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UV-VIS Spectroscopy of 2,4,6-Trinitrotoluene-Hydroxide Reaction

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Final report

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Preface

The work reported herein was conducted at the U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, MS, as part of cleanup technology development supported by the Environmental Quality Technology Program.

This report was prepared by Ms. Deborah R. Felt, Applied Research Associates, Inc., Southern Division; Dr. Steven L. Larson, Environmental Engineering Branch (EEB), Environmental Laboratory (EL), ERDC; and Dr. Edward J. Valente, Department of Chemistry and Biochemistry, Mississippi College, Clinton, MS.

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At the time of publication of this report, Director of ERDC was Dr. James R. Houston, and COL John W. Morris III, EN, was Commander and Executive Director of ERDC.

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1 Introduction

A major issue facing the Army is the restoration of explosive and energetics contaminated soil and groundwater. Explosives contamination may result from a variety of activities including: explosives and energetics manufacturing; munitions maintenance, load and pack facilities; and live fire training activities. Of particular concern to the Army is the wide distribution of relatively low concentrations of explosives and energetics on many live fire training and testing ranges. The U.S. Army Engineer Research and Development Center (ERDC) is actively pursuing development of low-cost remediation technologies to restore these lands and groundwaters to environmentally acceptable conditions.

Base-induced transformation (BIT) of explosives has shown promise as a rapid, low-cost technology for remediating explosives in soil and water. When used as a restoration technology, the BIT process incorporates the addition of highly basic material to the soil or groundwater, resulting in the transformation of the parent compound. Ideally, the process would drive the degradation of the parent to environmentally benign compounds.

Although the BIT process has been known for decades, the majority of work reported on the phenomena has been related to treating much higher concentrations than generally found on sites requiring remediation. The mechanism and products of the Hydroxide- (OH-) 2,4,6-Trinitrotoluene (TNT) reaction at concentrations of environmental concern are poorly understood. Previous kinetics studies of the OH-TNT reaction have only considered the reduction of the TNT analyte concentration, not the reaction of intermediates or final products. During these previous studies, TNT quickly degraded in less than 40 min at room temperature in basic solution, but the overall OH-TNT reaction may not have been completed. Early toxicological studies have shown that the final products of the OH-TNT reaction may be benign (Hansen et al. 2001), but intermediate products may be toxic to inherent bacteria or bind with environmental matrices (Michels and Gottschalk 1994; Pennington et al. 1995).

Identification and quantification of the reaction mechanism and all reaction components (reactants, intermediates, and final products) of the OH-TNT reaction are necessary to determine the technical feasibility of BIT as a remediation technology. The rate constants for each step in the reaction derived from the reaction mechanism could be used to guide engineers and technicians responsible for designing and operating the technology.

Detailed study of the mechanism of degradation and the interactions of the individual degradation products requires an analytical technique that enables separation of the individual compounds. Typically, the individual reaction components are separated using techniques such as liquid chromatography and identified using mass spectroscopy. Unfortunately, the final products of the OH-TNT reaction make this process problematic because of limitations on standard separation techniques. The polymers (Felt, Larson, and Hansen 2001b) that form as a result of the OH-TNT reaction often foul the separation column because of their large molecular size. To overcome this difficulty, the study reported here evaluates an alternate technique, ultraviolet-visible (UV/VIS) spectral analysis, to obtain similar information using factor analysis (FA) of kinetic spectral data. The knowledge of basic properties of the OH-TNT reaction presented in this report adds to our understanding of the BIT process.

2 Literature Review

Contamination of groundwater, surface water, and soil by explosives has occurred at military sites throughout the world as a result of manufacture of explosive compounds, assembly of munitions, and deployment of explosives containing devices (Roberts and Hartley 1992; Jenkins, Thorne, and Walsh 1994; Pennington et al. 1995). TNT has been listed as a priority pollutant, a Class C carcinogen, and has adverse effects on humans, plants, and animals (Rosenblatt et al. 1991; Smith 1991; Won, DiSalvo, and Ng 1976; Palazzo and Leggett 1986; Simini et al. 1995). TNT remediation methods, such as incineration, composting, bioremediation, and photolysis, have been used with mixed success (Bruns-Nagel et al. 1998; Dillert et al. 1995; Lang et al. 1998; Haselhorst 1999; Hawari et al. 2000). Existing technologies are hindered by problems such as high energy costs, costly equipment, extensive soil excavation, very slow degradation rates, or incomplete degradation of the explosive contaminants.

The transformation of TNT in basic solutions has long been established (Janowsky 1891) and could potentially be part of a rapid and low-cost technology to remediate TNT contamination. The rate of TNT transformation when exposed to ultraviolet light (Dillert et al. 1995), to iron (II) (Brannon, Prince, and Hayes 1998), or to a combination of UV light, ozone, and electrohydraulic discharge (Lang et al. 1998) is enhanced at alkaline pH. Dunnivant and Schwarzenbach (1992) reported that TNT degradation caused by natural organic matter (NOM) was increased by elevated pH. Previous work in our laboratory has shown that degradation rates of TNT associated with base-induced transformation technology is rapid, with complete TNT degradation realized in <40 min at room temperature (Felt, Larson, and Hansen 2001a). Kinetics studies of TNT and other nitroaromatics after alkaline hydrolysis demonstrated similar results in aqueous solutions and in highly contaminated soils using calcium hydroxide (Emmrich 1999, 2001).

Previous kinetics studies concentrated on the degradation of the parent compound, TNT, but gathered little data on the kinetics of the over-all OH-TNT reaction mixture as a whole. There is also a need to determine information on the transformation products of the OH-TNT reaction. A common analytical method used to identify individual components in a reaction mixture is liquid chromatography-mass spectroscopy (LC-MS), which separates the components of a mixture on the chromatography column and identifies them by comparing their mass spectrum to spectrum of known standards (Willard et al. 1988). From a previous study in our laboratory, it was determined that roughly 50 percent of the final products of the OH-TNT reaction are polymers, with molecular weights

above 1,000 Daltons (Felt, Larson, and Hansen 2001b). Polymers cannot be identified using LC-MS, because their large molecular size causes them to foul the chromatography column. An alternative method that could yield kinetic data of the overall reaction and theoretically separate the reaction components is a factor analysis of UV/VIS spectral data.

UV/VIS spectral analysis is based on the Lambert-Beer Law that relates the absorbance of a chemical species to its concentration,

$$A^\lambda = \varepsilon^\lambda\, bC \tag{1}$$

where

A^λ = absorbance of a compound at a given wavelength (λ)

ε^λ = molar absorptivity of the compound at wavelength λ

b = pathlength of the sample cell

C = concentration of the compound (Willard et al. 1988)

In a spectral experiment, a real experimental data matrix of absorbance over time $[A^\lambda(t)]$ may be rationally constructed from a row matrix $[\varepsilon^\lambda]$ of molar absorptivities and a column matrix $[c(t)]$ such that

$$[A^\lambda(t)] = [\varepsilon^\lambda]\,[c(t)] \tag{2}$$

The pathlength, b, of the sample cell is usually 1 cm and it remains constant over the experiment, so it is dropped from Equation 2. In application, there will be as many rows in $[\varepsilon^\lambda]$ as there are spectral wavelengths observed and as many columns as there are reaction components, i (Malinskowski 1989). Similarly, there will be in $[c(t)]$ as many rows as there are reaction components, i, and as many columns as there are times observed during the course of the reaction. While the overall dimensionality for the system ($r \times c$) is known from the design of the experiment, the number of reaction components is hidden in the matrix multiplication where an $[r \times i]$ matrix is multiplied by an $[i \times c]$ matrix to produce the $[r \times c]$ data matrix. The minimum number of *abstract terms* (n) required to account for the missing reaction component information can be determined without *a priori* information about i by using principal component analysis (PCA).

The real data matrix and its abstract row and column matrix constituents are defined as

$$[D] = [R][C] \tag{3}$$

The raw experimental data are not analyzed directly but converted to a covariance matrix $[Z]$ by multiplying the data matrix by its transpose

$$[Z] = [D]^T [D] \tag{4}$$

The diagonalization of this matrix by the eigenvalue-eigenvector method produces

$$[Z] = [C]^T[\lambda][C] \tag{5}$$

where $[\lambda]$ is an $i \times i$ (diagonal) matrix of eigenvalues which are ordered from most to least important. Only the first and larger n terms of $[\lambda]$ account for these data, with the remaining i-n terms being essentially nil and attributable to noise. The abstract matrix $[C^\ddagger]$ is the diagonalization matrix, since

$$[C^\ddagger]^T = [C^\ddagger]^{-1} \tag{6}$$

$$[C^\ddagger][Z][C^\ddagger]^{-1} = [\lambda] \tag{7}$$

Hence $[\lambda]$ is essentially an $n \times n$ matrix, and the abstract matrix $[C^\ddagger]$ contains the eigenvectors and has dimensions $n \times c$.

The abstract row matrix $[R^\ddagger]$ of eigenvalues can then be calculated from

$$[R^\ddagger] = [D][C^\ddagger]^T \tag{8}$$

which has $r \times n$ dimensions. These data matrix can then be reconstructed from the abstract row and column matrices from the n principal components, which are derived from the larger terms in $[\lambda]$ using PCA. This process has been coded into a FORTRAN program "PCA.F90" given in Appendix A.

PCA produces factors which are implicitly irrational, orthogonal, and account for $[D]$ to within experimental error. The chemical details of the system, a rational system, are embedded in $[D]$ and cannot be revealed by a simple inspection of the eigenvalues and eigenvectors of PCA. The abstract factors can be mathematically transformed into rational factors by using target testing analysis which tests suspected factors representing a row of the row matrix or column of the column matrix against the experimental data to determine if it is a real factor. The most readily testable target factors are initial and final spectral factors taken directly from the data. Other factors may suggest themselves on the basis of the kinetics or intermediates observed during the course of the reaction.

A row test vector R'' (eigenvalue) can be shown using a least squares method to be a real factor if the transformation vector, T'_r, implied by

$$T'_r = [\lambda]^{-1}[R^\ddagger]R'' \tag{9}$$

produces vector R' which closely agrees with R'' on application as follows:

$$R'' \approx R' = [R^{\ddagger}]\, T'_r \tag{10}$$

A similar target approach with the eigenvectors in $[C^{\ddagger}]$ also can be done. In this case, a single column test vector C'' (eigenvector) is a real factor if the transformation vector, T'_c, implied by

$$T'_c = C''\, [Z][C^{\ddagger}]^{T}[\lambda]^{-1} \tag{11}$$

produces vector C' which closely agrees with C'' on application as follows:

$$C'' \approx C' = T'_c\, [C^{\ddagger}] \tag{12}$$

Individual vectors can be tested in either the row or column categories and discover whether they are real factors independent of any undetermined factors. By doing so, and developing a theoretical or experimental model, one can in principle reconstruct a set of n real factors that accounts for the data to within experimental error.

In summary, experimental spectral data (absorbance versus time) can be used to create a data matrix of molar absorptivities and concentrations containing information about each reaction component in the reaction mixture over time. The row matrix in the kinetic spectroscopic application contains the spectra of the n components, while the column matrix contains the time relative concentration data for the same n components. In principle, the spectra and rate data for each component can be retrieved using PCA and target testing analysis and be used to develop kinetic models of the reaction using a least squares method without the use of separation techniques or mass spectrometry.

3   Materials and Methods

Previous experiments had studied the kinetics of the degradation of TNT after base addition, but the overall reaction kinetics had not been studied. In this study, UV/VIS spectral analysis of the OH-TNT reaction was conducted over time and at different temperatures. An FA program was used to analyze the spectral data and determine the number of major chemical species in the overall reaction without using separation technologies (e.g., gas chromatography (GC), high-pressure liquid chromatography (HPLC), or liquid chromatography-mass spectroscopy (LC-MS). Test spectral vectors were developed and tested against abstract vectors. Results were used to indicate possible kinetic models.

Materials

Chemicals and glassware

Chemicals used in this study included TNT supplied by the Rock Island Arsenal, Rock Island, IL, reagent grade potassium hydroxide purchased from Fisher Scientific, and dionized water. Glassware used in this study included beakers, pastuer pipettes, and volumetric flasks.

Instrumentation

The UV/VIS spectrometer was a Hewlett Packard 8453 with a diode array detector (DAD) with a 1-nanometer (nm) resolution purchased from Agilent Technologies. The instrument was equipped with UV/VIS HPChem software and a jacketed 1.0-cm quartz sample cell that was thermostated by connection to a recirculating water bath to maintain a given temperature.

Methods

Spectroscopy experiment

UV/VIS spectral analyses of the OH-TNT reaction were conducted at four different temperatures to develop information concerning the reaction mechanism and the individual components of the OH-TNT reaction as they change over time.

Two milliliters (mL) of water was added to 1 mL TNT solution (102 ppm) in a 25-mL flask and the solution was equilibrated at 25 °C. At time zero, 1 mL 1 N KOH was added and the mixture was homogenized by swirling briefly to yield a reaction mixture of 2:1:1 (water: 100 ppm TNT: 1N KOH). A representative sample (1 mL) was pipetted into a jacketed 1.0-cm quartz cell and analyzed using UV/VIS spectrometry from 190 to 1,100 nm. The cell was thermostated by connection to a recirculating water bath maintained at 25 °C. These data were collected in a darkened room to prevent TNT degradation as a result of photolysis. A diluted (1:3) sample of the initial TNT solution was analyzed to provide a reference spectrum.

From a previous kinetics study, it was known that the OH-TNT reaction had a very fast initial decay and a much slower secondary decay (Felt, Larson, and Hansen 2001a). The sample spectral runs were set up in two parts to take this into account. The spectrometer was programmed to yield numerous data points early in the reaction to measure the very fast initial decay. Allowance for a longer sampling cycle during the second part of the test is necessary because the secondary degradation is much slower. The initial settings for the instrument included a 10- to 12-s delay, a 20-s sampling cycle, and a total run time of 1,200 s (20 min). No incremental increase in the sampling cycle was programmed for this part of the experiment. Data collection settings were changed after the first protocol to remove the delay and modify the sampling cycle to 300 s with an increment of 25 percent after 1,800 s, with an additional run time of 43,200 s (12 h). The instrument was started, and the time elapsed between the two runs was noted. The experimental protocol described above was repeated using incubation temperatures of 20, 15, and 12 °C.

Factor analysis

FA was applied to the experimental data using the method described by Malinskowski (1989). The PCA process has been coded into a FORTRAN program "PCA.F90" and is given in Appendix A. The program used to test vectors derived from PCA is given in Appendix B.

The FA method selected for evaluation is a multivariate analysis that can be applied to a large data set from superposed, multiple sources such as individual compounds in a reaction mixture (Malinskowski 1989). Chemical transformations result in varying quantities of reactants, intermediates, and products over time, each with their characteristic spectral signatures. During spectral analysis, a detector measures transmitted light intensity (which is converted to the derivative unit "absorbance") over a range of wavelengths and at time intervals during the course of the reaction. Each chemical species is independently associated with its own absorbance and the absorbance of the reaction mixture that is indicated by the instrument is a combination of these signals. Chemical interference is possible, but it is rare and was assumed to be inconsequential in this study.

In the FA procedure used in this study, the experimental data are represented by a spectral data matrix, consisting of molar absorptivities and concentrations as a function of time. The experimental data matrix is mathematically converted to an abstract matrix that is analyzed using PCA to yield the minimum number of

factors necessary to reconstruct the abstract row matrix within the experimental error. The principal components are irrational factors that do not directly represent the actual reaction components of the OH-TNT reaction. The irrational factors indicated by PCA are transformed into rational (real) components using target testing. Test spectral vectors for four factors, including the reactant (TNT), two intermediates, and the final product, were developed and tested against the abstract vectors. There was good agreement between the test vectors and the abstract vectors, indicating the test vectors were real factors, corresponding to real components of the reaction. Two kinetic models that incorporated the test vectors were developed and refined using a nonlinear regression method. Figure 1 is a flowchart that summarizes the FA process.
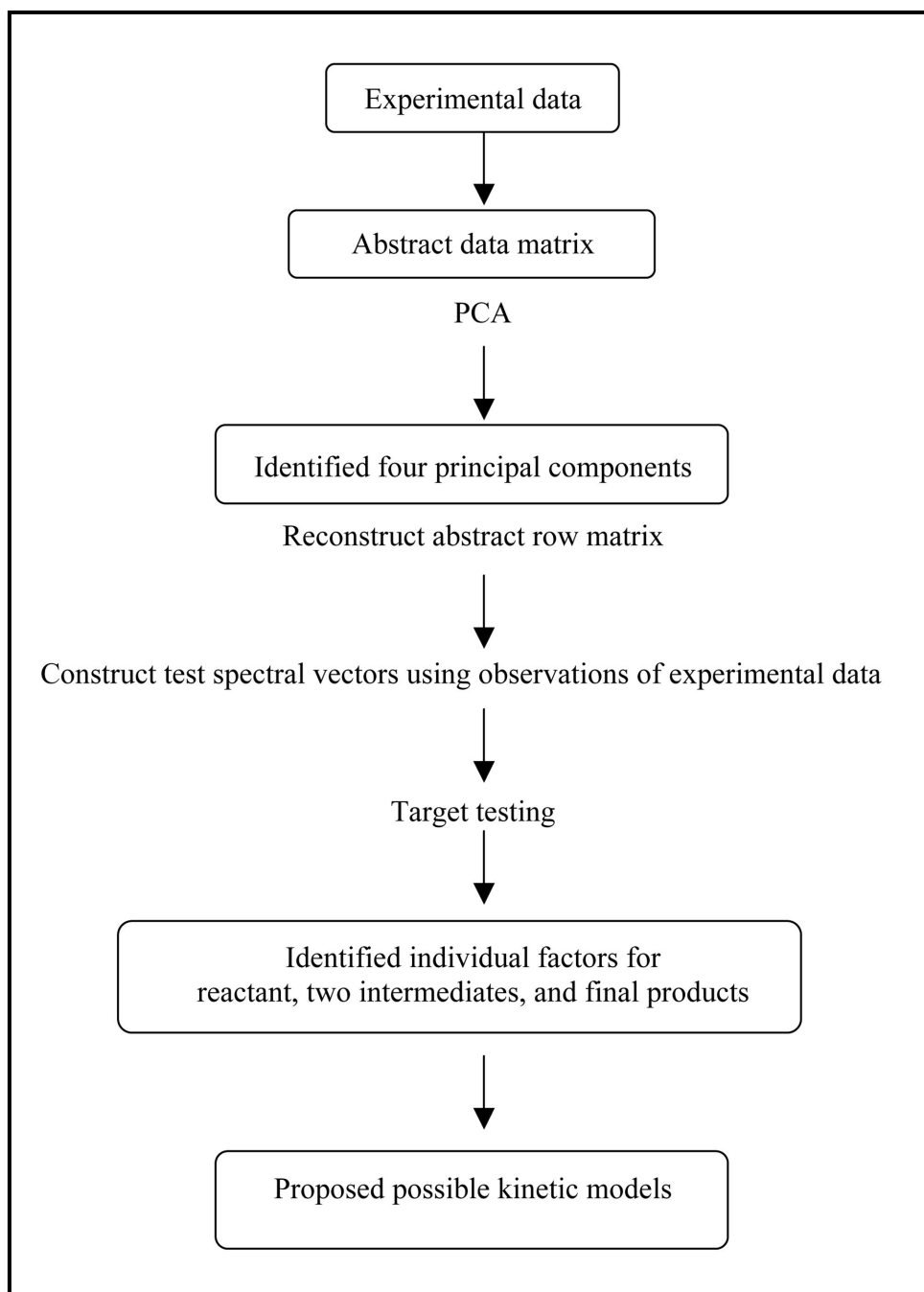
Figure 1.   Flowchart for factor analysis of spectral kinetic data

