyl-2-benzothiazolone hydrazone (MBTH), dimedon, and 2,4-dinitrophenylhydrazine, for this purpose is summarized by Yoon [34].

B—
Near-Infrared Spectroscopy

When compared to UV-VIS and IR spectroscopy, NIR is a new and developing tool for both qualitative and quantitative applications. Background information and some practical aspects concerning the use of NIR spectroscopy may be found in Ref. 36. NIR is a secondary technique; that is, it requires calibration models to be developed from a reference analytical method. Ghosh et al. [37] developed NIR calibrations for amounts of DMDHEU and DMDHI on cotton fabrics. Kjeldahl nitrogen determinations were used as the reference data for regression. A three-wavelength model successfully predicted percent nitrogen with an $r^2 = .97$ and a standard error of prediction (SEP) of 0.198% for fabrics treated with either DMDHEU or DMDHI. Ghosh and Brodmann [38] developed a system for online monitoring of DMDHEU in a polyester/cotton fabric. Another three-wavelength regression model from Kjeldahl values and second derivative NIR spectra gave $r^2 = .98$ and SEP = 0.2%. Use of second-derivative spectra reduced baseline shifts by removing or reducing differences caused by surface effects.

Morris and co-workers [39] determined the amount of BTCA on finished fabric by NIR. The reference method involved measurement of the ratio of the carbonyl stretching and CH_2 bending absorbances by FTIR. This ratio varied linearly ($r = .999$) with percent wet pickup. The FTIR ratio was used to determine a NIR model. The model predicted percent BTCA with a SEP of 0.33 and $r = .99$. Use of second derivative NIR spectra only improved the SEP to 0.31.

C—
Infrared Spectroscopy

General information on infrared spectroscopy can be found in any introductory organic chemistry text or in specific references, such as Colthup et al. [40]. Berni and Morris [41] provided information on experimental techniques useful in textile applications and briefly discuss IR analysis of DP agents.

The literature is replete with references to the use of IR spectroscopy as a tool for studying DP finishes. Most of the early IR investigations of DP finishes were by authors at the Southern Regional Research Center. The references discussed here are meant to be representative, rather than all-inclusive, of those publications. McCall et al. [42] described the following four techniques for obtaining infrared spectra of DP agents on finished cotton fabrics-potassium bromide disc, differential disc (KBr disc containing cotton placed in reference beam and disc containing

finished cotton placed in sample beam), acid hydrolysis, and multiple internal reflectance. The differential disc method was an early version of the subtractive techniques that are now possible with Fourier-transform infrared (FTIR) instruments. In the acid hydrolysis method, the finished cotton fabric was hydrolyzed with HCI and the hydrolysate mixed with KBr. This mixture was evaporated, dried, and pressed into a pellet for spectral determination. In the reflectance method, fabrics were pressed against a KRS-5 plate for spectral measurements. The authors identified absorption bands that were characteristic of DMU, DMEU, methylolated melamine, and some other finishes. In most cases, positive identification required spectra of known finishes for comparison with those obtained by one or more of these methods. Vail et al. [43] obtained IR spectra of cellulose films that had been reacted with either DMEU or DMMC. The authors concluded that both of these reagents gave monomeric crosslinks when reacted with cellulose. In a study of catalysis of the cross-linking reaction, Pierce and Vail [44] synthesized a series of complexes between 2-imidazolidinone (EU) or tetrahydro-2-pyrimidone (propyleneurea, PU) and some metal perchlorates. They concluded that the position of the carbonyl absorption band in these complexes could not be used to predict the mode of bonding. Vail et al. [45] reported the formation of DMDHI from DMU and glyoxal and characterized both the trans- and cis-isomers by IR and proton NMR. Petersen [46] described the influence of structure on the position of the carbonyl absorption band in several precursors of DP finishes. In addition, he showed that there is a linear relationship between carbonyl wavenumber and both the rate constant and energy of activation for the first methylolation of these amides. Electron density on nitrogen atoms, steric effects, and planarity of ring structures were reasons given for the differences in position of the carbonyl absorbtion bands. Jung and co-workers [47] studied the fine structural changes in cotton that accompany DP finishing and subsequent hydrolysis of the cross-linked fabric. They found that all traces of finish absorbances were removed if fabrics finished with DMEU or MMEU were hydrolyzed with urea-phosphoric acid (UPac), but DMDHEU signals remained even after several hydrolytic treatments. This information, coupled with data from strength measurements, led the authors to conclude that the DMDHEU cross-link is different from that of DMEU, either in its nature or site of attachment to cellulose.

