1990

Quantitative FTIR Analysis of Gas Phase Cigarette Smoke.

Rafael Cueto
Louisiana State University and Agricultural & Mechanical College

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Quantitative FTIR analysis of gas phase cigarette smoke

Cuetto, Rafael, Ph.D.

The Louisiana State University and Agricultural and Mechanical Col., 1990
QUANTITATIVE FTIR ANALYSIS OF GAS PHASE CIGARETTE SMOKE

A dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Chemistry

by

Rafael Cueto
B.S., Universidad Nacional de Colombia, 1981
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LIST OF ABBREVIATIONS

CLS - Classical least squares
cm - centimeter
DTGS - Deuterated triglycine sulfate
ESR - Electron spin resonance
FID - Flame ionization detector
FTIR - Fourier transform infrared
GC - Gas chromatography
ILS - Inverse least squares
Mb - Megabyte
μg - microgram
ml - milliliter
mm - millimeter
NaCl - Sodium chloride
NaNO₃ - Sodium nitrate
NO - Nitric oxide
NOCl - Nitrosyl chloride
NOₓ - Nitrogen oxides
NO₂ - Nitrogen dioxide
PCR - Principal component analysis
PLS - Partial least squares
ppm - parts per million
ABSTRACT

A new method, using Fourier transform infrared spectroscopy (FTIR), was developed for the simultaneous determination of nitrogen dioxide and nitric oxide in gas phase cigarette smoke and in model systems. The FTIR method also allows the simultaneous determination of other components.

The method uses multivariate least-squares regression analysis, that allows simultaneous quantitation of several components even in the presence of overlapping peaks, and fast data acquisition for kinetic analysis. For the preparation of the gas mixtures an apparatus that uses mass flow controllers, check-valves, and ground glass joints was constructed. This apparatus gives very exact metering, allowing the preparation of mixtures of precise concentrations, reducing the variations in the results between replications of experiments.

Using the developed method, model systems containing mixtures of nitric oxide/air with isoprene, methanol, acrolein, and acetaldehyde were studied using concentrations similar to those found in gas phase cigarette smoke. The "steady state" mechanism for the production of free radicals in gas phase cigarette smoke was substantiated, and a more realistic model for the continuous formation of free
radicals in gas phase cigarette smoke was proposed. The concentrations of nitric oxide and nitrogen dioxide in the new proposed model (a mixture of nitric oxide, air, methanol, and isoprene) follow time courses that duplicate very closely those found for the same components in gas phase cigarette smoke.
INTRODUCTION

GAS PHASE CIGARETTE SMOKE* CHEMISTRY

It has been known for many years that cigarette smoke contains free radicals\(^1\). It has often been assumed that these radicals are involved in smoking-induced diseases (e.g. cancer\(^2\)-\(^4\), and emphysema\(^5\),\(^6\)). The radicals in gas-phase cigarette smoke are very reactive and therefore short lifetimes are expected. However, these radicals appear to survive even if smoke is aged for 5-10 minutes\(^7\),\(^8\). Even more surprisingly, the concentration of radicals actually increases in smoke as it ages, reaching a maximum after about 1-2 minutes\(^9\),\(^10\). Previous reports suggest that the radicals in cigarette smoke are continuously produced in a steady-state mechanism that depends on nitrogen oxides (NO\(_x\))\(^7\),\(^8\). In this mechanism, nitric oxide (NO), which is relatively unreactive toward organic molecules, serves as the radical reservoir. The steady state mechanism postulates that NO slowly oxidizes to the reactive nitrogen dioxide (NO\(_2\)) (eq 1). NO\(_2\) adds to unsaturated compounds present in the smoke (e.g. isoprene), producing alkyl

---

\* Gas phase cigarette smoke is defined as the fraction of cigarette smoke that passes through a Cambridge filter, a glass fiber filter that retains 99.9% of all particulate matter with a size greater than 0.1 \(\mu\)M.