4   Results

Spectral Data Collected at 25 °C

Initial TNT spectrum

UV/VIS spectroscopy charted the chemical changes that occurred during the OH-TNT reaction from the initial TNT spectra (Figure 2) through the intermediates until final products were formed. The initial TNT spectrum indicated that TNT absorbs in the ultraviolet range, with a shoulder at 254 nm. The spectrum is flat in the visible range (400 to 700 nm), which is consistent with a colorless fluid.
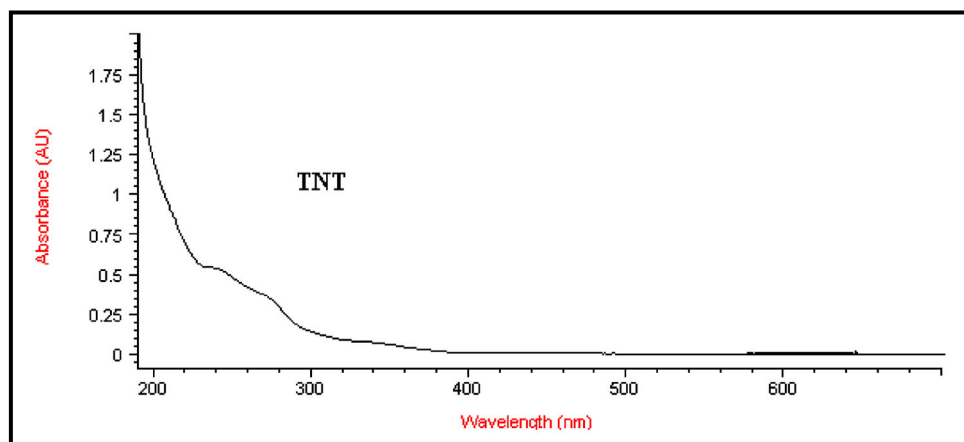
Figure 2.   Spectrum of diluted (1:3) TNT stock solution

Spectra of reaction mixture at 25 °C

Figure 3 shows the spectra generated during the initial run at 25 °C. The arrows indicate the direction of the spectral changes over the course of data collection. The first spectrum at 10 s shows a defined shoulder at 240 nm. The spectrum reaches a minimum at 360 nm, rises to another maximum of about 0.8 AU at 450 nm, and reaches a final minimum at 650 nm. No absorbance is seen from 650 to 1,100 nm. The second and subsequent spectra show that the 240-nm shoulder has been shifted to 260 nm. The minimum has shifted to 340 from 360 nm, and the maximum at 450 nm has shifted slightly to the left and continues to rise. This maximum reaches its peak by 191 s, before it slowly
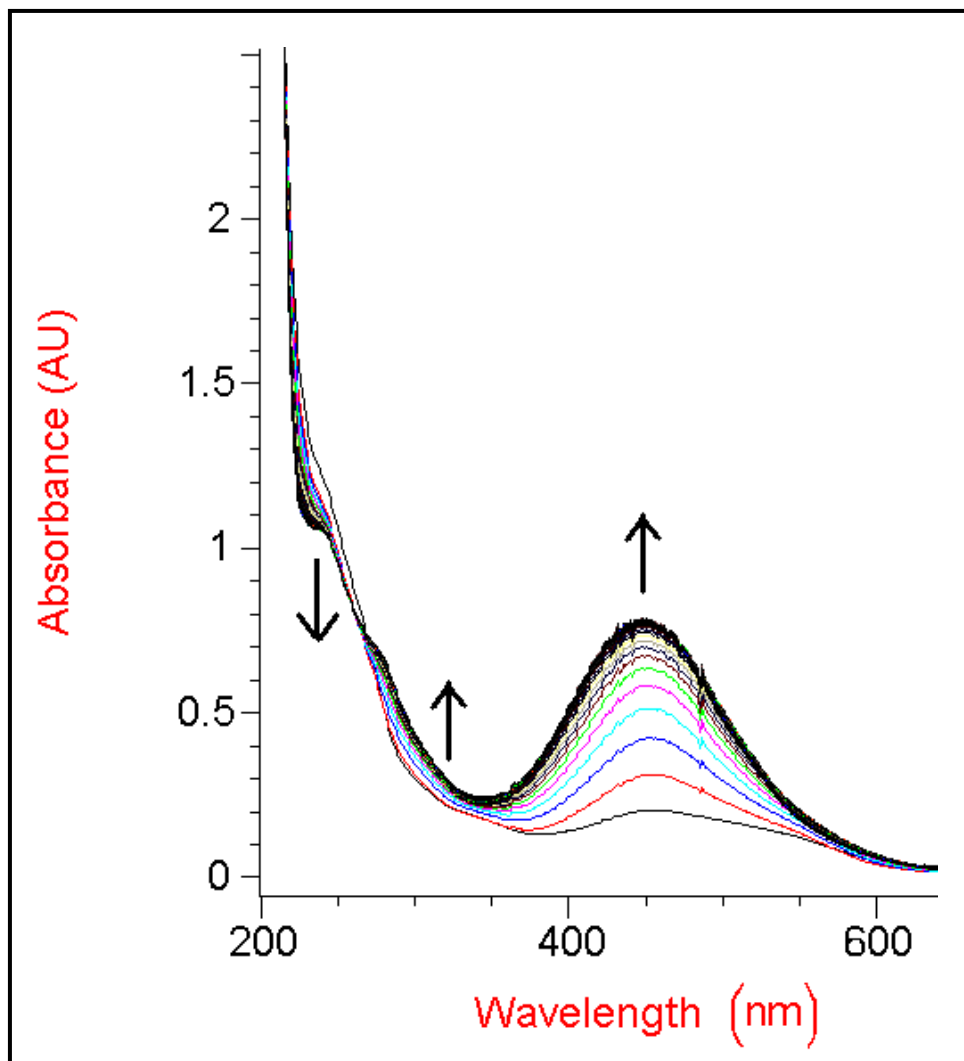
Figure 3.   Spectra of OH-TNT reaction at 25 °C – first 20 min

begins to decrease over the remainder of the reaction. A slight shoulder developed at 510 nm, and a foot developed between 510 and 550 nm.

Figure 4 shows the spectra generated during the latter portion of the experiment at 25 °C. The most obvious feature is the slow decrease in the spectral feature at 450 nm. The spectra have an approximate isosbestic point at 340 nm. The feature at 330 nm has risen and remains constant. A shoulder is still obvious at 260 nm and slowly decreases. A foot is still visible between 510 and 550 nm.

Spectrum of Final Products

The spectrum of the final products was collected after 48 h at which time the reaction was judged to be complete and is illustrated in Figure 5. A broad feature at 330 nm and a shoulder at 270 nm are evident. The spectrum has a low
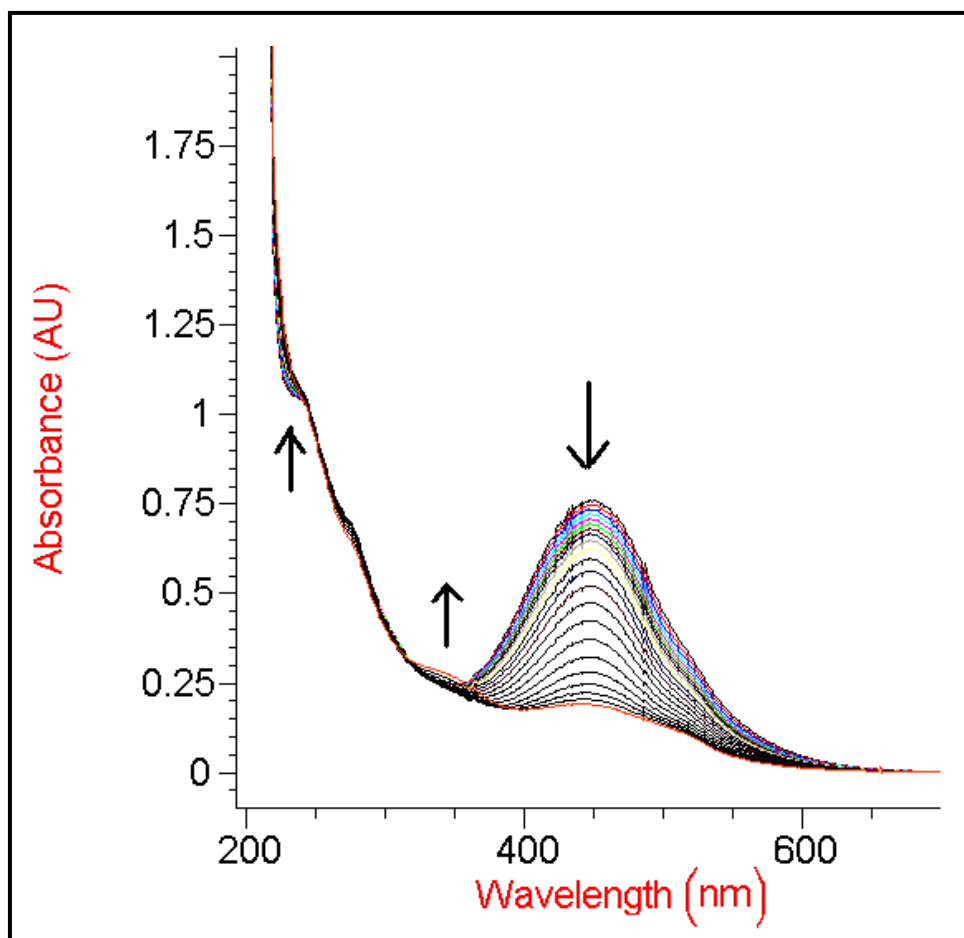
Figure 4.   Spectra of OH-TNT reaction at 25 °C – 12 h
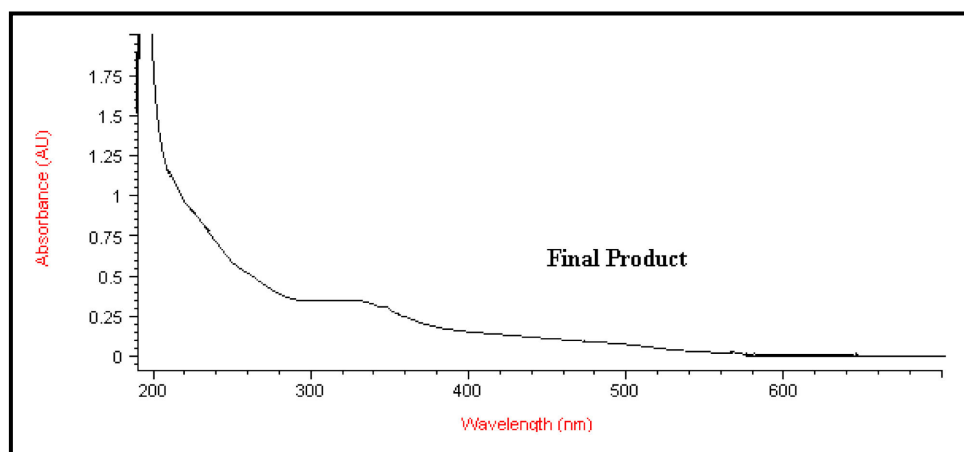
Figure 5.   Spectrum of final products of OH-TNT reaction

absorption in the visible range decreasing for 400 to 600 nm. This result is consistent with the light straw yellow color of the final reaction mixture.

Spectral data collected at 20, 15, and 12 °C

In order to collect more kinetic data about the OH-TNT reaction, the experiment described above was repeated at different temperatures (20, 15, and 12 °C). These spectra showed the rise of a major spectral feature with a maximum of 0.8 AU at 450 nm at all temperatures, but the features appear after longer times at cooler temperatures. These data correspond to the data recorded at 25 °C, except that the maximum was reached more slowly at the lower temperature (191 s at 25 °C, 230 s at 20 °C, and 419 s at 15 °C).

Factor analysis results

PCA indicated that six principal components explained the spectra to within experimental error, with four factors explaining the majority of the variance. Test spectral vectors for four components were developed, including TNT, two intermediates, and the final product, and were tested against abstract vectors. There was good agreement between the test vectors and the abstract vectors, indicating the test vectors were real factors, corresponding to real components of the reaction.

5   Discussion

Spectroscopy

Temperature dependence of OH-TNT reaction

A previous study using HPLC indicated that the second phase of the OH-TNT reaction, the slower secondary degradation, is temperature-dependent (Felt, Larson, and Hanson 2001a). The rate of this phase of the OH-TNT reaction decreased as the temperature decreased. In this study, it appears that the OH-TNT reaction proceeded by the same mechanism at all temperatures that were monitored and the differences in the spectra were a result of the temperature dependence of the OH-TNT reaction.

The 450-nm feature reached a maximum of about 0.8 AU, regardless of the incubation temperature and the run time that the feature occurred. This may indicate that the 450-nm feature is a pure spectral feature of the second intermediate and that this component has a large concentration and a relatively small molar absorptivity.

Primary and secondary intermediates

There was spectral and visual evidence that indicated a primary intermediate was formed and quickly replaced by a secondary intermediate. In the current study, the spectral feature at 450 nm on the first spectrum (A1) at 25 °C was visually different in shape than those of successive spectra at that incubation temperature. The reaction mixture changed from a colorless solution to a pink shade after addition of the base, and then quickly changed to a reddish orange, indicating at least two separate reaction intermediates. The OH-TNT reaction mixture was a light yellow color at the end of 48 h, indicating the final product is another chemical species.

In order to determine if a primary intermediate had been formed, A1 was scaled and compared to a successive spectrum at 25 °C. If A1 contained information associated with a different component than the successive spectra at 25 °C, A1 would have a different shape than that of the other spectra. If the components of A1 and A10 were the same, the two peaks should be different from each other only in size, not shape. A1 was scaled with the spectra that yielded the 450-nm maximum (A10, time = 191 s) and is illustrated as the thin solid line in the middle of Figure 6. The scale was the absorbance of A10 at
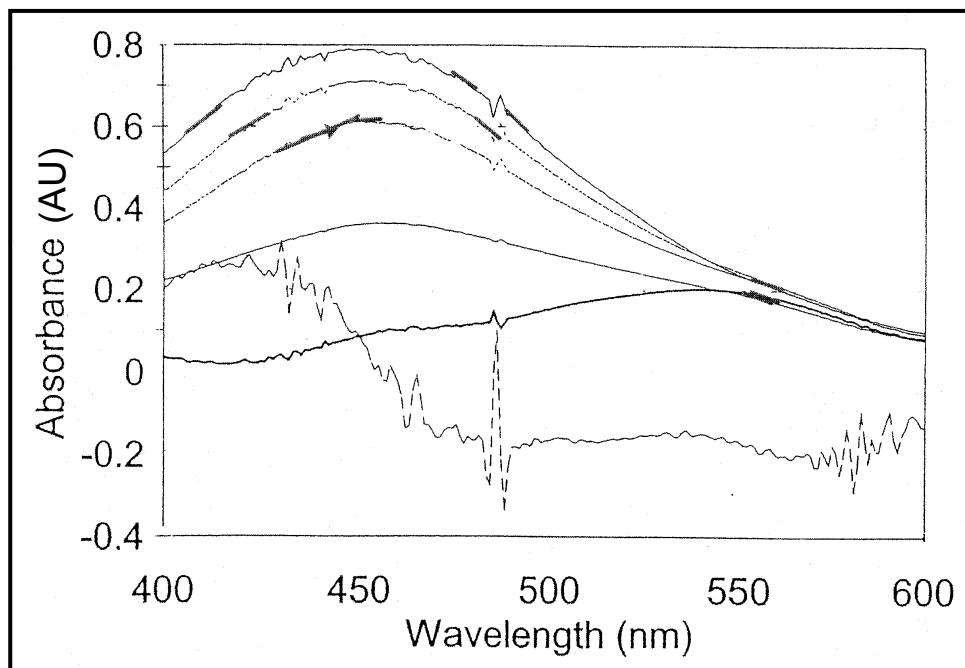
Figure 6. Spectral features of the first intermediate of OH-TNT reaction at
25 °C

450 nm divided by the absorbance of A1 at 450 nm. A plot of the difference of
scaled A1 less A10 in absorbance units versus wavelength would be a straight
line through zero if the reaction components that make up A1 were the same as
those that make up A10. When the difference was plotted (the bold line in Fig-
ure 6), the line did not go through zero but increased to a maximum at 550 nm.
This could indicate that a reaction component appears at 11 s (A1), which is
distinct from the species producing the large 450-nm peak that reaches its maxi-
mum at 191 s (A10). The first derivative of the difference also shows inflections
at 450 and 490 nm, as shown by the dashed line in Figure 6. Spectrum A1 is also
different than the initial TNT spectra, which would indicate an intermediate had
formed in this early reaction time. This intermediate seemed to be very reactive,
as the absorbance of 500 nm at 32 s (A2) had already decreased relative to the
first spectra. This indicates that a second intermediate had already started to form
by 32 s into the reaction, which appeared to be producing the significant absorp-
tion at 450 nm.

These conclusions are consistent with the color changes noted for the reac-
tion mixtures and results from a previous kinetic study of TNT degradation after
introduction of base using HPLC (Felt, Larson, and Hansen 2001a). The results
of this study indicated a two-phase reaction, a very fast initial rate, followed by a
much slower degradation rate, which is consistent with the formation and degra-
dation of two intermediates. Chromatograms of the base-challenged TNT solu-
tions showed a feature that had formed quickly at a 3.5-min retention time that
was indicative of an intermediate. The peak height of this intermediate dimin-
ished over time, indicating follow-on degradation. The short retention time on the
reverse phase C-18 column indicated a compound that was more polar than TNT
(retention time 17.5 min). The majority (98 percent) of the final reaction products

of the OH-TNT reaction are also polar compounds, as indicated by a study that separated the reaction products by molecular weight and solubility (Felt, Larson, and Hansen 2001b).

Factor Analysis of Spectral Data

Chemical transformations often result in varying quantities of starting material, intermediates, and products over time, each with their characteristic spectral signatures. FA has particular applicability in these chemical systems in which detector output records events containing information from superposed, multiple components. Absorbance was assumed to be independently associated with each chemical species. Chemical interference was possible, but it was assumed to be inconsequential.

Absorbance data for multicomponent mixtures can be approximated using the Lambert-Beer Law, where each data point can be represented by the equation, $A_{ik} = \sum \in_{ij} c_{jk}$. $\in_{ij}$ is the molar absorptivity per unit path length of component j at wavelength i, and c_{jk} is the concentration of component j in the kth mixture. Spectral data can theoretically be explained by a hypothetical experimental data matrix containing row matrix $[\varepsilon^{\lambda}]$ of molar absorptivities (spectra) and column matrix $[c(t)]$ of time-dependent concentrations (Malinskowski 1989). FA identifies the number of principal reaction components in the reaction mixture and produces irrational, orthogonal factors that account for this experimental matrix to within experimental error. The abstract matrix can be converted into real factors (chemically relevant data) by either using an appropriate transformation matrix or by using target testing, which is the method used in this study. In order to test the evolving model, suspected factors must be identified that can be used as starting points for the model. Factors are suggested on the basis of spectral and other experimental data and tested against the spectral data to determine if they are real factors.