Morris et al. [48] determined the amount of DMDHEU on finished fabric from FTIR spectra. By normalizing the calibration and sample spectra and applying a scaling factor, they developed a regression model ($r = .9876$) that predicted percent DMDHEU within about 12% of the Kjeldahl value. In a subsequent publication [49] Morris compared the previously mentioned KBr disc and multiple internal reflectance techniques with diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS). Samples investigated were cotton fabrics treated with sodium hypophosphite (NaH_2PO_2, catalyst for cross-linking with BTCA) and BTCA/NaH_2PO_2. Of the four DRIFTS sampling techniques investigated, the best

spectra were obtained using discs cut from fabric with no additional sample preparation, such as grinding or addition of KBr. The KBr disk technique gave more reproducible spectra than DRIFTS, which was better than the multiple internal reflectance method.

Investigations of both the mechanism of cross-linking with DMDHEU and BTCA or other polycarboxylic acids with cellulose, and the nature of those crosslinks have utilized FTIR and other analytical techniques. Yang et al. [50] used photoacoustic spectroscopy (PAS) to determine the distribution of finishing agent (DMDHEU or methylated DMDHEU) in foam-finished and normally finished fabrics. They found that finish distribution was more uniform in foam-finished fabrics and that this led to higher wrinkle recovery angles. The PAS technique allows the acquisition of IR spectra from material near the surface (to a depth of a few micrometers) and it requires little sample preparation. A comparison of FTIR/PAS and DRIFTS for analysis of textile fibers and chemically modified fabrics is given by Yang [51]. DRIFTS showed an enhancement of band intensifies for near-surface species compared to FTIR/PAS, but FTIR/PAS gave spectra from chromophores closer tothe surface. Yang and Perenich [52] described information obtained by FTIR/PAS on DHDHEU and polycarboxylic acid treated fabrics. These studies compared the intensities of carbonyl bands in powdered samples and in the near-surface regions to determine finish distribution. Polycarboxylic acids studied were BTCA, all-*cis*-l,2,3,4-cyclopentanetetracarboxylic acid, and *trans*-aconitic acid. Finish distribution differences for the polycarboxylic acids were explained by the size and diffusion characteristics of the molecules. Using FTIR/PAS, Yang [53] has determined the degree of ester cross-linking in BTCA treated fabrics. This technique involves conversion of all carboxylate ions to carboxyl groups with dilute acid and then comparing the intensity of the acid and ester carbonyl peaks. This method has been used by Morris and co-workers [54] to determine the amount of BTCA or citric acid in polycarboxylic acid-finished cotton fabrics. These authors obtained spectral information from KBr discs.

Yoon (55) has employed FTIR as an HPLC detector to identify components of durable press mixtures. Figure 9 showed the liquid chromatogram reconstructed from infrared absorbance. The structure of one possible monoglycolated DMDHEU isomer is shown in Figure 13. Figures 14 and 15 are FTIR spectra of DMDHEU (peak at 3.85 min) and glycolated DHDHEU (peak at 23.23 min).

D—
Nuclear Magnetic Resonance Spectrometry

Nuclear magnetic resonance is an extremely powerful instrumental technique for determining structures of materials. General information on NMR principles may be found in any introductory organic chemistry text or in specific references, such as Sanders and Hunter [56]. Discussion in this chapter is divided into references

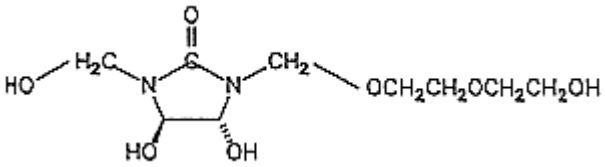

Figure 13
Glycolated DMDHEU.