\*\* NO\(_x\) may be either nitric oxide or nitrogen dioxide.
radicals (eq 2). These alkyl radicals rapidly react with oxygen to form peroxyl radicals (eq 3). The peroxyl radicals then rapidly react with another NO to form alkoxyl radicals and NO₂ (eq 4). The final products formed from this scheme are alkyl peroxy-nitrates (eq 5), alkyl nitrate or nitrite esters (eq 6'), and nitroalkanes or nitrosoalkanes (eq 7).

\[
\begin{align*}
\text{NO} & + \frac{1}{2} \text{O}_2 \xrightarrow{\text{slow}} \text{NO}_2 \quad (1) \\
\text{NO} & + \overset{\cdot}{\text{C}}=\overset{\cdot}{\text{C}} \quad \xrightarrow{} \text{NO}_2-\overset{\cdot}{\text{C}}-\overset{\cdot}{\text{C}} \quad (R^+) \\
\text{R}^+ & + \text{O}_2 \quad \xrightarrow{} \text{RO}_2^+ \quad (3) \\
\text{RO}_2^+ & + \text{NO} \quad \xrightarrow{} \text{RO}^+ + \text{NO}_2 \quad (4) \\
\text{RO}_2^+ & + \text{NO}_2 \quad \xrightarrow{} \text{RO}_2^-\text{NO}_2 \quad (5) \\
\text{RO}^+ & + \text{NO}_x \quad \xrightarrow{} \text{RO}^-\text{NO}_x \quad (6) \\
\text{R}^+ & + \text{NO}_x \quad \xrightarrow{} \text{R}^-\text{NO}_x \quad (7)
\end{align*}
\]

The rate of oxidation of NO to NO₂ in air is slow\textsuperscript{11}. Studies of smog chemistry\textsuperscript{12} have shown, however, that the presence of reactive olefins increases the rate of oxidation of NO to NO₂, since peroxyl radicals are formed that react
with NO to give alkoxy radicals and NO₂ (eq 4). If a major fraction of the radicals in smoke is produced by this mechanism, then the changes in NO₂ concentration in smoke must parallel the changes in concentrations of oxidizing free radicals.

A synthetic model system for the production of free radicals in cigarette smoke has been proposed by Pryor et al.6. This model system consists of a gaseous mixture of NO/air/isoprene with similar concentrations to those found in gas phase cigarette smoke. The NO/air/isoprene model gives essentially the same types of radicals (oxygen and carbon centered) as does cigarette smoke.

There are several components in gas-phase cigarette smoke such as acetaldehyde, acrolein, and methanol (Table 1) that may also react with NO₂ or NO. It is important to know the kinetic behavior of NO and NO₂ in both cigarette smoke and the model system, in order to confirm the steady state mechanism described above. It is also important to see how other components present in high concentrations in gas phase cigarette smoke affect the kinetic behavior of NO and NO₂ in the NO/air/isoprene model system.

NOₓ DETERMINATION TECHNIQUES

Several techniques have been used for the determination of nitrogen oxides in cigarette smoke. For many years NOₓ was determined using the Saltzman procedure, or a
Table 1. Some chemical constituents found in gas-phase cigarette smoke

<table>
<thead>
<tr>
<th></th>
<th>µg/cigarette</th>
<th>ppm**</th>
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<tbody>
<tr>
<td>nitric oxide</td>
<td>300</td>
<td>700</td>
</tr>
<tr>
<td>hydrogen cyanide</td>
<td>300</td>
<td>720</td>
</tr>
<tr>
<td>hydrogen sulfide</td>
<td>90</td>
<td>185</td>
</tr>
<tr>
<td>ammonia</td>
<td>100</td>
<td>410</td>
</tr>
<tr>
<td>methane</td>
<td>800</td>
<td>3,500</td>
</tr>
<tr>
<td>ethylene</td>
<td>160</td>
<td>400</td>
</tr>
<tr>
<td>isoprene</td>
<td>400</td>
<td>410</td>
</tr>
<tr>
<td>acetylene</td>
<td>25</td>
<td>70</td>
</tr>
<tr>
<td>toluene</td>
<td>80</td>
<td>60</td>
</tr>
<tr>
<td>methyl chloride</td>
<td>160</td>
<td>220</td>
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<td>methanol</td>
<td>180</td>
<td>390</td>
</tr>
<tr>
<td>acetaldehyde</td>
<td>900</td>
<td>1,430</td>
</tr>
<tr>
<td>formaldehyde</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>acrolein</td>
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<td>90</td>
</tr>
<tr>
<td>acetone</td>
<td>350</td>
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<td>30</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>140</td>
<td>240</td>
</tr>
<tr>
<td>water</td>
<td>4,000</td>
<td>15,500</td>
</tr>
<tr>
<td>carbon monoxide</td>
<td>16,000</td>
<td>40,000</td>
</tr>
<tr>
<td>carbon dioxide</td>
<td>68,000</td>
<td>108,000</td>
</tr>
</tbody>
</table>

* Adapted from reference (24)