PCA indicated six factors were required to reduce the reproduced data matrix to within the estimated measurement errors. Using four principal components leaves a residual data matrix with all elements less than 0.010 AU; the estimated measurement errors were less than this, at 0.002 AU. The two additional factors were very small contributors to the spectral variance, were without spectral features of note, and were therefore ignored. Table 1 shows the results of the PCA of the 25 °C spectral data. Eigenvalues are listed in order of the largest to the smallest, and the associated eigenvector for each time is given. The size of the eigenvalue signifies the amount of the variance in these data that is explained by that eigenvalue. The eigenvectors associated with the eigenvalues mimic concentration versus time for the abstract components. The first eigenvalue, 517, indicates that this eigenvalue explains most of the spectral data. The next three eigenvalues are significant (22.47, 1.02, and 0.27) and represent the other three principal components of the reaction as identified by PCA.

Table 1
Spectral Vectors for TNT-Hydroxide Reaction at 25 °C

```
EIGENVALUE #  1          517.212
   0.11     0.14     0.16     0.16     0.17     0.17     0.17     0.17     0.17     0.17
   0.17     0.17     0.17     0.17     0.17     0.17     0.17     0.17     0.17     0.17
   0.16     0.16     0.16     0.16     0.16     0.15     0.15     0.15     0.14     0.14
   0.14     0.13     0.13     0.13     0.13     0.13     0.13     0.13     0.13     0.13
   0.13     0.13     0.12     0.12
REAL ERROR-   0.11 EMBEDDED ERROR-    0.02
EIGENVALUE #  2           22.471
   0.30     0.10    -0.03    -0.09    -0.12    -0.14    -0.15    -0.15    -0.15    -0.15
  -0.15    -0.15    -0.15    -0.14    -0.14    -0.14    -0.13    -0.12    -0.12    -0.11
  -0.10    -0.08    -0.08    -0.05    -0.01     0.01     0.04     0.07     0.10     0.13
   0.15     0.17     0.17     0.18     0.19     0.20     0.20     0.20     0.20     0.20
   0.20     0.21     0.21     0.22
REAL ERROR-   0.03 EMBEDDED ERROR-    0.01
EIGENVALUE #  3            1.020
   0.79     0.33     0.18     0.11     0.07     0.04     0.03     0.02     0.01     0.00
   0.00    -0.01    -0.02    -0.03    -0.04    -0.04    -0.04    -0.04    -0.04    -0.04
  -0.03    -0.02    -0.02     0.01     0.03     0.04     0.06     0.06     0.06     0.05
   0.02    -0.03    -0.06    -0.08    -0.11    -0.12    -0.13    -0.13    -0.13    -0.14
  -0.14    -0.14    -0.14    -0.15
REAL ERROR-   0.01 EMBEDDED ERROR-    0.00
EIGENVALUE #  4            0.270
  -0.13     0.38     0.31     0.24     0.20     0.17     0.15     0.13     0.12     0.10
   0.10     0.08     0.03     0.01    -0.01    -0.03    -0.07    -0.10    -0.12    -0.14
  -0.18    -0.19    -0.20    -0.23    -0.25    -0.24    -0.23    -0.21    -0.17    -0.12
  -0.07    -0.02     0.00     0.03     0.04     0.07     0.07     0.07     0.08     0.07
   0.08     0.08     0.07     0.07
REAL ERROR-   0.01 EMBEDDED ERROR-    0.00
EIGENVALUE #  5            0.077
   0.46    -0.22    -0.22    -0.15    -0.09    -0.04    -0.01     0.01     0.03     0.05
   0.05     0.06     0.09     0.10     0.11     0.12     0.12     0.13     0.12     0.12
   0.10     0.07     0.06    -0.03    -0.10    -0.16    -0.22    -0.27    -0.30    -0.30
  -0.24    -0.14    -0.09    -0.04     0.01     0.06     0.07     0.08     0.09     0.10
   0.10     0.12     0.14     0.14
REAL ERROR-   0.00 EMBEDDED ERROR-    0.00
EIGENVALUE #  6            0.024
   0.12    -0.20    -0.36    -0.24    -0.08     0.03     0.11     0.15     0.17     0.17
   0.17     0.17     0.14     0.12     0.09     0.08     0.02    -0.02    -0.06    -0.09
  -0.15    -0.19    -0.20    -0.25    -0.21    -0.15    -0.07     0.05     0.17     0.25
   0.26     0.20     0.16     0.12     0.07     0.00    -0.01    -0.02    -0.03    -0.03
  -0.04    -0.08    -0.13    -0.18
REAL ERROR-   0.00 EMBEDDED ERROR-    0.00
EIGENVALUE #  7            0.002
   0.12    -0.51    -0.07     0.17     0.23     0.23     0.19     0.16     0.11     0.07
   0.07     0.07    -0.06    -0.10    -0.13    -0.11    -0.16    -0.18    -0.18    -0.14
  -0.11    -0.08    -0.09     0.03     0.11     0.14     0.14     0.12     0.09     0.02
  -0.06    -0.13    -0.17    -0.16    -0.11    -0.03    -0.01    -0.01    -0.02    -0.01
  -0.01     0.10     0.22     0.31
REAL ERROR-   0.00 EMBEDDED ERROR-    0.00
EIGENVALUE #  8            0.001
  -0.12     0.57    -0.41    -0.32    -0.13    -0.01     0.05     0.08     0.12     0.10
   0.10     0.06     0.04     0.00     0.02    -0.07    -0.04    -0.07    -0.02    -0.04
  -0.04     0.05     0.04     0.09     0.02     0.04     0.06     0.04     0.03     0.05
  -0.02    -0.09    -0.12    -0.14    -0.17    -0.10    -0.08    -0.07    -0.07    -0.07
  -0.04     0.10     0.21     0.37
REAL ERROR-   0.00 EMBEDDED ERROR-    0.00
EIGENVALUE #  9            0.000
   0.00    -0.08     0.26     0.07    -0.07    -0.08    -0.13    -0.09    -0.14    -0.12
  -0.12    -0.02     0.05     0.06     0.08     0.24     0.19     0.19     0.12     0.18
   0.07    -0.14    -0.18    -0.26    -0.17    -0.15    -0.06     0.04     0.23     0.23
   0.14    -0.03    -0.14    -0.16    -0.07    -0.09    -0.09    -0.12    -0.12    -0.06
  -0.10    -0.03     0.25     0.41
REAL ERROR-   0.00 EMBEDDED ERROR-    0.00
EIGENVALUE # 10            0.000
  -0.02     0.12     0.01    -0.16    -0.13    -0.02     0.04     0.07    -0.01    -0.02
  -0.02     0.10     0.00     0.00    -0.03     0.26     0.09     0.14    -0.05     0.03
  -0.09    -0.30    -0.34    -0.20     0.25     0.25     0.23     0.21     0.07    -0.25
  -0.22    -0.20    -0.19    -0.07     0.18     0.18     0.15     0.13     0.04     0.11
  -0.02    -0.14    -0.07    -0.11
REAL ERROR-   0.00 EMBEDDED ERROR-    0.00
```

The eigenvalues and eigenvectors were used to reconstruct the abstract row matrix. Row matrices (Table 2) mimic the spectral data, are part of an abstract matrix, but may have little rational significance. The four factors listed in Table 2 represent the four principal components identified by PCA, as described above. The listed values illustrate trends of the abstract matrix compared to measurable spectral values.

Table 2
Reconstructed Abstract Row Matrix for Four Important Factors for OH-TNT Reaction at 25 °C

Wavelength (nm)	1	2	3	4
220.	11.40	1.81	0.02	0.06
230.	7.44	1.11	0.25	0.05
240.	6.80	0.72	0.25	-0.01
250.	6.10	0.57	0.21	-0.04
260.	5.22	0.40	0.17	-0.06
270.	4.59	0.23	0.09	-0.09
280.	4.17	0.10	-0.08	-0.12
290.	3.49	0.09	-0.19	-0.07
300.	2.93	0.11	-0.20	-0.02
310.	2.55	0.16	-0.23	0.01
320.	2.27	0.25	-0.27	0.02
330.	2.10	0.34	-0.30	0.03
340.	2.00	0.39	-0.32	0.04
350.	1.95	0.36	-0.33	0.04
360.	1.90	0.24	-0.31	0.04
370.	1.97	0.06	-0.28	0.02
380.	2.08	-0.18	-0.23	0.00
390.	2.28	-0.42	-0.18	-0.01
400.	2.55	-0.67	-0.14	-0.03
410.	2.86	-0.89	-0.09	-0.05
420.	3.15	-1.08	-0.05	-0.07
430.	3.35	-1.21	-0.01	-0.09
440.	3.55	-1.34	0.02	-0.10
450.	3.58	-1.38	0.05	-0.10
460.	3.51	-1.38	0.06	-0.07
470.	3.31	-1.32	0.06	-0.02
480.	3.00	-1.20	0.05	0.05
490.	2.65	-1.04	0.04	0.12
500.	2.30	-0.87	0.04	0.15
510.	2.01	-0.73	0.03	0.15
520.	1.75	-0.62	0.03	0.14
530.	1.48	-0.51	0.03	0.13
540.	1.24	-0.42	0.04	0.14
550.	1.04	-0.34	0.04	0.14
560.	0.88	-0.28	0.03	0.13
570.	0.75	-0.22	0.02	0.11
580.	0.64	-0.17	0.01	0.09
590.	0.54	-0.14	0.01	0.06
600.	0.47	-0.11	0.00	0.05
610.	0.41	-0.08	-0.01	0.03
620.	0.38	-0.06	-0.01	0.02
630.	0.34	-0.05	-0.01	0.02
640.	0.31	-0.03	-0.01	0.01
650.	0.29	-0.03	-0.01	0.01
660.	0.27	-0.02	-0.01	0.01
670.	0.26	-0.02	-0.01	0.01
680.	0.25	-0.01	-0.01	0.01
690.	0.25	-0.01	-0.01	0.01
700.	0.24	-0.01	-0.01	0.00

The experimental data were then examined for information that would suggest possible factors. A factor for one component, the reactant, was taken directly from the initial TNT spectrum. The first few spectra of the OH-TNT reaction revealed a possible spectrum of a material with a broad, possibly divided absorption centered about 510 nm (Figure 3). This was rapidly overcome by the appearance of a species with a strong absorption at 450 nm that built to a maximum intensity at 191 s, then slowly declined over the next several hours. Late in the reaction, a chemical species with a significant absorption feature at 330 nm was noted and comprised the final spectra.

Test spectral vectors were constructed for the second intermediate, the final product, initial TNT, and the first intermediate using these observations of the experimental data. The second intermediate was modeled by the spectrum for which the absorbance at 450 nm reaches a maximum (191 s at 25 °C) and corresponds to spectral vector 1 on Table 2. The values start off very high, drop to a minimum at 360 nm, rise to a maximum at 450 nm, and then continue to fall to the end, which corresponds to the spectral data. The final product was modeled by the last spectrum (at 161,400 s at 25 °C) and relates to spectral vector 2. The values of this row start very high, drop slightly, come back to a maximum at 340 nm, then quickly decrease before reaching 400 nm. This is similar to the trend seen at the 24-h spectra at 25 °C. An initial TNT spectrum was used for the third spectral vector. This row begins with a maximum at 240 nm, drops quickly to a minimum at 350 nm, and is essentially constant at higher wavelengths. Most of the features of TNT are in the UV range, with a maximum at 240 nm, and the spectrum is constant in the visible range (400 to 700 nm). The fourth vector was modeled by altering the TNT spectrum with a broad double peak with absorbance of 0.1 AU centered at 520 nm, which corresponds to spectral vector 4. This row exhibits a maximum at 340 nm and a divided peak at 510 and 550 nm, which is consistent with the spectral data. Overall, there is good agreement between the trends of the factors in the reconstructed row matrix and trends in the observed spectra of the reaction over time.

The model that emerges is a four-component reaction with the parenthetical distinctive features:

TNT → Intermediate 1 (530 nm) →Intermediate 2 (450 nm)
→ Final Products (340 nm)
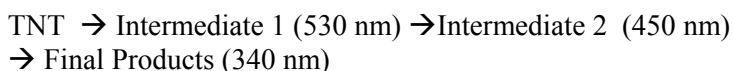
Fast   Very fast   Slow

Test Vectors for Four Components

Malinskowski has shown that, given an FA solution, the abstract row vectors can be transformed into a matrix of real (chemically meaningful) row vectors, if the transformation matrix can be established and if it describes the details of the transformation of the row vectors. In order to check a theoretical model, spectral vectors must be identified, as described above, and used as starting points. Table 3 shows the abstract row, test, and confirmation spectral vectors for the reaction at 25 °C for 220- to 700-nm wavelengths. The vectors marked "rows" were

Table 3
Abstract Row, Test, and Confirmation Spectral Vectors for the 25 °C Reaction

1st Spectral Vector   SSI>= 0.00095
ROW   11.40 7.444 6.804 6.096 5.217 4.595 4.173 3.495 2.930 2.547 2.273 2.099 2.003 1.946 1.897 1.968 2.079 2.279 2.554 2.860 3.150 3.348 3.547 3.576 3.505 3.3 13 3.005 2.652 2.300 2.006 1.749 1.483 1.237 1.040 0.884 0.752 0.640 0.537 0.466 0.4 13 0.377 0.340 0.306 0.287 0.273 0.262 0.255 0.247 0.243
Trial   1.632 1.080 1.033 0.937 0.811 0.729 0.673 0.565 0.471 0.400 0.341 0.297 0.277 0.274 0.286 0.327 0.382 0.453 0.535 0.6 17 0.689 0.734 0.782 0.790 0.780 0.748 0.690 0.6 19 0.539 0.467 0.402 0.339 0.282 0.237 0.200 0.169 0.141 0.117 0.099 0.084 0.074 0.065 0.057 0.052 0.048 0.046 0.044 0.042 0.041
Confirmation   1.639 1.082 1.028 0.931 0.806 0.725 0.671 0.564 0.471 0.402 0.344 0.301 0.2790.2740.283 0.321 0.375 0.444 0.526 0.609 0.684 0.735 0.788 0.799 0.789 0.753 0.689 0.6 0.532 0.461 0.400 0.339 0.284 0.240 0.203 0.170 0.142 0.117 0.098 0.084 0.074 0.066 0.058 0.053 0.0500.04 0.045 0.044 0.043

2nd Spectral Vector   SSE= 0.00274
ROW   1.809 1.106 0.724 0,565 0.404 0.228 0.103 0.089 0.1100.1570.247 0.344 0.386 0.357 0.244 0.060 -.177 -.423 -.667 -.888 -1.08 -1.21 -1.34-1.38-1.38-1.32-l.20-1.04-.869-.726 -.615 -.512 -.420 -.343 -.279 -.222 -.175 -.137 -.105 -.079 -.058 -.046-034-.028-.021-.017-.014-.012 -.011
Trial   1.829 1.139 0.960 0.839 0.698 0.585 0.521 0.457 0.405 0.379 0.374 0.381 0.382 0.370 0337 0.302 0.2.59 0.226 0.202 0.185 0.172 0.158 0.147 0.137 0.128 0.1190.113 0.106 0.099 0.093 0.083 0.073 0.063 0.056 0.051 0.048 0.044 0.039 0.037 0.036 0.035 0.033 0.031 0.030 0.029 0.029 0.028 0.028 0.028
Confirmation   1.807 1.130 0.964 0.847 0.707 0.601 0.545 0.476 0.416 0.384 0.376 0.380 0.381 0.369 0.335 0.299 0.253 0.217 0.191 0.175 0.163 0.153 0.143 0.134 0.126 0.1180.1120.1070.103 0.0980.0900.078~.~~67 0.058 0.053 0.049 0.045 0.040 0.038 0.037 0.038 0.035 0.033 0.032 0.032 0.03 1 0.031 0.030 0.030

3rd Spectra1 Vector   SSE= 0.01702
ROW   0.018 0.249 0.250 0.205 0.167 0.092 -.083 -.186 -.203 -.225-.268-.302 -.324 -.329-.307 -.277 -.225 -.178 -.135 -.095 -.054 -.0 14 0.022 0.045 0.056 0.055 0.048 0.042 0.036 0.030 0.027 0.032 0.039 0.039 0.034 0.023 0.014 0.006 -.002 -.007 -.012 -.012 -.013 -.013 -.013 -.013 -.014 -.013 -.014
Trial   1.759 1.332 1.166 1.004 0.821 0.623 0.374 0.214 0.155 0.121 0.092 0.083 0.074 0.060 0.044 0.030 0.018 0.010 0.005 0.003 0.003 0.003 0.003 0.003 0.002 0.002 0.002 0.002 0.002 0.002 0.002 0.002 0.002 0.002 0.002 0.002 0.002 0.002 0.002 0.002 0.001 0.002 0.002 0.002 0.001 0.002 0.001 0.001 0.001 0.001 0.001 0.001
Confirmation   1.763 1.315 1.141 0.987 0.817 0.644 0.427 0.262 0.187 0.140 0.102 0.085 0.069 0.049 0.028 0.007 -.009 -.022 -.029 -.028 -.018 -.002 0.010 0.019 0.017 0.007 -.004 -.010 -.006 0.000 0.006 0.013 0.019 0.021 0.021 0.018 0.015 0.013 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011

4th Spectral Vector   SSE 0.01078
ROW   0.061 0.046 -.010 -.038 -.059 -.092 -.121 -.069 -.016 0.008 0.018 0.027 0.037 0.042 0.035 0.020 0.003 -.013 -.031 -.050 -.070 -.088 -.101 -.098 -.074 -024 0.048 0.116 0.153 0.154 0.137 0.133 0.139 0.140 0.129 0.109 0.085 0.063 0.046 0.032 0.023 0.017 0.012 0.010 0.008 0.007 0.006 0.005 0.005
Trial   1.759 1.332 1.166 1.004 0.821 0.623 0.374 0.214 0.155 0.121 0.092 0.083 0.074 0.060 0.044 0.030 0.018 0.010 0.005 0.003 0.003 0.003 0.003 0.006 0.010 0.025 0.040 0.080 0.100 0.100 0.095 0.098 0.100 0.100 0.080 0.060 0.040 0.020 0.016 0.015 0.013 0.012 0.011 0.010 0.008 0.006 0.005 0.004 0.004
Confirmation 1.779 1.337 1.147 0.981 0.803 0.616 0.383 0.236 0.180 0.140 0.103 0.085 0.071 0.054 0.033 0.011 -.004 -.015 -.022 -.021 -.013 0.000 0.011 0.024 0.032 0.041 0.056 0.075 0.089 0.091 0.086 0.088 0.093 0.093 0.086 0.073 0.058 0.045 0.034 0.027 0.023 0.020 0.017 0.016 0.015 0.015 0.015 0.014 0.014

the same rows from the matrix identified in Table 2. The vectors marked "Trial" are the test spectral vectors constructed previously based on experimental obser- vations. The rows labeled "Confirmation" are the vectors that resulted after trans- formation of the abstract row vectors with the transformation matrix. Sum of squares error (SSE) in this method is defined as:

$$SSE = \sum (A^\lambda (t)_{calc} - A^\lambda(t)_{obs}) \tag{13}$$

The four test vectors appear to agree with the transformed vectors as judged by the small errors between them. This suggests that the four test vectors are real factors (spectral components) in the reaction.