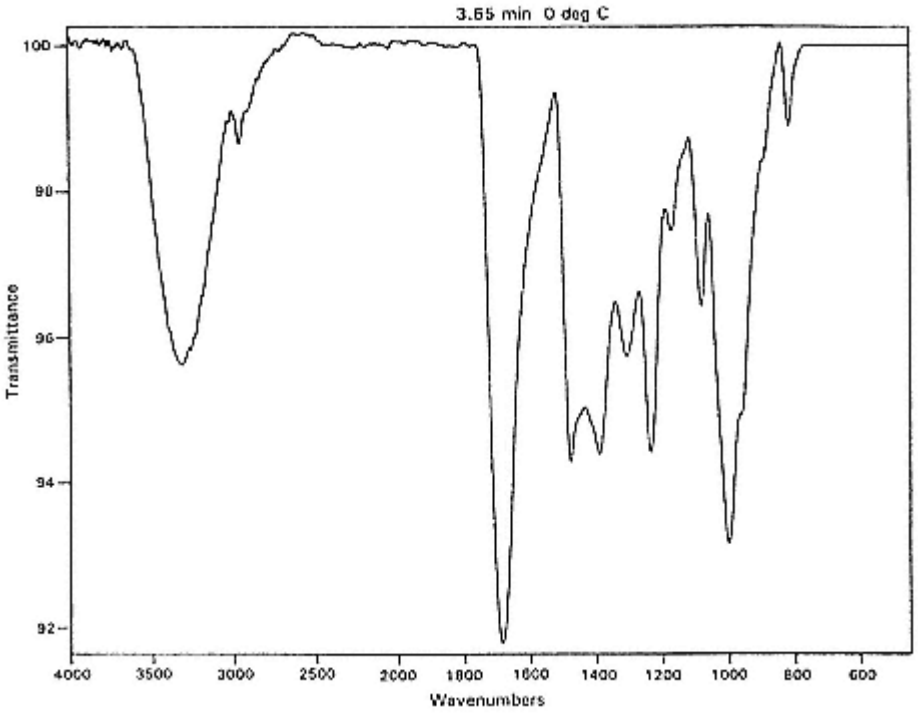

Figure 14
FTIR spectrum of DMDHEU as eluted from a C 18 HPLC column.
(Courtesy S. Yoon, Sequa Chemicals, Inc., Chester, S.C.)

dealing with proton magnetic resonance (^{1}H-NMR) and carbon-13 magnetic resonance (^{13}C-NMR).

1—
^{1}H-NMR

As with infrared analysis of DP agents, many of the early ^{1}H-NMR studies were carded out at the USDA Southern Regional Research Center. References included

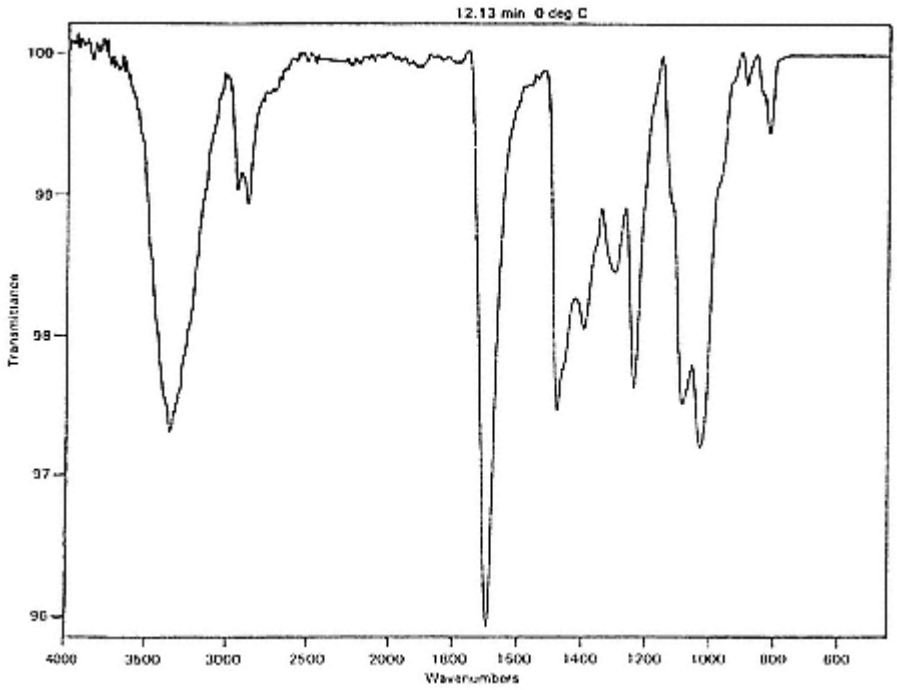

Figure 15
FTIR spectrum of glycolated DMDHEU as eluted from a C 18 HPLC column.
(Courtesy S. Yoon, Sequa Chemicals, Inc., Chester, S.C.)

here are representative, but not all-inclusive, of that work. Unless otherwise specified, all ^{1}H-NMR spectral data were measured in solution at 60 MHz.