** Based on 350 ml of smoke per cigarette, 298 K, 760 mm of mercury.
modification thereof\textsuperscript{13-19}. A few procedures involve other color forming reagents\textsuperscript{20-23}, but almost all require oxidation of NO to NO\textsubscript{2}, and absorbance of the NO\textsubscript{2} in solution before measurement of the absorption of the colored solution. These procedures are time consuming and can be used only for measuring total content of NO\textsubscript{2}. Also, many compounds interfere in the results obtained using these methods\textsuperscript{13-23}. Other procedures used for the measurement of NO\textsubscript{2} in cigarette smoke are electrochemistry\textsuperscript{25}, gas chromatography\textsuperscript{26}, non-dispersive infrared analysis\textsuperscript{27}, and chemiluminescent analysis\textsuperscript{28}.

Chemiluminescence has been adopted as the standard technique for the analysis of NO\textsubscript{x} in environmental work\textsuperscript{29-33}, and this method also has been used on cigarette smoke\textsuperscript{28,34-42}, mainly to measure total content of NO\textsubscript{x}. The most relevant results using chemiluminescence in cigarette smoke were published by Borland \textit{et al.}\textsuperscript{39}. These researchers reported the time course for the disappearance of NO both in whole smoke and in filtered gas-phase smoke using a chemiluminescence analyzer. The chemiluminescence method does not permit continuous monitoring of concentrations, does not differentiate between NO and NO\textsubscript{2}, and is subject to interferences. Borland \textit{et al.} remark on the importance of a method to monitor the change in NO and NO\textsubscript{2} concentrations continuously.
Comparison studies of some of the methods described above have also been reported\textsuperscript{15,41,42}. None of the techniques described above allow the simultaneous measurement of NO and NO\textsubscript{2} without interference from other compounds. One technique that permits simultaneous, real time determination of NO and NO\textsubscript{2} is infrared spectroscopy.

Infrared analysis of cigarette smoke was first reported in 1956 by Philippe and Hobbs\textsuperscript{43}: they used dispersive infrared spectroscopy to identify new compounds in cigarette smoke, and semiquantitate some of them. In 1975, Vilcins\textsuperscript{44} used FTIR for the determination of ethylene and isoprene and Vilcins and Lephardt\textsuperscript{45,46}, for the analysis of NO\textsubscript{x}, methanol and methyl nitrite in cigarette smoke. Later, (1977) Maddox and Mamantov\textsuperscript{47} used FTIR to measure CO, CO\textsubscript{2}, methane, ethylene, and methanol in cigarette smoke. The work by Vilcins and Lephardt shows a preliminary analysis of NO and NO\textsubscript{2} in cigarette smoke, however, their results are of limited utility since they report only relative absorbances.

**FTIR ADVANTAGES**

The advantages of FTIR instruments over conventional dispersive instruments are well documented\textsuperscript{48-50}: (1) Very high signal-to-noise ratio (Fellgett's advantage, or multiplex advantage), because of short spectral acquisition times and signal averaging, (2) High light throughput to the detector.
(Jaquinot advantage), and (3) high precision and accuracy in wavenumber determination (Conne's advantage).

In the last ten years several high-performance, low-cost FTIR instruments have been introduced. As a result, FTIR spectroscopy has become a very popular technique and has replaced conventional dispersive infrared spectroscopy in many laboratories. At the same time, the development of more powerful, inexpensive computers has resulted in the availability of spectral data processing techniques. Some of the biggest advances have been made in the development of new mathematical methods for multicomponent quantitative analysis. The most common chemometric methods used today for multicomponent quantitative analysis are: Beer's law K-matrix calculations or classical least squares (CLS)\textsuperscript{51-54}, inverse Beer's law P-matrix or inverse least squares (ILS)\textsuperscript{51,52,55,56}, partial least squares (PLS)\textsuperscript{53,57-60}, and principal component regression (PCR)\textsuperscript{58,61-63}. Each method has been applied to different systems, but guidelines on the applicability of each method under specific experimental conditions do not exist.

The use of FTIR spectroscopy for the determination of trace gases has become important in the analysis of air pollutants\textsuperscript{65-69} and studies of atmospheric chemistry\textsuperscript{70,71}. There has also been a great interest in the kinetic study of photochemical reactions, related to the upper atmosphere,
using FTIR spectroscopy\textsuperscript{72-77}. Most of these studies were made using long-path cells, and include determination of NO\textsubscript{x}.