Modeled Spectra

The spectra of the reaction components were then modeled and the concentrations of the reaction components were determined over time using the test spectral vectors and the abstract matrix. Absorbance data of base hydrolysis of TNT were interpreted as consistent with a reactant, two intermediates, and a product and suggests that the reaction may be crudely modeled by a sequence of first-order reactions. A model was assembled for the sequential first-order reaction scheme

$$a \rightarrow b \rightarrow c \rightarrow d$$
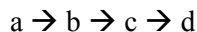
The composite absorbance for this reaction scheme at any time and wavelength, A_{ij}, is the sum of the absorbances of all the species present and follows from the Lambert-Beer Law,

$$A_{ij} = [a]g_a + [b]g_b + [c]g_c + [d]g_d = \sum\sum g_{ik}c_{kj} \tag{14}$$

where the g's are the molar absorptivity vectors taken over the i wavelengths, that is, they are the spectra of the absorbing species, and the concentrations of the k species are followed over the j times. Substituting for g's from the abstract row vectors V_k, we have

$$
\begin{aligned}
A = \ & [a](\tau_{11}V_1 + \tau_{12}V_2 + \tau_{13}V_3 + \tau_{14}V_4) \\
& + [b](\tau_{21}V + \tau_{22}V_2 + \tau_{23}V_3 + \tau_{24}V_4) \\
& + [c](\tau_{31}V_1 + \tau_{32}V_2 + \tau_{33}V_3 + \tau_{34}V_4) \\
& + [d](\tau_{41}V_1 + \tau_{42}V_2 + \tau_{43}V_3 + \tau_{43}V_4)
\end{aligned}
\tag{15}
$$

and collecting terms in V, we have

$$
\begin{aligned}
A = \ & [(a)\tau_{11} + (b)\tau_{21} + (c)\tau_{31} + (d)\tau_{41}]\,V_1 \\
& + [(a)\tau_{21} + (b)\tau_{22} + (c)\tau_{32} + (d)\tau_{42}]\,V_2 \\
& + [(a)\tau_{31} + (b)\tau_{32} + (c)\tau_{33} + (d)\tau_{34}]\,V_3 \\
& + [(a)\tau_{41} + (b)\tau_{42} + (c)\tau_{43} + (d)\tau_{44}]\,V_4
\end{aligned}
\tag{16}
$$

Defining ξ as the coefficients of V, defined over the l components as

$$\xi_{kl} = \tau_{lk}\,c_1 \tag{17}$$

the composite spectrum at any time is

$$A_i = V_1\xi_{11} + V_2\xi_{21} + \ldots = V_{1k}\,\xi_{kl} \tag{18}$$

and the whole absorbance versus time data set becomes

$$A_{IJ} = \sum\sum\sum V_{ik} \, \tau_{lk} \, c_{lj} \tag{19}$$

It is seen that the number of the square transformation matrix elements (τ's) is $1 \times k$, where $l = k$ and the number of important factors accounting for these data.

In order to derive the concentration of each reaction component over time, knowledge of the rate constants ($k_1 \ldots k_{k-1}$) for the reaction is required. For example, the concentration of the kth component, c_k, is

$$c_k(t) = C_1 e^{-k_1 t} + C_2 e^{-k_2 t} \ldots + C_k e^{-k_k t} \tag{20}$$

where $C_1 = (k_1, k_2 \ldots k_{k-1}) / (k_2 - k_1)(k_3 - k_1) \ldots (k_k - k_1)$

and

where $C_2 = (k_1, k_2 \ldots k_{k-1}) / (k_1 - k_2)(k_3 - k_2) \ldots (k_k - k_2)$, etc. (Friedlander, Kennedy, and Miller 1964).

Estimates of the rate constants were approached by ignoring the fast initial reaction (and ignoring the first few data) and examining the behavior of the reaction component producing the 450-nm absorption. Since the model is non-linear in all of the variables, the variables were refined against the absorbance versus time data array using a nonlinear least squares procedure.

Spectral components were separated by a nonlinear least squares method. The chi-squared definition, χ^2, was used as an appropriate gauge of the agreement between a developing model and the entire spectra when fitting the whole spectra measured over time. The best model for k components would have a set of variables that produces a minimum value for χ^2. The spectra are given as a function of the PCA row vectors and a transformation matrix, T

$$(spectra)_{i,k} = u \, (Tmn) \, (row)_{i,k}$$
$$m = 1 \ldots k; n = 1 \ldots k \tag{21}$$

and the concentrations are given by a kinetic model tied to the rate constants.

$$(concentrations)k_j = u \, (k_1, \ldots k_{k-1})_{kj} \tag{22}$$

There are $1[= k^2 + (k-1)]$ variables for k components. These are the normal equations.

$$\partial\chi^2/\partial a = -2 \sum [w_{ij}(A_{obs\,ij} - A_{calc\,ij})][\partial A_{calc\,ij}/\partial a_1] \tag{23}$$

In this case, $\partial\chi^2/\partial a_1$ is a vector with l elements.

In order to obtain the best fit, the variables are considered parameters to be adjusted to minimize χ^2. The derivative of χ^2 is taken with respect to each variable; i.e., the gradient of χ^2 and set to zero. Taking the partial derivatives of each of the observational equations with respect to each variable, and substituting into the normal equations, the normal equations can be rearranged to segregate the changes in the variables, which minimize χ^2. These equations are solved by a Gaussian (linear) elimination method, whereupon the shifts are applied to the variables, and the process is repeated until convergence. Because the system is nonlinear, the shifts will often result in sudden, large increases in χ^2 rather than a smooth procession to the global minimum. Methods to handle this require a combination of the steepest descent method (linear least squares) with dampening of the shifts as the problem moves toward the minimum. The beginning model must resemble the final solution, since the polydimensional hypersurface is potentially filled with many false minima to which the calculation can descend.

After the variables were refined, the spectra of the four reaction components were predicted by the sequential first order kinetic model and were plotted as illustrated in Figure 7. The four components in this figure are: TNT, first intermediate, second intermediate, and the final product. TNT spectra plotted in Figure 7 mirror the observed spectra in Figure 2. The spectrum shows a maximum at 250 nm, decreases quickly, and remains featureless in the visible range.
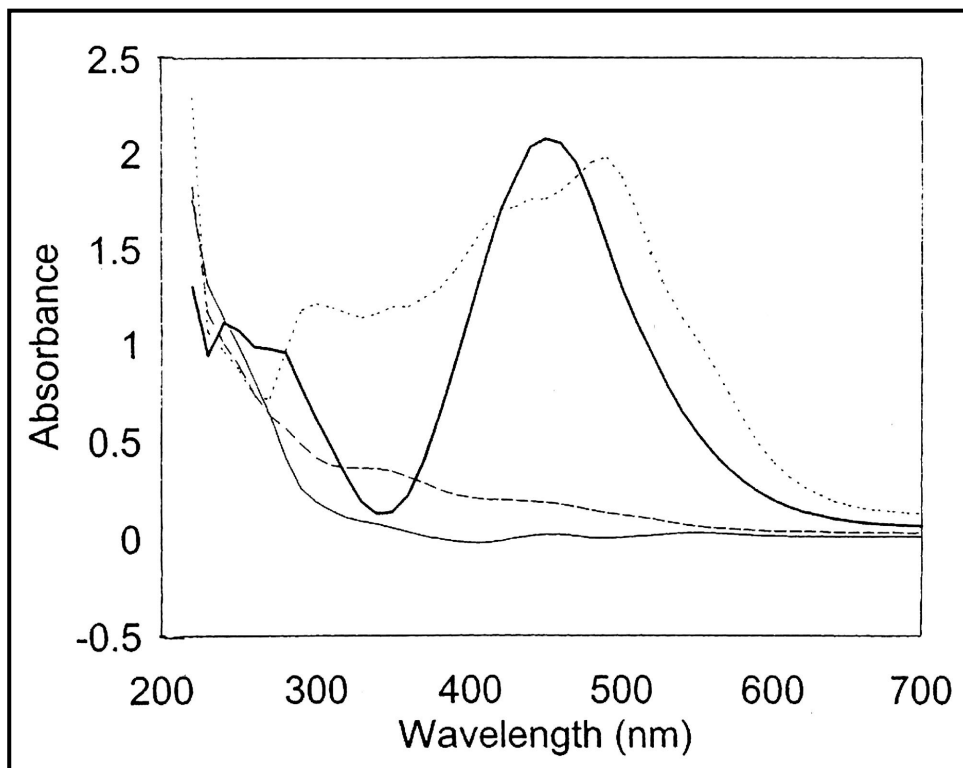

Figure 7.   Spectral features of four components at 25 °C using sequential first-order kinetic model
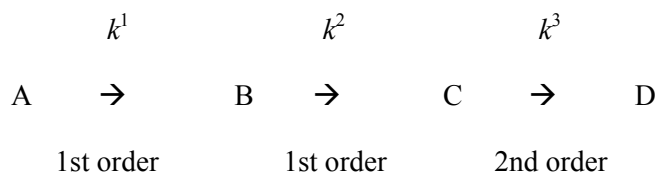
The first intermediate shows features at 330 and 500 nm, which are similar to the features seen growing into the observed spectra. The model indicates that the first intermediate is a major component of the 450-nm feature because its spectrum is strong at that wavelength. Spectrum of the second intermediate also exhibits a dominant 450-nm feature that rises quickly and decreases slowly over the remainder of the reaction, comparable to the observed spectra. The spectrum of final products calculated by this model exhibits a broad feature at 330 nm, similar to the observed spectra of the final product (Figure 5). The calculated spectra show reasonable agreement with the observed spectra, indicating this model may be useful to explain the experimental spectral data.

Predicted Concentrations of Individual Reaction Components

The concentration curves calculated using the sequential first-order kinetic model for the four components at 25 ºC for the first 3,000 s of the TNT-hydroxide reaction are shown in Figure 8. TNT concentration, the initial component, quickly goes to extinction as indicated by the thin solid line. The concentration of the first intermediate, illustrated by the dotted line, rises and falls quickly in the reaction. The second intermediate, represented by the bold solid line, grows to a maximum at 191 s at 25 ºC and very slowly decreases over time. The final concentration of the product slowly increases over the course of the reaction, as shown by the dashed line on Figure 8. The bottom plot illustrates the concentration curves for the four components at 25 ºC for the first 500 s of the reaction as fit by the sequential first-order model. A plot of the entire sampling time was not illustrated, as the smaller features were obscured in the plot.

Other Kinetic Models

In this work, the slow formation of the final component in the four-component model suggested that the final product might be produced in a second-order step. A reaction scheme for this model is

$$k^1 \qquad\qquad k^2 \qquad\qquad k^3$$

$$A \quad \rightarrow \quad B \quad \rightarrow \quad C \quad \rightarrow \quad D$$

$$\text{1st order} \qquad \text{1st order} \qquad \text{2nd order}$$

for which $-dC/dt = k_2 \, [B] - k_3 \, [C]^2$ and the other terms can be written accordingly. A four-component, first-order, first-order, second-order kinetics model was applied to 20 °C spectral data. Figure 9 illustrates the spectra of the four components of the TNT-hydroxide reaction using this model. TNT, first intermediate, second intermediate, and the final products follow very similar trends at 20 °C for this model at 25 °C for the sequential first-order kinetics model (Figure 7). This may indicate that the plotted spectra are not sensitive to the models.
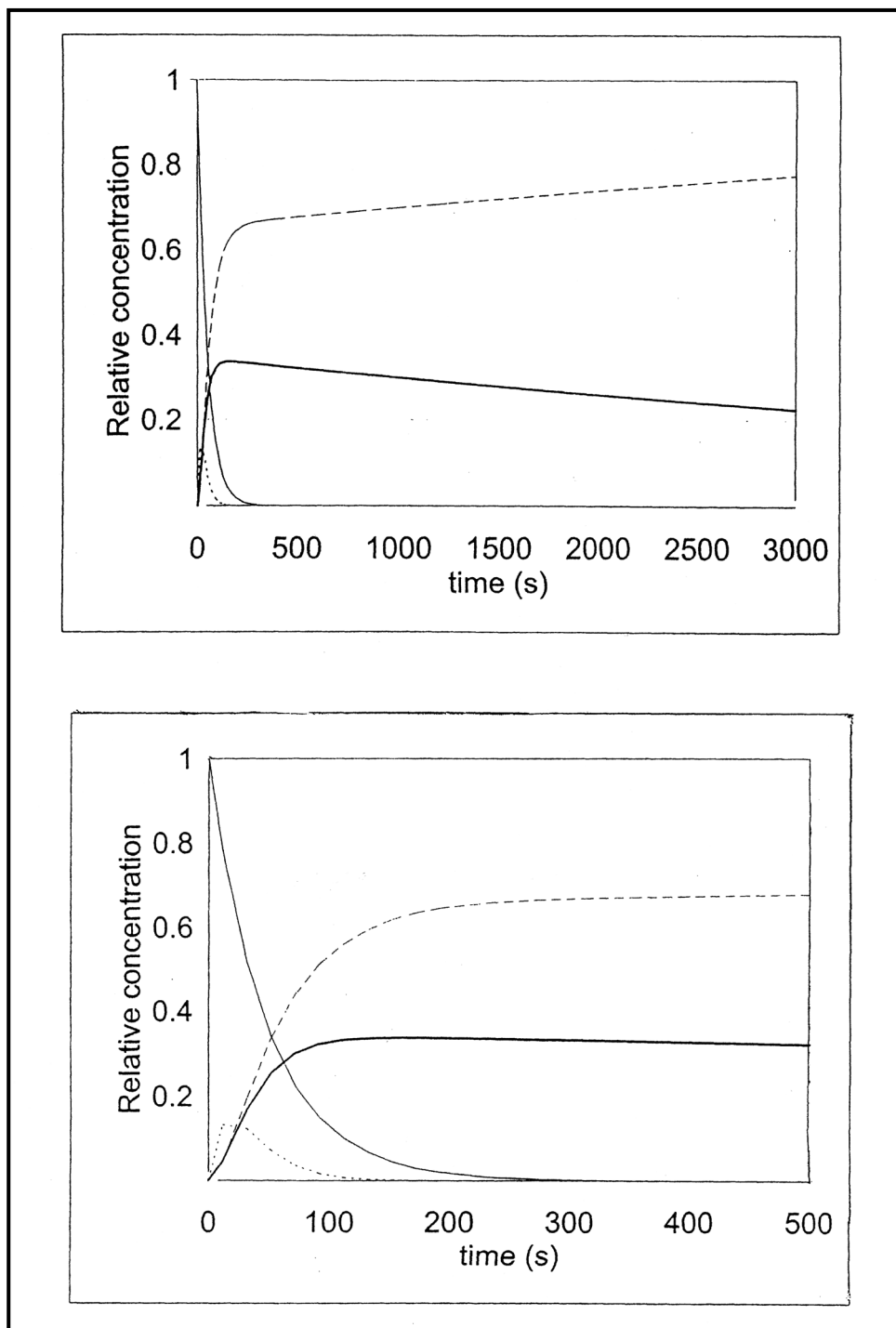
Figure 8.   Plot of concentration data for the four components at 25 °C using sequential first-order kinetic model

The kinetic (concentration) plots for 20 °C in Figure 10 also reflect similar trends as those at 25 °C in the sequential first-order model (Figure 8). This may indicate that both models are working reasonably well to predict the spectral and kinetic data of the TNT-hydroxide reaction.

Figure 9.   Spectral features of four components at 20 °C using first-order, first-order, second-order kinetics models

Table 4 shows the rate constants that were calculated using both four-component models that were described previously. The values for k_1 and k_3, calculated using the sequential first-order kinetics model, have equal and opposite values. The third rate constant is negative for all temperatures, which is not physically possible. χ^2 were in the order of 10^5, and SSE was calculated using the entire experimental matrix. The first-order, first-order, second-order kinetics model did show an improvement from the sequential first-order model in that all the rate constants were positive. Second-rate constants are at least an order of magnitude smaller in this model. χ^2 and SSE are in the same order of magnitude in both models. This table shows that the rate constant for the initial step in the reaction (k_1) is much larger (faster) than the second rate constant (k_2). This corresponds to results from a kinetics study that followed TNT decay using HPLC (Felt, Larson, and Hansen 2001a). Rate constants were calculated in that study using a second exponential decay to model TNT transformation.

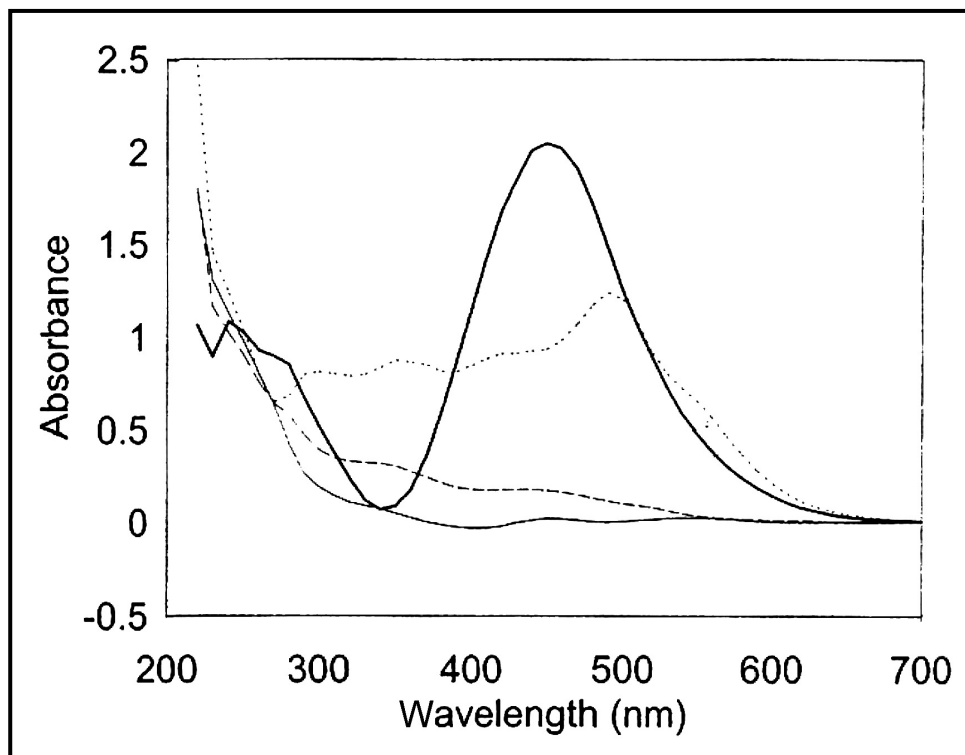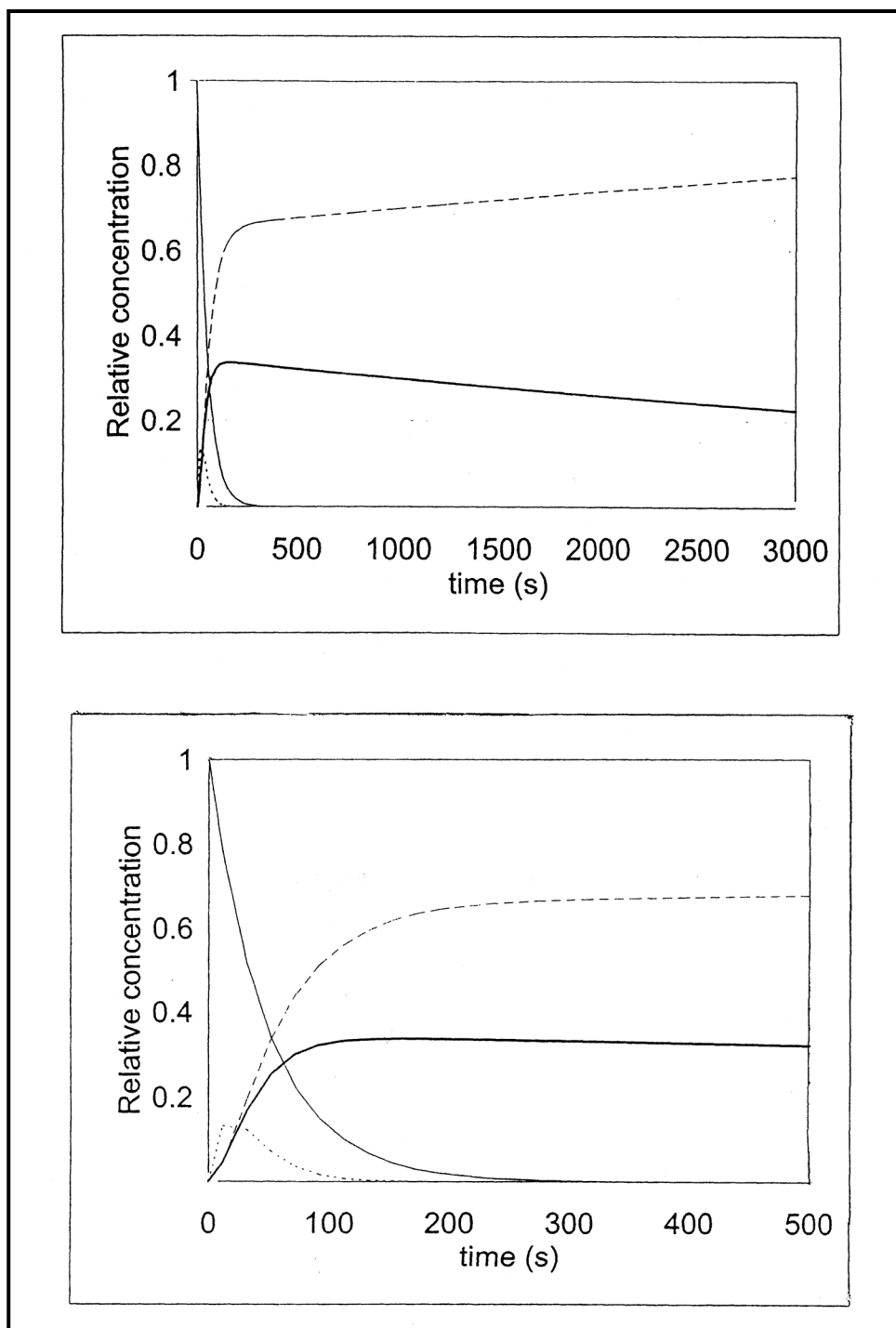Figure 10. Plot of concentration data for four components at 20 °C using a first-order, first-order, second-order kinetics model