Several groups investigated the structure of UF condensates with ^{1}H-NMR. Kumlin and Simonsen [19] identified and separated the products of urea formaldehyde reactions by HPLC and identified those compounds by NMR. Chemical shifts for MMU, *N*, *N´*-DMU, *N*, *N*-DMU, and trimethylolurea were given. These spectral characteristics allowed the symmetrical (*N*, *N´*-DMU) and unsymmetrical (*N*, *N*-DMU) disubstituted products to be differentiated. Chiavarini and co-workers [57] also characterized MMU, *N*, *N´*-DMU, methylenediurea, methoxymethylurea, dimethoxymethylurea, and dimethylolmethylenediurea by NMR in dimethyl sulfoxide-d_6 and dimethyl sulfoxide-d_6/$CaCl_2$ solutions. The latter solvent gave sharper peaks that led to better resolution, especially for NH and OH protons. Andrews [29] determined the distribution of MMU, *N*, *N*-DMU, *N*, *N´*-DMU, and TMU in mixtures of varying urea/formaldehyde ratios with ^{1}H-NMR.

In the course of studies with 1-(hydroxymethyl)-2-pyrrolidone (NMP) (Fig. 16) as a model monofunctional durable press agent, Beck et al. [58] isolated

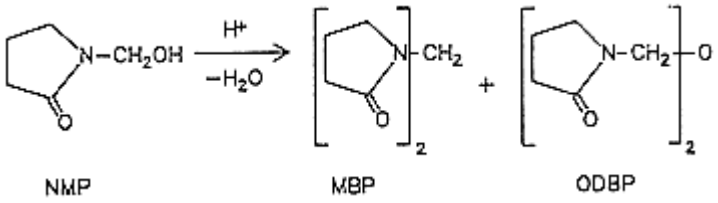

Figure 16
Dehydration products from *N*-(hydroxymcthyl)-2-pyrrolidone.

both *N, N´*-methylenebis-2-pyrrolidone [MBP] and *N, N´*-(oxydimethylene)bis-2-pyrrolidone (ODBP) (Fig. 16). These species were characterized both by ^{1}H-NMR and ^{13}C-NMR. The oxydimethylene compound was convened to MBP and formaldehyde in the presence of acid at room temperature, on passage through a silica gel column, and on distillation, which indicates that this type of species may be relatively unstable in a fabric.

Vail and Beck [29] used both HPLC and ^{1}H-NMR to determine the effect that U and EU scavengers have on the composition of extracts from DMMC finished fabrics. HPLC was shown to be more reliable in the determination of low concentrations of MC.

Vail and co-workers [59] used ^{1}H-NMR to determine the composition, both qualitatively and quantitatively, of methyl carbamate/formaldehyde reaction mixtutes. They also used ^{1}H-NMR to determine relative reactivity of the *N*-CH_2OH (*N*-methylol) and *N*-CH_2OCH_3 (mcthoxymethyl) moieties in acid-catalyzed reactions of the type found in cellulose cross-linking. From this work the authors concluded that the stem (atoms connected to the nitrogen) is more important in stabilizing the incipient carbocation (N-CH_{2+}) than the nature of the leaving group (-OH or -OCH_3 in this example). In a related study, Xiang and co-workers [60] used ^{1}H-NMR to determine the rate constants for methylolation and demethylolation of methyl carbamate (MC) at different pH levels and ratios of MC/formaldehyde. To study the relationship between ease of hydrolysis of methoxy derivatives of DMDHEU and DMDHI, Vail [61] measured appropriate proton resonances at various temperatures up to 80°C. He concluded that bond cleavage occurs first at the carbon oxygen of the methylol group, regardless of the nature of the urea adduct. From NMR studies of methylated DMDHEU, Vail and Arney [62] concluded that the ring and pendant groups in DMDHEU are equal in reactivity toward small reagents, but steric hindrance reduces the reactivity of the ring groups toward larger reagents, such as cellulose. These data were confirmed on a 100-MHz instrument [63]. In further studies by Vail and Petersen [64] to determine the influence of leaving group effects on reactivity of substituted DMDHI molecules, $_{1}$H-NMR showed that both the basicity of the leaving group and the inductive effects of remaining substituents and leaving group are determining factors. Rela-

tive rates of hydrolysis under mildly acidic conditions were determined by placing pairs of several alkoxy (or one acetoxy)derivatives of DMDHI in an NMR tube and monitoring increases and decreases in appropriate resonances.