Table 4
Rate Constants Calculated Using the Sequential First-Order, Four-Component Model and the First-Order, First-Order, Second-Order, Four-Component Model (12′ represents 12-°C data that had been recalculated using the 15-°C data as a starting point for the calculations)

Sequential First-Order Model		Temperature (°C)			
		12	15	20	25
k_1		0.0205	0.0206	0.0206	0.0206
k_2		0.0029	0.00684	0.04529	0.04396
k_3		-0.0204	-0.0204	-0.0205	-0.0205
χ^2		9.82E+05	6.60E+05	8.84E+05	6.78E+05
SSE		0.826	0.556	0.678	0.571

1-1-2 Model			Temperature (°C)		
	12'	12	15	20	25
k_1	0.02173	0.1234	0.0208	0.0526	0.076
k_2	0.000116	0.000171	0.000143	0.0002	0.000234
k_3	0.00676	0.00855	0.00583	0.0228	0.03151
χ^2	5.09E+05	4.95E+05	3.53E+05	6.22E+05	5.22E+05
SSE	0.429	0.417	0.297	0.524	0.465

The fits for the four-component models are interesting but not perfected. χ^2 are in the order of 10^5, were reduced from 10^{12}, and the values were set at the initial step of the calculation. The overall fit to the absorbance differences are on the order of 0.04 AU, and most below 0.008 AU, but these values are above the estimated error of an absorbance reading (0.002 AU). Judging from the χ^2 criteria, the exact rate model is as yet not sufficiently characterized. The exact rate model does not alter the basic features of the rise and fall of the first three components and the growth of the terminal component to represent the spectra at long reaction times. The four-component models based on PCA therefore reasonably map out the course of the reaction.

A kinetics model that represents multiple products may be illustrated as:

$$a \rightarrow b \rightarrow c \begin{array}{c} \nearrow d \rightarrow e \\ \rightarrow f \\ \searrow g \rightarrow h \end{array} \qquad (23)$$

(TNT)   (Int. 1)   (Int.2)
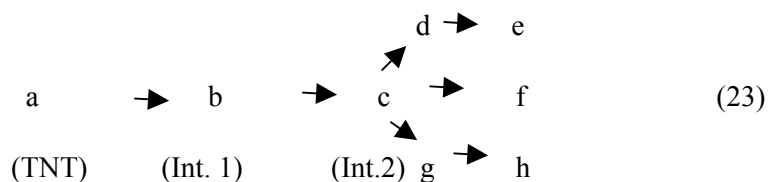
Other kinetics models for the TNT-hydroxide reaction are possible. The observed spectra indicate that TNT degrades to form a first intermediate (b) that rapidly degrades to form a second intermediate (c). The second intermediate may degrade to form more than one product, which was indicated by a previous study that was conducted in our laboratory. Using gel permeation chromatography

(GPC), OH-TNT final reaction products were separated into molecular weight fractions (Felt, Larson, and Hansen 2001b). TNT final products varied in molecular weight from 3,000 to 6,000 to <100 Da. GPC results do not contradict the spectral model offered here, since the PCA would not necessarily differentiate between similar chemical compounds.

It should be noted that the order of the OH-TNT reaction has not been established experimentally. Knowing the order of the reaction could verify a kinetics model for the OH-TNT reaction. The smaller principal components of the OH-TNT reaction could be identified using an LC-MS technique after filtration of the polymers. The overall order of the reaction could be determined after the components were identified and the order for each component was determined. Kinetic models could be refined and tested, if the order of the reaction were known. Establishing the order of the reaction could be a topic for future work.

6   Conclusions

OH-TNT reaction mixtures were analyzed over time using UV/VIS spectroscopy at different temperatures. The spectra indicated that the OH-TNT reaction requires 48 h to come to completion at room temperature, long after TNT itself has degraded (< 40 min). An intermediate of the reaction produced a dominant spectral feature with a maximum of 0.8 AU at 450 nm, regardless of temperature. This suggested that the component was a real reaction component, and the spectrum containing a maximum 450-nm feature was its true spectrum. Results indicate an initial reaction intermediate is rapidly formed after the addition of the base that quickly transforms into a polar, secondary intermediate. The secondary intermediate, in turn, slowly degrades to form polar final products. These results were supported by a previous kinetic study using HPLC.

The observed spectral data were analyzed by FA. PCA of the observed data indicated that there were six principal components in the reaction, four of which explained most of the variance in the data matrix. A sequential first-order model and a first-order, first-order, second-order model were tried and were judged to be interesting. The models and rate measurements were abstract and exhibited trends similar to rate measurements calculated for HPLC data by a second exponential decay fit. The rate order of the OH-TNT reaction has not been established experimentally. Identification of individual reaction components and the order of the reaction would help determine an accurate kinetics model for the OH-TNT reaction.

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Appendix A
Principal Component Analysis (PCA) for Spectral Data

```
!------PRINCIPAL COMPONENT ANALYSIS FOR SPECTRA
    implicit real*8(A-H,O-Z)
    CHARACTER*1 TITL(80)
    DIMENSION D(100,100),T(100),WAV(100)
    DIMENSION DT(100,100),COVAR(100,100)
    DIMENSION ANORM(100),DNORM(100,100),Z(100,100)
    DIMENSION DNORMT(100,100),EIGEN(100)
    DIMENSION V(100),VE(100),VT(100)
    DIMENSION C(100,100)
    DIMENSION ADIFF(100,100),DDIFF(100,100)
    DIMENSION RE(100),EMBE(100)
    DIMENSION CPRIME(100,100),DPRIME(100,100),ROW(100,100)
    DIMENSION CPRIMET(100,100)
!
!  READ DATA MATRIX
!   FIRST READ NUMBER OF ROWS (IR) THEN NUMBER OF COLUMN (IC)
!   FOR ABSORBANCE VS. TIME: (OTHER 2D VARIABLE JUST AS ACCEPTABLE)
!   THE ROW ENTRIES ARE THE ABSORBANCES AT VARIOUS TIMES
!   AND SUCCESSIVE ROWS ARE ADDITIONAL ABSORBANCES AT VARIOUS
TIMES
!   THE TIME DATA SHOULD BE IN THE LAST ROW RECORD
    OPEN(3,FILE='HPDATA.DAT',STATUS='UNKNOWN')
!  OPEN OUTPUT FILE, TOO
    OPEN(10,FILE='PCA.OUT',STATUS='UNKNOWN')
    READ(3,10)IR,IC
 10   FORMAT(2I5)
    DO I=1,IR
     READ(3,*) (D(I,J),J=1,IC)
     ENDDO
     READ(3,*) (T(J),J=1,IC)
     WRITE(6,25)IR,IC
     WRITE(10,25)IR,IC
 25   FORMAT(1X,'Principal Component Analysis ',&
     /1X,I5,' x',I5,' DATA MATRIX READ FROM "HPDATA.DAT"')
    DO I=1,IR
     WRITE(10,30)(D(I,J),J=1,IC)
 30   FORMAT(1X,6(E12.4,1X))
     ENDDO
     WRITE(10,31) (T(J),J=1,IC)
 31   FORMAT(1X,'TIMES:',/1X,6(E12.4,1X))
     WRITE(10,*)
! READ WAVELENGTH
    READ(3,*)(WAV(I),I=1,IR)
    READ(3,33)(TITL(I),I=1,80)
 33  FORMAT(80A1)
    CLOSE(3)
! COMPUTE THE TRANSPOSE OF THE DATA MATRIX;
! THEN THE COVARIANCE MATRIX DT.D    DIMENSION NOW ICxIR
    CALL TRANSPOS(IR,IC,D,DT)
    CALL MATMULT(IC,IR,IC,DT,D,COVAR)
```

```fortran
       WRITE(10,29)
 29    FORMAT(1X,'TRANSPOSED DATA MATRIX:')
       DO I=1,IC
        WRITE(10,30)(DT(I,J),J=1,IR)
       ENDDO
        WRITE(10,32)
 32     FORMAT(1X,'COVARIANCE MATRIX:')
       DO I=1,IC
        WRITE(10,30)(COVAR(I,J),J=1,IC)
       ENDDO
!
!    NOW NORMALIZE THE COVARIANCE MATRIX
!    FIRST GET THE NORMALIZATION CONSTANTS FOR EACH COLUMN
       DO I=1,IR
        DO J=1,IC
         ANORM(J)=ANORM(J)+(D(I,J)**2)
        ENDDO
       ENDDO
!     WRITE(10,*)ANORM(1),ANORM(2),ANORM(3),ANORM(4)
       DO I=1,IC
        ANORM(I)=1/ANORM(I)
        ANORM(I)=DSQRT(ANORM(I))
       ENDDO
!     WRITE(10,*)ANORM(1),ANORM(2),ANORM(3)
! COMPUTE NORMALIZED DATA MATRIX DNORM
       DO I=1,IR
        DO J=1,IC
         DNORM(I,J)=D(I,J)*ANORM(J)
        ENDDO
       ENDDO
       WRITE(10,51)
 51    FORMAT('NORMALIZED DATA MATRIX:')
       DO I=1,IR
        WRITE(10,30)(DNORM(I,J),J=1,IC)
       ENDDO
! AND CALCULATE THE CORRELATION MATRIX, Z=DNORM*(DNORM)T
       CALL TRANSPOS(IR,IC,DNORM,DNORMT)
       CALL MATMULT(IC,IR,IC,DNORMT,DNORM,Z)
        WRITE(10,59)
 59    FORMAT(1X,'NORMALIZED CORRELATION MATRIX AS COR TRIANGLE:')
       DO I=1,IC
        WRITE(10,60)(Z(I,J),J=1,I)
 60     FORMAT(13(F5.3,1X))
       ENDDO
!
! NOW DETERMINE THE EIGENVECTORS IN THE SPACE;& THE EIGENVALUES
! BY ITERATION, WE SATISFY [Z]*C1=EIG1*C1
! INTITIAL ESTIMATES OF EIGENVECTOR
       WRITE(10,*)"DETERMINE EIGENVECTORS BY ITERATION"
       DO I=1,IC
```

```fortran
      DO J=1,IC
       C(I,J)=0.58
      ENDDO
      ENDDO
! BEGIN ITERATION
      DEL=1.0D-9
      START=-1.0D-10
! COMPUTE IC EIGENVALUES AND EIGENVECTORS
      DO 121 N=1,IC
      DO 110 L=1,50
      DO I=1,IC
       V(I)=C(N,I)
      ENDDO
      CALL MATVEC(IC,IC,COVAR,V,VE)
!     WRITE(10,104)(VE(J),J=1,IC)
  104 FORMAT(1X,10(1X,E10.5))
! MORMALIZE THE VECTOR
      XNORM=0.0D0
      DO I=1,IC
       XNORM=XNORM+(VE(I)**2)
      ENDDO
      XNORM=DSQRT(XNORM)
      DIFF=DABS(XNORM-START)
      WRITE(10,109)L,XNORM,DIFF
  109 FORMAT(1X,'ITER# ',I3,'EST. EIGENVALUE = ',F12.3,&
      ' CHANGE = ',F10.5)
      DO I=1,IC
       VE(I)=VE(I)/XNORM
      ENDDO
!     WRITE(10,104)(VE(J),J=1,IC)
      DO I=1,IC
       C(N,I)=VE(I)
      ENDDO
      START=XNORM
      IF(DIFF.LT.DEL)GOTO 111
  110 CONTINUE
  111 CONTINUE
      WRITE(10,105)N,XNORM,(C(N,J),J=1,IC)
  105 FORMAT(1X,'EIGENVALUE ',I2,' IS ',F12.5,/1X,&
      'VECTOR IS ',3(1X,F12.5))
! END ITERATION
! COMPUTE RESIDUAL MARIX R, =COVAR - LAM*C*C'
      EIGEN(N)=XNORM
      DO I=1,IC
       VT(I)=VE(I)*EIGEN(N)
      ENDDO
      CALL VECMULT(IC,1,VT,VE,ADIFF)
!     DO I=1,IC
!     WRITE (10,*) (ADIFF(I,J),J=1,IC)
!     ENDDO
```

```
! SUBTRACT FROM COVARIANCE MATRIX
      DO I=1,IC
       DO J=1,IC
        COVAR(I,J)=COVAR(I,J)-ADIFF(I,J)
       ENDDO
      ENDDO
  121 CONTINUE
! PRINT THE COVARIANCE MATIX AFTER ALL IS DONE (SHOULD BE ZEROS)
      WRITE(10,*)"FINAL COVARIANCE MATRIX:"
      DO I=1,IC
       WRITE(10,122)(COVAR(I,J),J=1,IC)
  122 FORMAT(1X,10(F6.4,1X))
      ENDDO
!
      IVEC=IC
      IMPTIVEC=IC
       CUT=1.0D0/IC
      DO I=1,IC
       IF(EIGEN(I).LT.CUT)IMPTIVEC=IMPTIVEC-1
      ENDDO
! OFFER THE OPPORTUNITY TO MODIFY THE NUMBER OF IMPORTANT
EIGENVECTORS
!    WRITE(6,*)'ENTER NUMBER OF EIGENVECTORS TO OVERRIDE CALC. (I1)
0=KEEP :'
!    READ(5,129)ICHOSE
! 129  FORMAT(I1)
!    IF(ICHOSE.EQ.0)GOTO 130
!    IMPTIVEC=ICHOSE
! CALCULATE REAL AND IMBEDDED ERRORS
! RE = THAT ACCOUNTED FOR BY THE OTHER FACTORS THAN THOSE
EXPLAINING THE
! VARIANCE
 130  DO I=1,IVEC
      K=I+1
      ANUM=0.0D0
      DO J=K,IVEC
       ANUM=ANUM+EIGEN(J)
      ENDDO
!     WRITE(6,*)I,J,ANUM
      ARG=ANUM/(IC*(IVEC-I))
      RE(I)=DSQRT(ARG)
      ANUM=I*ANUM
      ARG=ANUM/(IR*IC*(IVEC-I))
      EMBE(I)=DSQRT(ARG)
      ENDDO
! SOME SCREEN OUTPUT; EIGENVALUES AND EIGENVECTORS
      WRITE(6,135)IR,IC
  135 FORMAT(1X,'DATA MATRIX HAS ',I3,' ROWS AND ',I3,' COLUMNS')
      WRITE(6,139)IMPTIVEC
  139 FORMAT(1X,'PCA EXTRACTED ',I3,' IMPORTANT EIGENVECTORS')
```

```
      DO I=1,IVEC
       WRITE(6,143)I,EIGEN(I)
       WRITE(6,144)(C(I,J),J=1,IC)
       WRITE(6,145)RE(I),EMBE(I)
       WRITE(10,143)I,EIGEN(I)
       WRITE(10,144)(C(I,J),J=1,IC)
       WRITE(10,145)RE(I),EMBE(I)
  143 FORMAT(1X,'EIGENVALUE # ',I2,5X,F12.3)
  144 FORMAT(1X, 10(F7.2,1X))
  145 FORMAT(1X,'REAL ERROR= ',F6.2,' EMBEDDED ERROR= ',F6.2)
      ENDDO
!
!    COMPUTE THE DATA MATIX FROM THE PCA SOLUTION
!    D'=C*R  USING THE IMPTIVEC EIGENVECTORS AND EIGENVALUES
!    CONSTRUCT THE EIGENVECTOR APPROXIMATION
      DO I=1,IMPTIVEC
      DO J=1,IC
       CPRIME(I,J)=C(I,J)
      ENDDO
      ENDDO
!    WRITE(10,*)"CPRIME"
!    DO I=1,IMPTIVEC
!     WRITE(10,144)(CPRIME(I,J),J=1,IC)
!    ENDDO
!    AND GENEERATE THE ROW MATRIX FROM THE IMPORTANT
EIGENVECTORS
!    ACCORDING TO R=d*Ct
      CALL TRANSPOS(IMPTIVEC,IC,CPRIME,CPRIMET)
!    WRITE(10,*)"CPRIME TRANSPOSE"
!    DO I=1,IC
!     WRITE(10,144)(CPRIMET(I,J),J=1,IMPTIVEC)
!    ENDDO
!  AND MULTIPLY BY THE EIGENVECTORS TO GENERATE THE ROW MATRIX
      CALL MATMULT(IR,IC,IMPTIVEC,D,CPRIMET,ROW)
      WRITE(10,*)"RECONSTRUCTED ROW MATRIX BASED ON IMPORTANT
FACTORS"
      WRITE(10,146)
  146 FORMAT(1X,'LAMBDA    1    2    3    4    5    6')
      DO I=1,IR
       WRITE(10,147)WAV(I),(ROW(I,J),J=1,IMPTIVEC)
      ENDDO
  147 FORMAT(1X,F4.0,3X,10(F7.2,1X))
!  AND FINALLY, THE RECONSTRUCTED DATA IS ROW*CPRIME
      CALL MATMULT(IR,IMPTIVEC,IC,ROW,CPRIME,DPRIME)
      WRITE(10,*)"RECONSTR. DATA MATRIX BASED ON ",IMPTIVEC,"
IMPORTANT FACTORS"
      DO I=1,IR
       WRITE(10,30)(DPRIME(I,J),J=1,IC)
      ENDDO
!  AND THE DIFFERENCE BETWEEN THE DATA AND ITS RECONSTRUCTION
```

```fortran
      DO I=1,IR
       DO J=1,IC
        DDIFF(I,J)=D(I,J)-DPRIME(I,J)
       ENDDO
      ENDDO
      WRITE(10,*)"DIFF. BETW. DATA AND RECONSTRUCTION = ERROR"
      DO I=1,IR
       WRITE(10,151)(DDIFF(I,J),J=1,IC)
151   FORMAT(1X,10(F6.3,1X))
      ENDDO
!
!     ISSUE OUTPUT FOR READING TO TEST DIRECTED VECTORS
      OPEN(11,FILE='TESTVEC.DAT',STATUS='UNKNOWN')
      WRITE(11,10)IR,IC
!  10 FORMAT(2I5)
      DO I=1,IR
       WRITE(11,*)(D(I,J),J=1,IC)
      ENDDO
      DO I=1,IR
       WRITE(11,*)(DPRIME(I,J),J=1,IC)
      ENDDO
      WRITE(11,10)IVEC,IMPTIVEC
      DO I=1,IVEC
       WRITE(11,*)EIGEN(I)
      ENDDO
      DO I=1,IVEC
       WRITE(11,*)(C(I,J),J=1,IC)
      ENDDO
      DO I=1,IR
       WRITE(11,*)(ROW(I,J),J=1,IMPTIVEC)
      ENDDO
      WRITE(11,*)(WAV(I),I=1,IR)
      WRITE(11,*)(T(I),I=1,IC)
      WRITE(10,*)"DATA FOR MODEL TESTING WRITTEN TO 'TESTVEC.DAT'"
      WRITE(10,233)(TITL(I),I=1,80)
      WRITE(11,233)(TITL(I),I=1,80)
 233  FORMAT(1X,80A1)
      CLOSE(11)
      WRITE(6,*)"OUTPUT WRITTEN TO 'PCA.OUT'"
      STOP
      END
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
!
! SUBROUTINES
!
! COMPUTE THE TRANSPOSE OF A RECTANGULAR MATRIX   !!!!!!!!!!!!!!!!!!!!!!!!!
      SUBROUTINE TRANSPOS(II,JJ,A,B)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(100,100),B(100,100)
!     WRITE(6,*)"TRANSPOSE",II,JJ
```

```fortran
      DO I=1,II
       DO J=1,JJ
        B(J,I)=A(I,J)
!      WRITE(10,*)B(J,I)
       ENDDO
      ENDDO
      RETURN
      END
!
!
! COMPUTE THE MATRIX PRODUCT OF AN IxK AND KxJ ARRAYS TO PRODUCE
A
! THE GENERAL PRODUCT MATRIX OF DIMENSION IxJ
      SUBROUTINE MATMULT(II,KK,JJ,A,B,AB)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(100,100),B(100,100),AB(100,100)
! BY THE ROWxCOLUMN METHOD; AN II BY KK MATRIX IS MULTIPLIED BY A
! KK BY JJ PRODUCING AN II BY JJ MATRIX
      DO I=1,II
       DO J=1,JJ
        SUM=0.0D0
        DO K=1,KK
         SUM=SUM+(A(I,K)*B(K,J))
!        WRITE(10,40)I,J,K,B(I,K),A(K,J),SUM
! 40  FORMAT(1X,3I5,1X,3(F12.4,1X))
        ENDDO
        AB(I,J)=SUM
       ENDDO
      ENDDO
      RETURN
      END
!
! MULTIPLY A VECTOR (B) BY A MATRIX (A) [DOT PRODUCT]
! COLUMNS OF VECTOR MUST EQUAL ROWS OF MATRIX (IR)
! OUTPUT VECTOR (C) HAS IR ROWS
      SUBROUTINE MATVEC(IR,IC,A,B,C)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(100,100),B(100),C(100)
      DO I=1,IC
       SUM=0.0D0
       DO J=1,IR
        SUM=SUM+(A(I,J)*B(J))
!       WRITE(10,30)I,J,A(I,J),B(J),SUM
! 30   FORMAT(1X,I5,I5,3(F12.5,1X))
       ENDDO
       C(I)=SUM
      ENDDO
      RETURN
      END
!
```

```
! MULTIPLY TWO VECTORS (A) AND (B); (RxC)*(CxR) = (RxR)
! TO PRODUCE A MATRIX
      SUBROUTINE VECMULT(II,JJ,A,B,C)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(100),B(100),C(100,100)
      DO I=1,II
       DO J=1,II
        C(I,J)=A(I)*B(J)
!       WRITE(10,30)I,J,A(I),B(J),C(I,J)
! 30    FORMAT(1X,2I5,1X,3F12.5)
       ENDDO
      ENDDO
      RETURN
      END
!
```