When DMDHEU was being developed as a cross-linking agent, it was intensly studied by many people using many different techniques. Vail et al. [65] concluded from proton NMR and other data that the ring hydroxyls in DMDHEU are *trans*, and predominately *trans* in DMDHI. The *cis*-isomer of DMDHI can be isolated, but it is easily converted to trans in solution by either acid or base catalysis. A summary of resonance assignments for ^{1}H-NMR spectra of a variety of substituted cyclic ureas, including EU, DHEU, DMEU, DMDHEU, DMDHI, and DMPU, is given by Soignet and co-workers [66]. Spectral effects caused by substitution on the parent ring, splitting patterns, and hydrogen,bonding effects were also discussed for these cyclic ureas.

Frick and Harper [67] used ^{1}H-NMR and HPLC to show that the glyoxal adducts shown in Fig. 8 existed in aqueous solution as mixtures of the possible *cis—trans* isomers. The substituted ethane (x = 2) was purified by recrystallization and showed sharp NMR signals consistent with one pure compound in DMSO. This compound in water gave multiple methyl resonances in the NMR spectrum and showed five peaks in the liquid chromatogram. In a related study, these authors [67] reacted 1 mole of EU with 1 mole of glyoxal and obtained a watersoluble adduct. Methylation of this adduct gave a solid that showed two sets of multiple signals representing hydroxymethylene and methylene/methoxy protons. Nine peaks were present in the liquid chromatogram of the water-soluble product. These data plus those from ^{13}C-NMR, which are discussed later, led the authors to assign the oligomeric structure shown in Figure 17.

With 300-MHz ^{1}H-NMR spectra, Chen [10] showed that tartaric acid does complex with aluminum sulfate. These data supported the results he had obtained on these durable-press catalysts with FTIR and TLC.

2—
^{13}C-NMR

Development of Fourier-transform ^{13}C-NMR gave chemists an exceptionally versatile tool for determining molecular structures. Unless otherwise specified, all spectra cited in this discussion were obtained in solution at 20 MHz. Frick and

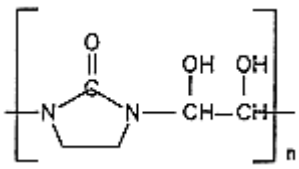

Figure 17
Adduct from glyoxal and EU.

Harper [67] observed two signals from methylene groups, four signals from hydroxymethylene groups, and three resonances for carbonyl groups in the ^{13}C-NMR spectrum of an aqueous solution of the adduct in Figure 17. Andrews [31] used this technique to determine the level of impurities in DMDHEU. Urea could be detected at 1 mol% by monitoring the carbonyl resonance. By comparison, HPLC was not able to detect urea in DMDHEU until the concentration reached 10 mol%. Beck et al. [58] reported ^{13}C-NMR chemical shifts for all three materials shown in Fig. 16.

Beck and Springer [68] reported ^{13}C-NMR chemical shift data for urea, MMU, monomethoxymethylurea, DMU, dimethoxymethylurea, methoxymethylhydroxymethylurea, DHEU, 4,5-dimethoxy-2-imidazolidinone, MMDHEU, DMDHEU, methoxymethylDHEU, DMDHEU methylated at one pendant group, DMDHEU dimethylated at both pendant groups and at both ring positions, both trimethylated DMDHEU isomers, tetramethylated DMDHEU, and DMDHI. Figure 18 shows the proton-decoupled ^{13}C-NMR spectrum of DMMDHEU. Two different tech-