Appendix B
Program to Test Vectors from Principal Component Analysis (PCA) Version for Various Consecutive First-Order Kinetics Treatment

```
!
!  PROGRAM TO TEST VECTORS FROM PCA
!  VERSION FOR TWO FIRST ORDER FOLLOWED BY SECOND ORDER KINETICS
!   TREATMENT
!  MODIFIED LEAST-SQUARES PROCEDURE
!  LOCAL NAME IS TESTVEC VERSION 7
!
      IMPLICIT REAL*8(A-H,O-Z)
      CHARACTER*1 TITLE
      DIMENSION D(100,100),DPRIME(100,100),C(100,100),CBAR(100,100)
      DIMENSION DD(100,100),ROWT(100,100),WAV(100)
      DIMENSION EIGEN(100),ALAM(100,100),ALAMINV(100,100),ROW(100,100)
      DIMENSION TT(100,100),TL(100),XFORM(100,100),TINV(100,100)
      DIMENSION DATA(100),UNITY(100),UNIQUE(100),SELF(100),TEST(100)
      DIMENSION TITLE(80)
      DIMENSION A(100,100),AA(100)
      DIMENSION SCRATCH(500)
      DIMENSION TIME(100),CONC(10,100)
!
      DIMENSION G(100,10)
      DIMENSION V(100),RATEK(10),CN(10),TAU(10,10),ZETA(10,10)
      DIMENSION ACALC(100,100),Q(100,100)
      DIMENSION SIG(100,100),D2XIDADB(100,100),DXIDV(100)
      DIMENSION ADEL(100,100),DELA(100)
      DIMENSION DADVAR(100,100,50)
      DIMENSION BLO(10),BHI(10),SCALE(10)
! RETRIEVE DATA FROM UNIT 11 'TESTVEC.DAT', MADE BY PCA.F90
      OPEN(11,FILE='TESTVEC.DAT',STATUS='UNKNOWN')
! OUTPUT IS UNIT 10
      OPEN(10,FILE='TESTVEC.OUT',STATUS='UNKNOWN')
      READ(11,10)IR,IC
 10  FORMAT(2I5)
      WRITE(6,*)IR,IC
      WRITE(10,*)IR,' ROWS',IC,' COLUMNS'
      DO I=1,IR
       READ(11,*)(D(I,J),J=1,IC)
      ENDDO
! GET LIMITS
      ALOW=1.0D+25
      AHI=1.0D-25
      DO I=1,IR
       DO J=1,IC
        IF(D(I,J).GT.AHI)AHI=D(I,J)
        IF(D(I,J).LT.ALOW)ALOW=D(I,J)
       ENDDO
      ENDDO
      WRITE(10,14)ALOW,AHI
 14  FORMAT(1X,'ABSORBANCE RANGE FROM ',F7.3,' TO ',F7.3)
!     WRITE(10,*)'DATA MATRIX'
!     DO I=1,IR
```

```
!      WRITE(10,11)(D(I,J),J=1,IC)
!     ENDDO
    DO I=1,IR
     READ(11,*)(DPRIME(I,J),J=1,IC)
     ENDDO
!    WRITE(10,*)'RECONSTRUCTED DATA MATRIX'
!    DO I=1,IR
!     WRITE(10,11)(DPRIME(I,J),J=1,IC)
!     ENDDO
 11  FORMAT(1X,6(F10.6,1X))
    READ(11,10)IVEC,IMPTIVEC
    WRITE(10,8)IVEC,IMPTIVEC
    WRITE(6,8)IVEC,IMPTIVEC
  8  FORMAT(1X,I3,' VECTORS WITH ',I3,' IMPORTANT ONES')
    DO I=1,IVEC
     READ(11,*)EIGEN(I)
     ENDDO
    WRITE(10,*)'EIGENVALUES'
    DO I=1,IVEC
     WRITE(10,*)EIGEN(I)
!     WRITE(6,*)EIGEN(I)
     ENDDO
    DO I=1,IVEC
     READ(11,*)(C(I,J),J=1,IC)
     ENDDO
    WRITE(10,*)'EIGENVECTORS FOR IMPORTANT ONES'
    DO I=1,IMPTIVEC
     WRITE(10,*)(C(I,J),J=1,IC)
     ENDDO
! READ IMPTIVEC RECONSTRUCTED ROW VECTORS (FOR TESTS)
    DO I=1,IR
     READ(11,*)(ROW(I,J),J=1,IMPTIVEC)
     ENDDO
! READ IN THE WAVELENGTHS FOR EACH ROW OF THE ROW MATRIX
     READ(11,*)(WAV(I),I=1,IR)
!     WRITE(6,*)(WAV(I),I=1,IR)
! READ IN THE TIMES FOR THE EIGENVECTORS
     READ(11,*)(TIME(I),I=1,IC)
!     WRITE(6,*)(TIME(I),I=1,IC)
     READ(11,3)(TITLE(I),I=1,80)
     WRITE(6,3)(TITLE(I),I=1,80)
  3  FORMAT(80A1)
    CLOSE(11)
! GENERATE DATA' MATRIX JUST TO BE SURE ALL IS WELL
    CALL MATMULT(IR,IC,IR,ROW,C,DD)
    DO I=1,IR
     DO J=1,IR
      DIFF=DD(I,J)-DPRIME(I,J)
      IF(DIFF.GT.1D-5.OR.DIFF.LT.-1D-5) GO TO 60
     ENDDO
```

```
      ENDDO
      GO TO 65
  60  WRITE(6,*)"ERROR ON DATA READ"
      WRITE(6,*)DD(I,J),DPRIME(I,J),DIFF
      GO TO 1001
!  FILL OUT EIGENVALUE DIAGONAL MATRIX (IVEC x IVEC)
  65  DO I=1,IVEC
      DO J=1,IVEC
       ALAM(I,J)=0.0D0
       ALAMINV(I,J)=0.0D0
       IF(I.EQ.J)ALAM(I,J)=EIGEN(I)
       IF(I.EQ.J)ALAMINV(I,J)=1.0D0/EIGEN(I)
       ENDDO
      ENDDO
      WRITE(10,*)'IMPORTANT EIGENVECTOR LAMBDA ARRAY'
      DO I=1,IMPTIVEC
      WRITE(10,13)(ALAM(I,J),J=1,IMPTIVEC)
!       WRITE(6,13)(ALAMINV(I,J),J=1,IVEC)
  13   FORMAT(1X,10(F8.3,1X))
      ENDDO
! GENERATE UNITY, UNIQUENESS, AND A SELF-ROW VECTOR
      DO I=1,IR
       UNITY(I)=1.0D0
       UNIQUE(I)=0.0D0
       SELF(I)=ROW(I,1)
      ENDDO
!  TESTVECTOR TT = (ALAM)-1 * ROW * TESTVECTOR
      CALL TRANSPOS(IR,IMPTIVEC,ROW,ROWT)
      CALL MATMULT(IMPTIVEC,IMPTIVEC,IC,ALAMINV,ROWT,TT)
!
! FIRST, TEST FIRST ROW VECTOR FROM THE RECONSTRUCTED [R] OF [R][C]
      WRITE(6,*)"DATA (ROW 1) TEST = SELF TEST"
      WRITE(10,*)"DATA (ROW 1) TEST = SELF TEST"
      J=1
      DO I=1,IR
       DATA(I)=ROW(I,J)
      ENDDO
! TL IS THE TRANSFORMATION FOR THE FIRST COLUMN OF THE ROW MATRIX
      CALL MATMULT(IMPTIVEC,IR,1,TT,DATA,TL)
! TEST = [ROW]*TL
      CALL MATMULT(IR,IMPTIVEC,1,ROW,TL,TEST)
      WRITE(6,23) (ROW(I,J),I=1,IR)
      WRITE(6,*)'FIRST COLUMN OF THE RECONSTRUCTED ROW MATRIX:'
      WRITE(6,23) (TEST(I),I=1,IR)
      WRITE(10,23) (ROW(I,J),I=1,IR)
      WRITE(10,*)'FIRST COLUMN OF THE RECONSTRUCTED ROW MATRIX:'
      WRITE(10,23) (TEST(I),I=1,IR)
  23  FORMAT(11X,10(F5.2,1X))
  300 CONTINUE
! UNITY
```