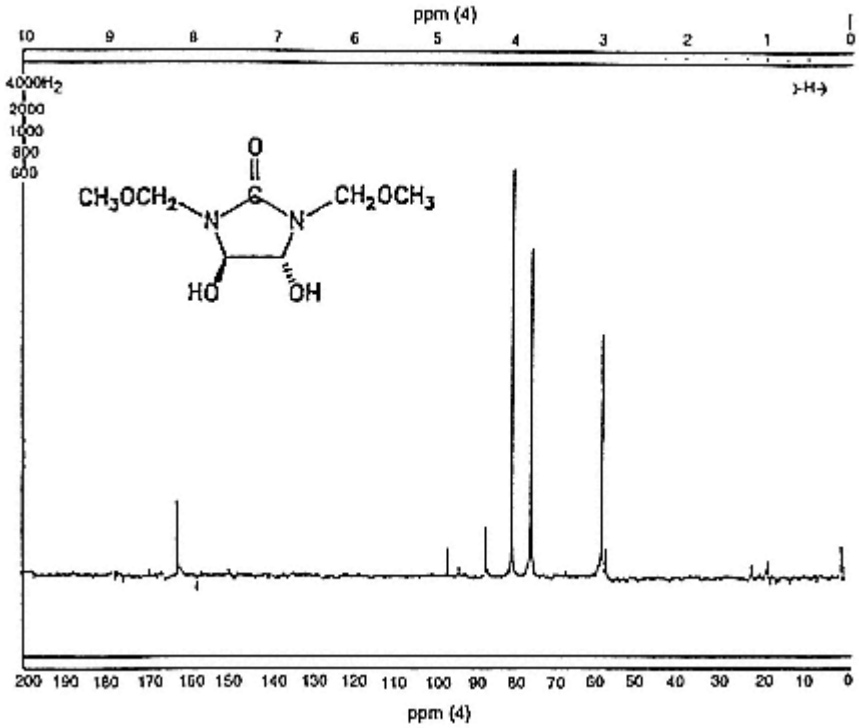

Figure 18
Proton decoupled ^{13}C-NMR spectrum of DMMDHEU.
(From AATCC.)

niques for structure elucidation [68], off-resonance and the attached proton test, are illustrated in Figures 19 and 20, respectively. In the off-resonance experiment, a small amount of coupling from protons to carbons is allowed. This splits the carbon resonance into n + 1 lines, where n is the number of attached protons. In the attached proton test, the experiment is run in a manner such that carbons bearing an even number (0 or 2) of protons exhibit an upward signal and carbons bearing an odd (1 or 3) number of protons exhibit a downward signal. Effects of structural changes, such as reaction with glyoxal, methylolation, and methylation, were also discussed. It was also concluded that the C_4 and C_5 carbons in *cis*-isomers of 4,5-dihydroxy-2-imidazolidinones resonate from 3 to 7 ppm upfield from the corresponding trans carbons. Steric crowding in the *cis*-isomer was given as the reason for this shielding effect, which was observed with both hydroxy and methoxy groups in these positions.

Hermanns et al. [69] used 50-MHz ^{13}C-NMR to determine the structure and composition of DMDHEU and DMDHI solutions. These authors [70] determined the materials extracted from DMDHEU- and DMDHI-finished fabrics by 50-MHz

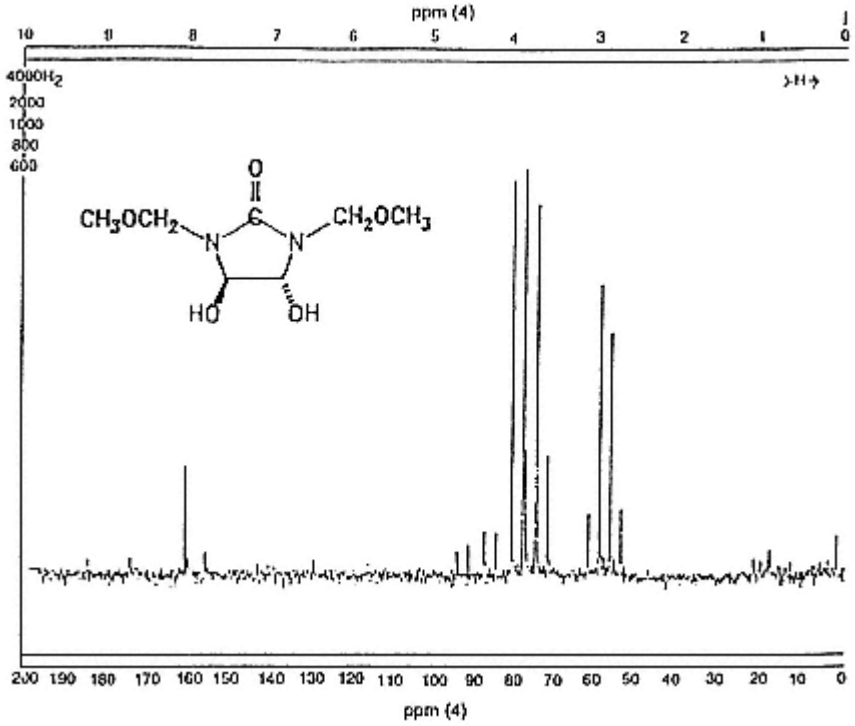

Figure 19
Off-resonance ^{13}C-NMR spectrum of DMMDHEU
(From AATCC.)

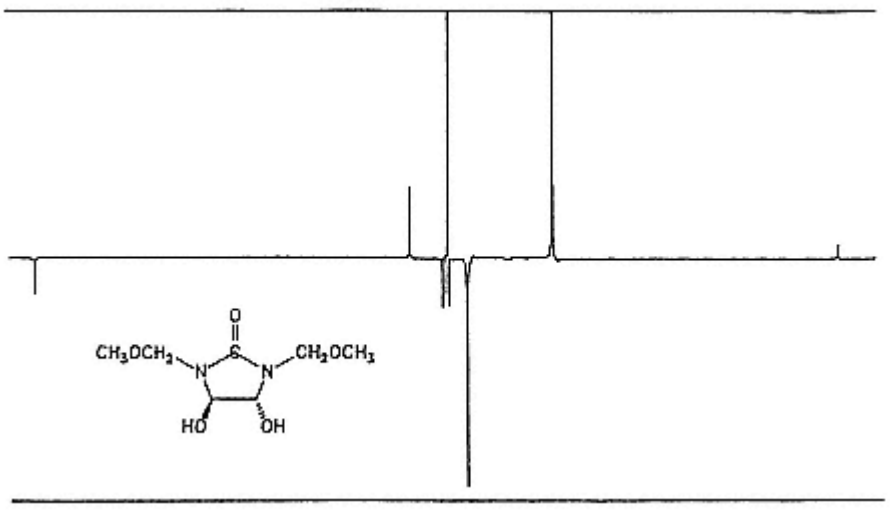

Figure 20
Attached proton test ^{13}C-NMR spectrum of DMMDHEU.
(From AATCC.)

^{13}C-NMR. Swatches of finished fabric and water were sealed in ampules and heated at 40°C for 1 week or at 80°C for 4 days. No DMDHI was detected in the extract of the DMDHI-finished fabric. DMDHEU, MMDHEU, DHEU, and formaldehyde were all detected in the extract from DMDHEU-finished fabric. Generation of these materials was explained by hydrolysis of the cellulose crosslinks and subsequent equilibration of the resulting products.

E—
Mass Spectrometry

The basic theory of mass spectrometry (MS) and interpretation of mass spectra can be found in any introductory organic chemistry text. More detailed information can be found in specific MS references, such as Chapman [71]. Representative references dealing with mass spectral analysis of the major classes of DP agents are discussed in this section.

Cashen [7] separated the methyl carbamate/formaldehyde reaction products by preparative TLC and analyzed each by MS. Based on MS fragmentation patterns and NMR data, structures for the products were suggested. Most were either oligomers or polymers of MC. Beck et al. [58] reported the major ions in the mass spectrum of ODBP (Fig. 16) as representative of this oxydimethylene structure. Similarities and differences in the electron impact (EI) mass spectra of 14 DP agents, including DMDHEU, DMDHI, and several alkylated derivatives of DMDHEU, were reported by Trask-Morrell et al. [72]. The presence of hydroxymethyl moieties was indicated by the presence of fragmentation of m/z 31 ions.

Electron impact and chemical ionization (CI) data for DMDHI, DHEU, DMDHEU, and several methylated derivatives of DMDHEU were described by Beck and co-workers [14]. Differences between fragmentation patterns caused by the two ionization techniques were discussed. These compounds were also silylated and analyzed by GC/MS in both EI and CI modes. Cleavage patterns that assisted in identification of some of the compounds were described. One such fragmentation allowed the identification of the *cis*-DMDHEU. Another fragmentation pattern led to the structure of the monoglycolated DMDHEU (Fig. 13) in a commercial DP finish. Mass spectra of trimethylsilylated DMDHEU and its glycolated derivative are shown in Figures 21 and 22.

Mass spectrometry was used by Trask-Morrell et al. [73] to indicate the presence of an anhydride intermediate in the polycarboxylic acid cross-linking of cellulose. Heating seven different materials, including two di-, two tri-, and three tetracarboxylic acids in the presence and absence of catalyst showed loss of water. This, and the presence of other ions in the mass spectra, suggested the generation of an intermediate acid anhydride in the cross-linking of cellulose with polycarboxylic acids.