Appendix B   Program to Test Vectors from PCA Version

```fortran
      CALL MATMULT(IMPTIVEC,IR,1,TT,UNITY,TL)
      CALL MATMULT(IR,IMPTIVEC,1,ROW,TL,TEST)
      DIFF=0.0D0
      DO J=1,IR
       DIFF=DIFF+(UNITY(J)-TEST(J))**2
      ENDDO
      WRITE(6,21)DIFF
      WRITE(10,21)DIFF
 21  FORMAT(1X,"UNITY VECTOR: (ALL ONES)            SSE = ",F6.4)
! MAKE UNITY, SELF AND UNIQUENESS CHECKS
! SELF
      DO L=1,IMPTIVEC
       DO I=1,IR
        SELF(I)=ROW(I,L)
       ENDDO
       CALL MATMULT(IMPTIVEC,IR,1,TT,SELF,TL)
       CALL MATMULT(IR,IMPTIVEC,1,ROW,TL,TEST)
       DIFF=0.0D0
       DO J=1,IR
        DIFF=DIFF+(SELF(J)-TEST(J))**2
       ENDDO
       WRITE(6,29)L,DIFF
       WRITE(10,29)L,DIFF
 29   FORMAT(1X,"SELF VECTOR: ROW ",I2,"              SSE = ",F6.4)
      ENDDO
! UNIQUENESS (CYCLE OVER ALL EIGENVECTORS)
      DO I=1,IC
       UNIQUE(I)=1.0D0
       K=I-1
       IF(I.GT.1)UNIQUE(K)=0.0D0
       CALL MATMULT(IMPTIVEC,IR,1,TT,UNIQUE,TL)
       CALL MATMULT(IR,IMPTIVEC,1,ROW,TL,TEST)
       DIFF=0.0D0
       DO J=1,IC
        DIFF=DIFF+(UNIQUE(J)-TEST(J))**2
       ENDDO
       WRITE(6,22)I,DIFF
       WRITE(10,22)I,DIFF
 22   FORMAT(1X,I3,"TH UNIQUE VECTOR              SSE =",F6.4)
!       WRITE(6,23) (TEST(J),J=1,IR)
!       WRITE(10,22) I,DIFF
!       WRITE(10,23) (TEST(J),J=1,IR)
      ENDDO
!
! RETRIEVE SPECTROSCOPY INFORMTION >>  INFO.DAT CONTAINS
! A TITLE
! TEST VECTORS 1 ... IMPTIVEC AT IR WAVELENGTHS
! INSTRUCTIONS (3I1) ILSQ, NCOM, ICONTINUE
! THE BALANCE OF THE INFORMATION HAS COME FROM TESTVEC.DAT
      OPEN(8,FILE='INFO.DAT',STATUS='UNKNOWN')
```

```
      READ(8,201)(TITLE(I),I=1,80)
 201  FORMAT(80A1)
      WRITE(6,*)
      WRITE(10,*)
      WRITE(6,201)(TITLE(I),I=1,80)
      WRITE(10,201)(TITLE(I),I=1,80)
!  READ IN IMPTIVEC SPECTRA (GUESSES), AT IR WAVELENGTHS
      WRITE(6,223)(WAV(I),I=1,IR)
 223  FORMAT(11X,10(F4.0,2X))
      DO J=1,IMPTIVEC
      READ(8,*)(A(J,I),I=1,IR)
      ENDDO
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
! IF ILSQ = 1 PERFORM FURTHER ANALYSIS FOR THE MODEL CODED HERE
! IF NCOM = NUMBER OF COMPONENTS (DEFAULT = IMPTIVEC)
! IF ICONTINUE > 0 DO 2^(ICONTINUE) CYCLES
! IF IREAD =1, READ OLD PARAMETERS AND BEGIN THERE; WRITE NEW AT END
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
      READ(8,288)ILSQ,NCOM,ICONTINUE,IREAD
 288  FORMAT(I1,I1,I1,I1)
      IF(NCOM.EQ.0)NCOM=IMPTIVEC
      ICY=2**(ICONTINUE)
!! TEST THESE ROW MATRICES  - BIG LOOP
      DO 279 LL=1,IMPTIVEC
      DO I=1,IR
       AA(I)=A(LL,I)
      ENDDO
      CALL MATMULT(IMPTIVEC,IR,1,TT,AA,TL)
      CALL MATMULT(IR,IMPTIVEC,1,ROW,TL,TEST)
! WRITE COMPARISON
      DIFF=0.0D0
      DO J=1,IR
       DIFF=DIFF+(AA(J)-TEST(J))**2
      ENDDO
      WRITE(6,33)LL,DIFF
      WRITE(6,26) (ROW(I,LL),I=1,IR)
      WRITE(6,24) (AA(I),I=1,IR)
      WRITE(6,25) (TEST(I),I=1,IR)
  33  FORMAT(1X,I3,'TH SPECTRAL VECTOR              SSE= ',F7.5)
      WRITE(10,33)LL,DIFF
      WRITE(10,26) (ROW(I,LL),I=1,IR)
      WRITE(10,24) (AA(I),I=1,IR)
      WRITE(10,25) (TEST(J),J=1,IR)
  26  FORMAT(1X,'ROW   ',15(F5.3,1X))
  24  FORMAT(1X,'GUESS ',15(F5.3,1X))
  25  FORMAT(1X,'TEST  ',15(F5.3,1X))
! NEW IMPLIED ROW MATRIX IS AA
! SAVE THE TRANSFORM (XFORM), EACH HAS DIMENSION IMPTIVEC x 1
      DO KK=1,IMPTIVEC
       XFORM(LL,KK)=TL(KK)
```

```
       ENDDO
       WRITE(10,278)(XFORM(LL,KK),KK=1,IMPTIVEC)
! END LOOP OVER LL IMPTIVEC VECTORS
 279   CONTINUE
 278   FORMAT(1X,6(F12.5,1X))
     DO LL=1,IMPTIVEC
      DO KK=1,IMPTIVEC
       TINV(LL,KK)=XFORM(LL,KK)
      ENDDO
     ENDDO
     CALL MINV(TINV,IMPTIVEC,200,SCRATCH,DET,1.0D-4,1,1)
!     WRITE(6,*)'INVERSE TRANSFORM MATRIX (IMPTIVEC x IMPTIVEC)'
     WRITE(10,*)'INVERSE TRANSFORM MATRIX (IMPTIVEC x IMPTIVEC)'
     DO LL=1,IMPTIVEC
!     WRITE(6,278)(TINV(LL,KK),KK=1,IMPTIVEC)
      WRITE(10,278)(TINV(LL,KK),KK=1,IMPTIVEC)
     ENDDO
! AND GENERATE ROTATED EIGENVECTORS
     CALL MATMULT(IMPTIVEC,IMPTIVEC,IC,TINV,C,CBAR)
     WRITE(6,*)'OLD EIGENVECTORS'
     WRITE(10,*)'OLD EIGENVECTORS'
     DO I=1,IMPTIVEC
      WRITE(6,282)I,(C(I,J),J=1,IC)
      WRITE(10,282)I,(C(I,J),J=1,IC)
 282   FORMAT(1X,I1,':',15(F5.2))
     ENDDO
     WRITE(6,*)'ROTATED EIGENVECTORS'
     WRITE(10,*)'ROTATED EIGENVECTORS'
     DO I=1,IMPTIVEC
      WRITE(6,282)I,(CBAR(I,J),J=1,IC)
      WRITE(10,282)I,(CBAR(I,J),J=1,IC)
     ENDDO
     WRITE(6,*)'TIMES: '
     WRITE(10,*)'TIMES: '
     WRITE(6,283)(TIME(I),I=1,IC)
     WRITE(10,283)(TIME(I),I=1,IC)
 283   FORMAT(1X,10(F7.0))
     IF(ILSQ.EQ.0)GO TO 1001
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
! A TO B TO C ... FITTING ROUTINE; UP TO NINE IN SEQUENCE
! FIND THE RATE CONSTANTS AND THE TRANSFORMATION MATRIX THAT FITS THE
DATA
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
     WRITE(6,*)'PERFORMING NON-LINEAR LEAST-SQUARES ON SEQENTIAL MODEL'
! ESTIMATE TAU ELEMENTS OF TRANSFORMATION MATRIX FROM TEST VECTORS
! NUMBER OF VARIABLES = IMPTIVEC^2 + (IMPTIVEC-1)
     K=1
     DO I=1,IMPTIVEC
      DO J=1,IMPTIVEC
       V(K)=TINV(I,J)
```

```
       K=K+1
      ENDDO
      ENDDO
      NK=NCOM-1
      DO I=1,NK
! DO NOT LET INITIAL GUESSES OF RATEK'S BE EQUAL
      V(K)=1.0D-2+(K*3.0D-3)
      K=K+1
      ENDDO
! WILD GUESS AT RATE CONSTANTS
      V(37)=0.0221
      V(38)=0.03
      V(39)=0.0455
      V(40)=0.1420
      V(41)=0.00000000001
!
      NVAR=K-1
      WRITE(6,287)NVAR,NCOM,ICY
 287  FORMAT(1X,I3,' VARIABLES   ',I3,' COMPONENTS   ',I3,' CYCLES')
! READ OLD PARAMETERS IF IREAD =1
      IF(IREAD.EQ.1)READ(8,992)F
      IF(IREAD.EQ.1)READ(8,993)(V(I),I=1,NVAR)
! SET DELV FOR DIFFERENTIALS ON ANY VARIABLE
      DELV=1.0D-10
! PLACE VARIABLES INTO TAU AND RATEK ARRAYS
      DO I=1,NVAR
       CALL VARFIG(I,NCOM,TAU,RATEK,V)
      ENDDO
!     WRITE(10,278)(RATEK(I),I=1,NK)
! APPROXIMATE SIGMAS FOR ABSORBANCES
      DO I=1,IR
       DO J=1,IC
        SIG(I,J)=4.0D-3
       ENDDO
      ENDDO
      NCY=0
! ENTER ITERATION ROUTINE....................................................
      FUDGE=0.1D+003
      IF(IREAD.EQ.1)FUDGE=F
      CHISQ=1.0D+150
      IFLAG=0
 285  CHIOLD=CHISQ
      CHISQ=0.0D0
      NCY=NCY+1
! LOOP OVER ALL VARIABLES
      DO NV=1,NVAR
! CALC Q AND XI^2; LOOP OVER IR ROWS(LAMBDAS) AND IC COLUMNS(TIMES)
      DO I=1,IR
       DO J=1,IC
! THE SECULAR EQUATIONS ARE CODED HERE
```

```fortran
! CALUCLATE CONCENTRATIONS OF THE SPECIES (CN(1) .. CN(NCOM))
      CALL CONCEN(NCOM,J,RATEK,TIME,CN,CONC)
!      IF(J.EQ.6)WRITE(6,278)(CONC(K,J),K=1,NCOM)
! NOW COMPUTE THE ZETA
      CALL MODEL(I,NCOM,CN,TAU,ZETA,ROW,TERM)
      ACALC(I,J)=TERM
      Q(I,J)=D(I,J)-ACALC(I,J)
! NORMALIZE THE DATA
      CHISQ=CHISQ+(Q(I,J)/SIG(I,J))**2
!      WRITE(6,*)CHISQ
      ENDDO
      ENDDO
      ENDDO
      WRITE(6,293)NCY,CHISQ,CHIOLD,FUDGE
293   FORMAT(1X,'CY#',I3,'CHISQ =',E14.7,' CHIOLD =',E14.7,'  FUDGE =',E14.7)
      WRITE(10,293)NCY,CHISQ,CHIOLD,FUDGE
      IF(NCY.EQ.1)GOTO 299        ! FIRST CYCLE
! DECISION POINT: IF CHISQ<CHIOLD, DECREASE FUDGE, ACCEPT SHIFTS AND ITERATE
!          IF CHISQ>CHIOLD, INCREASE FUDGE, REJECT SHIFTS AND CYCLE
!      IFLAG=1 FROM PREV CYCLE WHERE XI^2 INCREASED
! STOP AFTER NCY=30 IF CHISQ<CHIOLD OR IF CHISQ < 1D-10
      IF(ICY.EQ.1)GOTO 1001
      IF(IFLAG.EQ.0.AND.NCY.GE.ICY)GOTO 415
      IF(CHISQ.LT.1.0D-010)GOTO 415
      IF(IFLAG.EQ.1)GOTO 299
      IF(CHISQ.GT.CHIOLD)GOTO 297
      FUDGE=FUDGE/1.25D0
      GOTO 299
297  FUDGE=FUDGE*15.0D0
      IFLAG=1
      DO NV=1,NVAR
       V(NV)=V(NV)-DELA(NV)
       CALL VARFIG(NV,NCOM,TAU,RATEK,V)
      ENDDO
      GOTO 285
! INCREMENT A VARIABLE AND SET THE TAU AND RATEK VALUES
299  IFLAG=0
! ENTER LEAST-SQUARES
      DO NV=1,NVAR
       V(NV)=V(NV)+DELV
       CALL VARFIG(NV,NCOM,TAU,RATEK,V)
! CALCULATE THE DERIVATIVE DY/DVAR
      DXIDV(NV)=0.0D0
      DO I=1,IR
      DO J=1,IC
       CALL CONCEN(NCOM,J,RATEK,TIME,CN,CONC)
       CALL MODEL(I,NCOM,CN,TAU,ZETA,ROW,TERM)
       ADEL(I,J)=TERM
       DADVAR(I,J,NV)=((ACALC(I,J)-ADEL(I,J))/DELV)
       DXIDV(NV)=DXIDV(NV)+Q(I,J)*(1.0D0/(SIG(I,J))**2)*DADVAR(I,J,NV)
```

```
      ENDDO
      ENDDO
! CALC DIFF OF XI WRT VARIABLE (A VECTOR DXIDV)
!     WRITE(6,*)DXIDV(NV)
      DXIDV(NV)=-2.0D0*DXIDV(NV)
      V(NV)=V(NV)-DELV
      CALL VARFIG(NV,NCOM,TAU,RATEK,V)
      ENDDO
! CALC APPROX SECOND DERIV DD XI WRT VAR A & VAR B (A MATRIX D2XIDADB)
! THIS IS APPROXIMATELY THE HESSIAN OR CURVATURE MATRIX
      DO NV=1,NVAR
      DO NVB=1,NVAR
      D2XIDADB(NV,NVB)=0.0D0
      DO I=1,IR
       DO J=1,IC
        ARG=(1.0D0/(SIG(I,J))**2)*DADVAR(I,J,NV)*DADVAR(I,J,NVB)
        D2XIDADB(NV,NVB)=D2XIDADB(NV,NVB)+ARG
       ENDDO
      ENDDO
      D2XIDADB(NV,NVB)=2.0D0*D2XIDADB(NV,NVB)
      ENDDO
      ENDDO
! AND SET UP LEVINSON-MARQUARDT FUDGE METHOD
      DO I=1,NVAR
      DO J=1,NVAR
      IF(I.NE.J)GOTO 295
      D2XIDADB(I,J)=D2XIDADB(I,J)*(1.0D0+FUDGE)
 295  ENDDO
      ENDDO
! SET UP MATRICES FOR GUASSIAN-JORDAN ELIMINATION SOLUTION OF SHIFTS
! GAUSSJ RETURNS THE SHIFTS AS VECTOR IN DXIDV
      CALL GAUSSJ(D2XIDADB,NVAR,100,DXIDV,1,100)
! STORE SHIFT IN DELA; RETURNED IN DXIDV
      DO I=1,NVAR
      DELA(I)=DXIDV(I)
      ENDDO
! UPDATE THE VARIABLES; ******************APPLY SHIFTS******************
!     WRITE(6,*)'VARIABLES   SHIFTS :'
!     WRITE(10,*)'VARIABLES   SHIFTS :'
      DO I=1,NVAR
!       WRITE(6,303)I,V(I),DELA(I)
!       WRITE(10,303)I,V(I),DELA(I)
 303  FORMAT(1X,'#',I2,' VAR=',F9.5,' SHIFT=',F9.5)
      V(I)=V(I)+DELA(I)
! DAMP KINETIC RATEK'S
      IF(I.LE.16)GOTO 304
      V(I)=V(I)-DELA(I)+0.60D0*(DELA(I))
 304  CALL VARFIG(I,NCOM,TAU,RATEK,V)
      ENDDO
! ESTIMATE RESTRAINTS BASED ON ALOW,AHI
```

```
      DO K=1,IMPTIVEC
       BLO(K)=1.0D+25
       BHI(K)=1.0D-25
      ENDDO
      DO I=1,IR
       DO K=1,IMPTIVEC
       SP=0.0D0
        DO L=1,IMPTIVEC
         SP=SP+TAU(K,L)*ROW(I,L)
        ENDDO
       IF(SP.LT.BLO(K))BLO(K)=SP
       IF(SP.GT.BHI(K))BHI(K)=SP
       ENDDO
      ENDDO
      DO I=1,IMPTIVEC
       DELOBS=AHI-ALOW
       DELCALC=BHI(I)-BLO(I)
       SCALE(I)=DELCALC/DELOBS
       WRITE(10,387)I,BLO(I),BHI(I),SCALE(I)
 387  FORMAT(1X,'SPECTRUM ',I3,' LOW ',F8.3,' TO ',F8.3,';   SCALE=',F8.3)
      ENDDO
! APPLY RESTRAINTS AFTER THE SHIFTS *IF OUT OF RANGE*
      DO L=1,IMPTIVEC
       IF(SCALE(L).LE.1.3D0)GOTO 391
       SCALE(L)=(1.0D0-NCY/ICY)+((NCY/ICY)*SCALE(L))
       DO K=1,IMPTIVEC
        TAU(K,L)=TAU(K,L)/SCALE(L)
       ENDDO
 391  ENDDO
! GO BACK AND ITERATE
       GOTO 285
! END LOOP OVER ALL VARIABLES
! END OF BIG VARIABLE ITERATION LOOP
! NV VARIABLES, NK RATE CONSTANTS
 415 NT=NVAR-NK
     NT1=NT+1
     WRITE(10,422)
     WRITE(10,424)(V(I),I=1,NT)
     WRITE(10,423)
     WRITE(10,424)(V(I),I=NT1,NVAR)
     WRITE(6,422)
     WRITE(6,424)(V(I),I=1,NT)
     WRITE(6,423)
     WRITE(6,424)(V(I),I=NT1,NVAR)
 422 FORMAT(1X,'VARIABLES:    TRANSFORM')
 423 FORMAT(1X,'VARIABLES:    RATE CONSTANTS')
 424 FORMAT(1X,4(E15.5,1X))
! SAVE THE CURRENT VARIABLE VALUES
     IF(IREAD.EQ.0)GOTO 994
! BACKSPACE THE POINTER
```

```
       NR=0
       NLINES=(NVAR/3)
       FLINES=(NVAR/3.0D0)
       RESID=FLINES-NLINES
       IF(RESID.NE.0.0D0)NR=1
       NLINES=NLINES+1+NR
       DO I=1,NLINES
        BACKSPACE(8)
       ENDDO
 994  WRITE(8,992)FUDGE
       WRITE(8,993)(V(I),I=1,NVAR)
 992  FORMAT(E15.6)
 993  FORMAT(3E15.6)
       WRITE(10,*)'DATA MATRIX FIT - CALCULATED'
       DO I=1,IR
        WRITE(10,11)(ACALC(I,J),J=1,IC)
       ENDDO
       SSE=0.0D0
       DO I=1,IR
        DO J=1,IC
!       Q(I,J)=Q(I,J)*(SIG(I,J)**2)
         SSE=SSE+Q(I,J)**2
        ENDDO
       ENDDO
       WRITE(10,419)SSE
 419  FORMAT(1X,'DIFFERENCE MATRIX   SSE=',E12.6)
       DO I=1,IR
        WRITE(10,428)(Q(I,J),J=1,IC)
       ENDDO
 428  FORMAT(1X,10(F6.4,1X))
! CALCULATE THE ROTATED SPECTRA
 999  CONTINUE
       WRITE(6,*)(TITLE(I),I=1,80)
       WRITE(10,*)(TITLE(I),I=1,80)
       DO I=1,NCOM
        WRITE(10,861)(CONC(I,J),J=1,IC)
 861  FORMAT(1X,10(F6.4,1X))
       ENDDO
! CALCULATE THE SPECTRA (ROTATED ROW VECTORS)
       DO I=1,IR
        DO K=1,IMPTIVEC
        SP=0.0D0
         DO L=1,IMPTIVEC
         SP=SP+TAU(K,L)*ROW(I,L)
         ENDDO
         G(I,K)=SP
        ENDDO
       ENDDO
       DO I=1,IR
        WRITE(10,865)WAV(I),(G(I,K),K=1,IMPTIVEC)
```

```
      ENDDO
 865  FORMAT(1X,F4.0,1X,9(F7.4,1X))
1001  WRITE(6,*)"INSPECT OUTPUT ON FILE TESTVEC.OUT"
      CLOSE(8)
      CLOSE(10)
      STOP
      END
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
!
!  SUBROUTINES
!
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
!  COMPUTE THE TRANSPOSE OF A RECTANGULAR MATRIX
      SUBROUTINE TRANSPOS(II,JJ,A,B)
! II ROWS AND JJ COLUMNS OF ORIGINAL MATRIX: JJ ROWS, II COLUMNS TRANSPOSED
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(100,100),B(100,100)
!     WRITE(6,*)"TRANSPOSE",II,JJ
      DO I=1,II
      DO J=1,JJ
       B(J,I)=A(I,J)
!     WRITE(10,*)B(J,I)
      ENDDO
      ENDDO
      RETURN
      END
!
!
!  COMPUTE THE MATRIX PRODUCT OF AN IxK AND KxJ ARRAYS TO PRODUCE A
!  THE GENERAL PRODUCT MATRIX OF DIMENSION IxJ
      SUBROUTINE MATMULT(II,KK,JJ,A,B,AB)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(100,100),B(100,100),AB(100,100)
!  BY THE ROWxCOLUMN METHOD; AN II BY KK MATRIX IS MULTIPLIED BY A
!  KK BY JJ MATRIX PRODUCING AN II BY JJ MATRIX
      DO I=1,II
      DO J=1,JJ
       SUM=0.0D0
       DO K=1,KK
        SUM=SUM+(A(I,K)*B(K,J))
!       WRITE(10,40)I,J,K,B(I,K),A(K,J),SUM
! 40  FORMAT(1X,3I5,1X,3(F12.4,1X))
       ENDDO
       AB(I,J)=SUM
      ENDDO
      ENDDO
      RETURN
      END
!
! MULTIPLY A VECTOR (B) BY A MATRIX (A) [DOT PRODUCT]
```

```
! COLUMNS OF VECTOR MUST EQUAL ROWS OF MATRIX (IR)
! OUTPUT VECTOR (C) HAS IR ROWS
    SUBROUTINE MATVEC(IR,IC,A,B,C)
    IMPLICIT REAL*8(A-H,O-Z)
    DIMENSION A(100,100),B(100),C(100)
    DO I=1,IC
     SUM=0.0D0
     DO J=1,IR
      SUM=SUM+(A(I,J)*B(J))
!      WRITE(10,30)I,J,A(I,J),B(J),SUM
! 30  FORMAT(1X,I5,I5,3(F12.5,1X))
     ENDDO
     C(I)=SUM
    ENDDO
    RETURN
    END
!
! MULTIPLY TWO VECOTRS (A) AND (B); (RxC)*(CxR) = (RxR)
! TO PRODUCE A MATRIX
    SUBROUTINE VECMULT(II,JJ,A,B,C)
    IMPLICIT REAL*8(A-H,O-Z)
    DIMENSION A(100),B(100),C(100,100)
    DO I=1,II
     DO J=1,II
      C(I,J)=A(I)*B(J)
!      WRITE(10,30)I,J,A(I),B(J),C(I,J)
! 30   FORMAT(1X,2I5,1X,3F12.5)
     ENDDO
    ENDDO
    RETURN
    END
!
!-------------------------------------------------------- ************
!                                    MINV
    SUBROUTINE MINV(AB,N,ND,SCRATCH,DET,EPS,M,MODE)
    IMPLICIT REAL*8(A-H,O-Z)
!
!    A subroutine that calculates the determinant and inverse of
!    a matrix, as well as solving systems of linear equations.
!    Martin J. McBride.  11/25/85.
!    General Electric CRD, Information System Operation.
!
    INTEGER N,ND,M,MODE,OUTER,ROW,COL,I,SCOL,SROW,PIVCNT
    DIMENSION AB(100,100),SCRATCH(500)
! Initialize scratch space, with 1 to N holding the diagonal of the identity
! matrix used to compute the inverse and N+1 to 2N holding the positions of
! the first N columns of the matrix (for use when pivot occurs).
    DO 5 I = 1,N
  5   SCRATCH(I) = 1.0
     COLNUM = 1.0
```

```fortran
      DO 6 I = N+1,2*N
        SCRATCH(I) = COLNUM
        COLNUM = COLNUM + 1.0
    6 CONTINUE
! Make left, square matrix an upper triangular matrix.
      DET = 0.0
      PIVCNT = 0
      DO 10 OUTER = 1,N-1
        IF (DABS(AB(OUTER,OUTER)) .LE. EPS) THEN
          CALL PIVOT(AB,N,ND,OUTER,SCRATCH,EPS)
          IF (AB(OUTER,OUTER) .EQ. 0.0) THEN
            WRITE(6,*)'***********************************'
            WRITE(6,*)'  MINV called with singular matrix.'
            WRITE(6,*)'***********************************'
            STOP
          ENDIF
          PIVCNT = PIVCNT + 1
        ENDIF
        DO 20 ROW = OUTER+1,N
          MULT = AB(ROW,OUTER)/AB(OUTER,OUTER)
          DO 30 COL = OUTER,N+M
   30       AB(ROW,COL) = AB(ROW,COL) - AB(OUTER,COL)*MULT
          DO 25 SCOL = 1,OUTER-1
   25       AB(ROW,SCOL) = AB(ROW,SCOL) - AB(OUTER,SCOL)*MULT
          AB(ROW,OUTER) = AB(ROW,OUTER) - SCRATCH(OUTER)*MULT
   20   CONTINUE
   10 CONTINUE
! Compute determinant.
      DET = AB(1,1)
      DO 40 I = 2,N
   40   DET = DET*AB(I,I)
      DET = (-1.0)**PIVCNT * DET
! Return if inverse is not to be found and there are no systems of equations
! to solve.
      IF (MODE .EQ. 0 .AND. M .EQ. 0) RETURN
! Place ones in diagonal of square matrix A.
      DO 80 ROW = 1,N
        DIV = AB(ROW,ROW)
        DO 90 COL = 1,N+M
          AB(ROW,COL) = AB(ROW,COL)/DIV
   90   CONTINUE
        SCRATCH(ROW) = SCRATCH(ROW)/DIV
   80 CONTINUE
! Reduce upper triangle to zeros to give matrix A = I.
      DO 50 OUTER = 2,N
        DO 60 ROW = OUTER-1,1,-1
          MULT = AB(ROW,OUTER)/AB(OUTER,OUTER)
          DO 70 COL = OUTER,N+M
   70       AB(ROW,COL) = AB(ROW,COL) - AB(OUTER,COL)*MULT
          DO 65 SCOL = 1,ROW-1
```

```fortran
 65       AB(ROW,SCOL) = AB(ROW,SCOL) - AB(OUTER,SCOL)*MULT
          SCRATCH(ROW) = SCRATCH(ROW) - AB(OUTER,ROW)*MULT
          DO 63 SCOL = ROW+1,OUTER-1
 63       AB(ROW,SCOL) = AB(ROW,SCOL) - AB(OUTER,SCOL)*MULT
          AB(ROW,OUTER) = AB(ROW,OUTER) - SCRATCH(OUTER)*MULT
 60    CONTINUE
 50 CONTINUE
! Move diagonals of inverse to matrix AB.
     DO 85 I = 1,N
 85    AB(I,I) = SCRATCH(I)
! If pivot was made, switch rows corresponding to the columns that were
! pivoted.
     IF (PIVCNT .EQ. 0) RETURN
     ROW = 1
     DO 95 I = 1,N-1
       SROW = INT(SCRATCH(ROW+N))
       IF (SROW .NE. ROW) THEN
         DO 92 COL = 1,N+M
           TEMP = AB(ROW,COL)
           AB(ROW,COL) = AB(SROW,COL)
           AB(SROW,COL) = TEMP
 92      CONTINUE
         TEMP = SCRATCH(ROW+N)
         SCRATCH(ROW+N) = SCRATCH(SROW+N)
         SCRATCH(SROW+N) = TEMP
       ELSE
         ROW = ROW + 1
       ENDIF
 95 CONTINUE
     RETURN
     END
!-------------------------------------------------------------
     SUBROUTINE PIVOT(AB,N,ND,OUTER,SCRATCH,EPS)
     IMPLICIT REAL*8(A-H,O-Z)
!
!    This subroutine switches two columns of a matrix to get
!      a nonzero entry in the diagonal.
!    Martin J. McBride.  12/04/85.
!    General Electric CRD, Information System Operation.
!
     INTEGER N,ND,COL,OUTER,I
     DIMENSION AB(100,100),SCRATCH(100)
! Get first column with non-zero element in row OUTER.
     COL = OUTER + 1
 10 IF (COL .GT. N) GO TO 90
     IF (ABS(AB(OUTER,COL)) .GT. EPS) GO TO 20
       COL = COL + 1
       GO TO 10
! Switch column OUTER with column COL, which has non-zero element in
! row OUTER.
```

```
   20 DO 30 I = 1,N
        TEMP = AB(I,OUTER)
        AB(I,OUTER) = AB(I,COL)
        AB(I,COL) = TEMP
   30 CONTINUE
      TEMP = SCRATCH(N+OUTER)
      SCRATCH(N+OUTER) = SCRATCH(N+COL)
      SCRATCH(N+COL) = TEMP
   90 CONTINUE
      RETURN
      END
!
      SUBROUTINE ALSQ(N,X,Y,SLOPE,ERSLOP,YINT,ERYINT,CORREL,SSE)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(100),Y(100)
      NT=N-2
      IF(NT.EQ.0)GO TO 80
      SUMX=0.0D0
      SUMY=0.0D0
      SUMXX=0.0D0
      SUMXY=0.0D0
      SUMYY=0.0D0
      SSE=0.0D0
      DO I=1,N
       SUMX=SUMX+X(I)
       SUMY=SUMY+Y(I)
       SUMXX=SUMXX+(X(I)*X(I))
       SUMYY=SUMYY+(Y(I)*Y(I))
       SUMXY=SUMXY+(X(I)*Y(I))
      ENDDO
      SLOPE=((N*SUMXY)-(SUMX*SUMY))/((N*SUMXX)-SUMX**2)
!    WRITE(6,*)SLOPE
      YINT=(SUMY/N)-(SLOPE*(SUMX/N))
      DO I=1,N
       SSE=SSE+((SLOPE*X(I))+YINT-Y(I))**2
      ENDDO
      DEL=(N*SUMXX)-(SUMX*SUMX)
      SIG2=(1.0D0/(N-2.0D0))*SSE
      ERSLOP=DSQRT((N*SIG2)/DEL)
      ERYINT=DSQRT(SIG2*SUMXX/DEL)
      CNUM=(N*SUMXY)-(SUMX*SUMY)
      TERM1=DSQRT((N*SUMXX)-SUMX**2)
      TERM2=DSQRT((N*SUMYY)-SUMY**2)
      CORREL=CNUM/(TERM1*TERM2)
!    WRITE(6,*)CORREL
      GO TO 90
   80  WRITE(6,82)
   82  FORMAT(1X,'INSUFFICIENT DATA FOR REGRESSION')
   90  RETURN
      END
```

```fortran
!
      SUBROUTINE VARFIG(L,NCOM,TAU,RATEK,V)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION TAU(10,10),RATEK(10),V(100)
! NUMBER OF VARIABLES IS NCOM^2 + (NCOM-1)
! AFTER DETERMINING WHAT VARIABLE "L" TRANSLATES INTO, IT CORRECTS ONLY
THIS
      NA=NCOM
      NB=NCOM-1
      IDIV=(NCOM**2)+1
      IF(L.GE.IDIV)GOTO 396
      IX=(L+NB)/NA
      IY=L+1-((NA*IX)-NB)
      GOTO 397
 396  IZ=L-(IDIV-1)
      RATEK(IZ)=V(L)
      GOTO 398
 397  TAU(IX,IY)=V(L)
 398  RETURN
      END
!
      SUBROUTINE CONCEN(NC,J,RATEK,TIME,CN,CONC)
! THIS ROUTINE FOR A=B=C=D (FOR 1ST 1ST 2ND ORDER, RESP) 7/1/00 EJV
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION RATEK(10),TIME(100),CN(10),CONC(10,100)
!     DIMENSION CNUM(10),CDEN(10)
! FIRST SPECIES
      CN(1)=DEXP(-RATEK(1)*TIME(J))
! SECOND SPECIES
      B=(DEXP(-RATEK(1)*TIME(J)))-(DEXP(-RATEK(2)*TIME(J)))
      CN(2)=B*(RATEK(1)/(RATEK(2)-RATEK(1)))
! THIRD SPECIES
      CALL RUNGE(J,CC,RATEK,TIME)
      CN(3)=CC
! AND ADD THE NCth SPECIES
      CAL=0.0D0
      DO I=1,3
       CAL=CAL+CN(I)
      ENDDO
      CN(4)=1.0D0-CAL
!
      DO I=1,NC
       CONC(I,J)=CN(I)
      ENDDO
      RETURN
      END
!
      SUBROUTINE RUNGE(J,CC,RATEK,TIME)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION RATEK(10),TIME(100)
```

```
!     DIMENSION DELC(100),DCDT(100)
      A1=(RATEK(1)*RATEK(2))/(RATEK(2)-RATEK(1))
! SPECIFY TIME INTERVAL (TINT)
      TINT=10.0D0
      IT=TIME(J)/TINT
      TIM=0.0D0
      CONC=0.0D0
      DO I=1,IT
! GENERATE THE FOUR RUNGE-KUTTA TERMS
      CALL KUTTA(TIM,CONC,A1,TINT,RATEK,A)
      RK1=A
      TH=TIM+TINT/2.0D0
      CH=CONC+A/2.0D0
      CALL KUTTA(TH,CH,A1,TINT,RATEK,B)
      RK2=B
      CI=CONC+B/2.0D0
      CALL KUTTA(TH,CI,A1,TINT,RATEK,C)
      RK3=C
      TI=TIM+TINT
      CJ=CONC+C
      CALL KUTTA(TI,CJ,A1,TINT,RATEK,D)
      RK4=D
      DELC=RK1+(RK2*2.0D0)+(RK3*2.0D0)+RK4
      CONC=CONC+DELC
      TIM=TIM+TINT
      ENDDO
      CC=CONC
      RETURN
      END
!
      SUBROUTINE KUTTA(T,C,A1,TINT,RATEK,A)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION RATEK(10)
      A=(A1*DEXP(-RATEK(1)*T)-A1*DEXP(-RATEK(2)*T)-RATEK(3)*(C**2))*TINT
      RETURN
      END
!
      SUBROUTINE MODEL(I,NCOM,CN,TAU,ZETA,ROW,TERM)
! THIS ROUTINE MADE GENERAL FOR UP TO 9 NCOM COMPONENTS 6/24/00 EJV
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION CN(10),TAU(10,10),ZETA(10,10),ROW(100,100)
      DO L=1,NCOM
      DO K=1,NCOM
      ZETA(K,L)=TAU(L,K)*CN(L)
      ENDDO
      ENDDO
! ACCUMULATE THE TERMS IN ABSORBANCE
      TERM=0.0D0
      DO L=1,NCOM
      DO K=1,NCOM
```

```fortran
        TERM=TERM+(ROW(I,K)*ZETA(K,L))
       ENDDO
      ENDDO
      RETURN
      END
!
      SUBROUTINE GAUSSJ(A,N,NP,B,M,MP)
! THIS ROUTINE SOLVES A x = B BY (AT.A).x=(AT.B)  (AT=Atranspose)
! IT TAKES MATRIX A(N,N) STORED IN AN ARRAY OF DIMENSIONS NPxNP
! B IS AN INPUT MATRIX NxM CONTAINING m RIGHT-SIDE VECTORS, STORED IN AN
! ARRAY OF DIMENSIONS NPxMP.  ON OUTPUT, A IS REPLACED BY ITS MATRIX
! INVERSE, AND B IS REPLACED BY THE CORRESPONDING SET OF SOLUTION VECTORS
      IMPLICIT REAL*8(A-H,O-Z)
!     PARAMETER (NMAX=50)
      DIMENSION A(100,100),B(100,100),IPIV(50),INDXR(50),INDXC(50)
      DO 11 J=1,N
      IPIV(J)=0.0D0
 11   CONTINUE
      DO 22 I=1,N
      BIG=0.0D0
      DO 13 J=1,N
       IF(IPIV(J).NE.1)THEN
       DO 12 K=1,N
        IF(IPIV(K).EQ.0)THEN
         IF(DABS(A(J,K)).GE.BIG)THEN
          BIG=DABS(A(J,K))
          IROW=J
          ICOL=K
         ENDIF
        ELSE IF (IPIV(K).GT.1) THEN
         PAUSE 'SINGULAR MATRIX'
        ENDIF
 12    CONTINUE
       ENDIF
 13   CONTINUE
      IPIV(ICOL)=IPIV(ICOL)+1
      IF(IROW.NE.ICOL) THEN
      DO 14 L=1,N
       DUM=A(IROW,L)
       A(IROW,L)=A(ICOL,L)
       A(ICOL,L)=DUM
 14   CONTINUE
      DO 15 L=1,M
       DUM=B(IROW,L)
       B(IROW,L)=B(ICOL,L)
       B(ICOL,L)=DUM
 15   CONTINUE
      ENDIF
      INDXR(I)=IROW
      INDXC(I)=ICOL
```

```fortran
      IF(A(ICOL,ICOL).EQ.0.0D0) PAUSE 'SINGULAR MATRIX'
      PIVINV=1.0D0/A(ICOL,ICOL)
      A(ICOL,ICOL)=1.0D0
      DO 16,L=1,N
       A(ICOL,L)=A(ICOL,L)*PIVINV
 16  CONTINUE
      DO 17 L=1,M
       B(ICOL,L)=B(ICOL,L)*PIVINV
 17  CONTINUE
      DO 21 LL=1,N
       IF(LL.NE.ICOL)THEN
        DUM=A(LL,ICOL)
        A(LL,ICOL)=0.0D0
        DO 18 L=1,N
         A(LL,L)=A(LL,L)-A(ICOL,L)*DUM
 18     CONTINUE
        DO 19 L=1,M
         B(LL,L)=B(LL,L)-B(ICOL,L)*DUM
 19     CONTINUE
       ENDIF
 21  CONTINUE
 22  CONTINUE
      DO 24 L=N,1,-1
       IF(INDXR(L).NE.INDXC(L))THEN
       DO 23 K=1,N
        DUM=A(K,INDXR(L))
        A(K,INDXR(L))=A(K,INDXC(L))
        A(K,INDXC(L))=DUM
 23     CONTINUE
       ENDIF
 24  CONTINUE
      RETURN
      END
!
```