V—
Summary

Modern analytical instrumentation has played a significant role in the development of DP finishing agents. These tools have been used for structure determina-

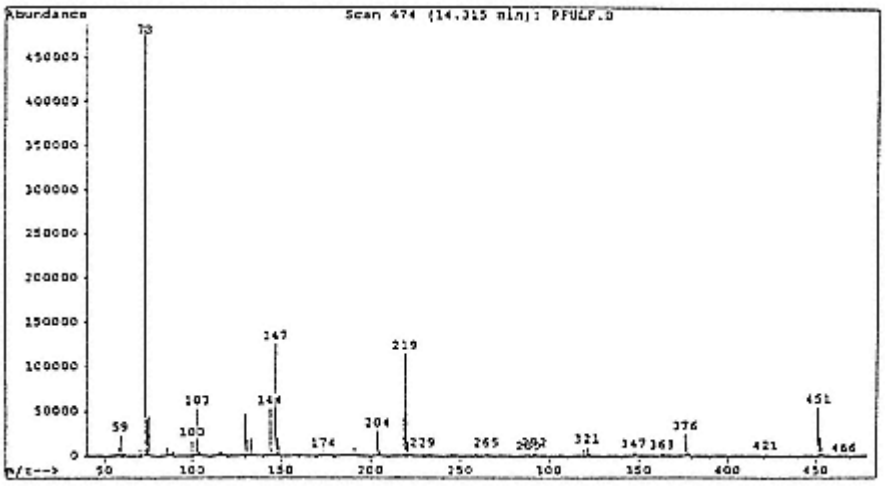

Figure 21
Mass spectrum of trimethylsilylated DMDHEU.
(Courtesy S. Yoon, Sequa Chemicals, inc., Chester, S.C.)

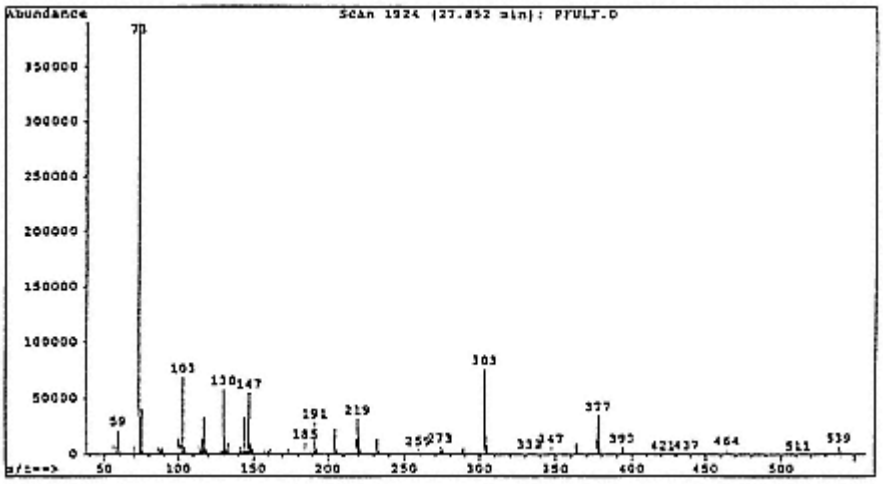

Figure 22
Mass spectrum of trimethylsilylated glycolated DMDHEU.
(Courtesy S. Yoon, Sequa Chemicals, Inc., Chester, S.C.)

tion, mixture composition, properties, and mechanisms of cross-linking. The intent of this chapter has been to give illustrative, but not exhaustive, examples of the uses of TLC, GC, HPLC, UV-VIS spectroscopy, NIR spectroscopy, IR spectroscopy, NMR spectrometry, and mass spectrometry. Other analytical techniques, such as thermal analysis, have given valuable information about the means by which the cross-linking reaction occurs, but they were not the focus of this chapter. It is certain that any new DP agents that are discovered in the future will be studied by the techniques included here.

Acknowledgments

The assistance of Paul Garwig in performing the computerized literature search that was a partial basis for this work is gratefully acknowledged. Special thanks go to Soon Yoon for helpful discussions about analytical techniques and for providing many of the chromatograms and spectra included in this chapter.

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