Appendix C
Program Directions

First Order Kinetics Experiments

Global analysis. ....Version 1.1 EJV 08/09/2000

Principal component analysis (PCA) method - HP8453 Array Detector Data

Obsrve the following data analysis scheme. The FORTRAN programs are on chelab10 under C:/LF90/CR/. The programs are preparation for principal component analysis (PREPPCA), principal component analysis (PCA), and vector testing and least-squares (TESTVEC).

Scheme: *activities*, **PROGRAMS**, files

	HP8453 - kinetics run	
	↓	
	transfer data as .dif *files to diskette*	
	↓	
PREPPCA		
↓	↓	↓
preppca.out	hptrial.dat	info.out
	inspect and rename hpdata.dat	*modify and rename* info.dat
	↓	
PCA		
↓	↓	
pca.out	testvec.out	
inspect	*inspect and rename* testvec.dat	
	↓	↓
TESTVEC		
↓	↓	
testvec.out		
inspect		

Detailed instructions.

Activity.

HP8453 Diode Array Spectometer. Kinetic Run.

1. Set up a kinetics run. Use the jacketted cell, a thermostated water bath with recirculating pump. Give the kinetics run datafile an appropriate name.

2. For a 25 °C run, use a 25-s 'start' time, and collect spectra every 60 s thereafter for a period of 3,600 s. Adjust this for higher or lower temperatures.

3. Combine thermal-equilibrated reagents at 0 time and initiate the kinetics run; mix!; transfer to the cell within 25 s. Sit back and collect data. Whole spectra are stored in the kinetics run file.

Data processing and transfer.

4. Selecting the individual spectra with the mouse (right click on spectra), save the spectra to be analyzed as .dif files to diskette. Note the times of the spectra. Each file should be saved as a filename that makes sense with regard to the time, like A85.dif for the file containing the data from the 85-s spectrum.

5. After selecting and saving as .dif files all the spectra of interest, place them in C:/LF90/CR/ on chelab10 (MSDOS prompt).

6. Run PREPPCA (invoke PREPPCA) to prepare the data for principal component analysis. In this program, you will be asked to:

a) Enter a range of wavelengths (in nm) to be analyzed (like 400, 700 [return])

b) Enter the uniform interval at which the spectra are to be tabulated (like 10 [return])

c) Enter the name of the .dif files in order of the times collected (like A85.dif [return]) followed by the time (in seconds) (like 85. [return]); and repeat this until all of the data have been entered. Then enter STOP [return]. If you make an error, execute <control>C, then rerun the program.

d) Enter a name for the data file (like Cr+6 to Cr+3, temperature, date, name, class [return]).

7. PREPPCA runs and outputs three files: hptrial.dat, preppca.out, and info.out.

Inspect the hptrial.dat file to see that it contains:

a) The data matrix preceded by the number of rows (wavelengths) and columns (times).

b) The wavelengths and then the times. Inspect these carefully to be sure they are correct.

c) The title of the kinetics run.

If all is well, *change the name of this file to* hpdata.dat. This will be an input file to PCA (principal component analysis). The file preppca.out contains similar information, and can be printed out if desired.

8. The file info.out contains representations of the first and last spectra which will be useful for vector testing later on. In fact, for a two-component system, the first spectra should be the Cr+6 spectrum, the second should be the Cr+3 spectrum. The last is approximated by the t = large spectrum collected; the Cr+6 spectrum is estimated from the first spectrum back extrapolated to t = 0.

Principal component analysis.

9. There is no program control for principal component analysis. Be sure that its input data are present in file hpdata.dat. Execute the program by invoking PCA.

10. PCA outputs two files: pca.out and testvec.out. The file pca.out can be inspected or printed out (partially, since it is possibly a large file) to answer the following questions:

a) How many factors are needed to explain the variance in the kinetics data?

b) How large are the eigenvalues, and how many are there before their magnitude vanishes?

c) Do the row vectors resemble the spectra of the components?

d) Do the column vectors resemble the concentration dependence of the components over time?

If the data can be explained with two components, then proceed to test spectral vectors and resolve the kinetics information.

Vector testing and least squares analysis.
11. Examine the info.out file. At the end of the file, control information for TESTVEC6 is required. It is contained in columns 1 - 5 on the line immediately after the second test vector.
These are ILSQ, NCOM,ICONT,IREAD,IFINISH (in 5I1 format; see below).
Recommended values at the start of a run are: 00000
Rename the file to info.dat.
ILSQ = 0 do not perform least squares; = 1 perform least squares.
NCOM = number of components; default (0) is the number of important vectors (or 2).
ICONT = run $2^{\wedge}(NCOM)$ cycles of least squares (if ILSQ = 1); default NCOM = 0 (i.e., 1 cycle).
IREAD = 0 do not read previous info.dat file results; = 1 read previous info.dat file results and begin least squares calculation from there, and write over old info.dat file after cycling.
IFINISH = 0 do not output spectral information at a particular wavelength; = 1 prompt at end of the run for a wavelength (λmax) at which to output time vs. absorbance data.
12. Execute TESTVEC6 (using 00000). This program evaluates the test vectors contained on info.dat file. It output is in one file: testvec.out.
13. Examine the file testvec.out. Answer the following questions:
a) Are the two test vectors likely to be real spectral vectors? (What are the sum-of-square-errors for the test and least squares trial?)
b) Do the transforms of the column vectors look like improved concentration vs. time data?
14. Now, fit the transformation matrix elements and a single rate constant by the nonlinear least squares method. This is done by reinvoking TESTVEC6 with the info.dat command of 10n10 (where n = $2^{\wedge}$n cycles; 10410 will run 16 cycles and save the results). Rerun until converged.
15. Examine the file testvec.out. Answer the following additional questions:
a) What rate constant accounts for the data?
b) How well does the kinetics model reproduce the spectral data? Are the residuals small?
16. Now, end the process by outputing the spectal information at the λmax (say, 440nm). This is done by reinvoking TESTVEC6 with the info.dat command of 10111. A prompt at the end of the program will inquire for a wavelength, and the output will be on file testvec.out.   This can be clipped out and plotted with the other spectral and time data.

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14. ABSTRACT

Contamination of groundwater, surface water, and soil by explosives has occurred at military sites throughout the world as a result of manufacture of explosive compounds, assembly of munitions, and deployment of explosives containing devices. As a result of the adverse effects of explosives on humans and environmental receptors, a low-cost means of decontaminating explosives and energetics contaminated areas is needed. Base-induced transformation of explosives shows promise as a rapid, low-cost technology for detoxifying explosives in soil and water. To understand the reaction mechanism, a reaction mixture of 2:1:1 (water: 100 ppm 2,4,6-trinitrotoluene (TNT): 1N KOH) was analyzed by ultraviolet-visible (UV/VIS) spectrometry from 190 to 1,100 nm. Time course measurements were conducted at 25, 20, 15, and 12 $^{\circ}$C. A factor analysis program was used to analyze the spectral data. Principal component analysis indicated that six principal components explained the spectra to within experimental error, with four factors explaining the majority of the variance. Test spectral vectors for four components were developed, including TNT, two intermediates, and the final product, and tested against the abstract vectors. Two possible reaction mechanisms were suggested and tested to explain the spectral data.

15. SUBJECT TERMS		
Base hydrolysis	Explosives	Spectroscopy
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