OBJECTIVES

The main objective of this dissertation was to develop a FTIR method that allows the simultaneous determination of NO and NO\textsubscript{2} in gas phase cigarette smoke and in model systems, in order to confirm the steady-state mechanism.

The second objective of this dissertation was to use the developed method to study the effect of components, other than isoprene (original model system), on the kinetic behavior of NO and NO\textsubscript{2} in different model systems, and if possible to suggest a better model.
MATERIALS AND EQUIPMENT

GASES

Commercial nitric oxide from Matheson was first passed through a thymol blue/KOH solution to remove nitrogen dioxide, and then through a dry ice/acetone trap to remove any remaining nitrogen dioxide and water. Matheson's certified standards of nitric oxide (554 ppm) and nitrogen dioxide (520 ppm) in helium were used for calibration. Nitrogen, compressed air, and helium from Liquid Carbonic were used for dilutions and gas phase reactions.

LIQUIDS AND SOLIDS

Isoprene (Aldrich "gold label"), acrolein (Aldrich), acetaldehyde (Aldrich), hexatriacontane (Aldrich), and absolute methanol (J.T. Baker Chemical Co.) were used without further purification.

CIGARETTES

Research cigarettes were obtained from the University of Kentucky, Tobacco and Health Research Institute, and commercial cigarettes were purchased in a local store. Cigarettes were conditioned by storing in a desiccator over a saturated aqueous solution of ammonium nitrate (60% relative humidity) for at least 48 hours. Several types
of cigarettes were analyzed, but for the modeling experiments the standard IR179 research cigarette was used.

FOURIER TRANSFORM INFRARED SPECTROMETER

Initially FTIR spectra were obtained with an IBM IR/32 FTIR spectrometer equipped with a DTGS detector and an IBM 9000 data system. Analyses were performed with the software supplied with the instrument. Later, the data system was upgraded to an IBM IR/44 which uses an 8 MHz IBM-AT computer with a 30 MB hard disk, 4 MB of memory, and a math coprocessor. This upgrade fixed some of the problems and inconveniences experienced with the IBM 9000 system, such as slow acquisition speed, and the fact that the software did not allow the storage of interferograms. The software used by the IBM IR/44 system is supported by Nicolet.

GAS CHROMATOGRAPHY

Gas Chromatography analyses were performed with a Varian Gas Chromatograph model 3700 with a 30 meter DB-5 capillary column (J&W Scientific), and a FID detector.

MASS FLOW CONTROLLERS

The mixing and control of the different gases was accomplished using mass flow controllers model 5850 series D from Brooks (Hatfield, Pa.), connected to a controller, readout and power supply unit model 5876 also from Brooks.
FTIR CONDITIONS

Several experiments were performed to determine the optimal data collection conditions; the main parameters studied were resolution and number of scans. Most experiments were performed using 4 cm\(^{-1}\) resolution, 5-10 scans, gain 2, Happ-Genzel apodization, and automatic correlation. To increase the acquisition speed and the number of data points per kinetic run, interferograms were collected, then saved in memory (RAM disk). The fast Fourier transformation was executed after all interferograms were collected. Baselines of the resulting spectra were corrected, and in some cases absorption due to water was subtracted from the total absorption. Water vapor absorbs around 1600 cm\(^{-1}\), and may interfere with the determination of NO\(_2\). It was also found that the use of disk caching in the computer, while collecting the data, decreases the time between data points (especially during kinetic runs).

For the multiple component quantitative analysis, the QUANT software package from IBM Instruments (later NICOLET instruments), was used. This software uses multivariate least-squares regression analysis, making it possible to simultaneously quantitate several components even in the presence of overlapping peaks.
GAS CELL

A 20 cm pathlength single-pass gas cell with sodium chloride windows and a total volume of 50.6 ml was built (Figure 1). This gas cell takes advantage of the size of the sample compartment of the FTIR and at the same time has a small volume to pathlength ratio. The longest single pass gas cell commercially available is a 10 cm cell, with a volume close to 50 ml. Teflon gaskets are used between the windows (25 mm diameter, 4–5 mm thickness) and the glass body. Neoprene o-rings are used between the windows and the cell mount.

Coating of gas-cell windows: It has been reported\textsuperscript{80,81} that NO\textsubscript{2} reacts with the NaCl of the gas-cell windows, producing NOCl (1790 cm\textsuperscript{-1}), and sodium nitrate (1340 and 840 cm\textsuperscript{-1}). To avoid this problem, the procedure of coating windows with commercial paraffin reported by Carlson et al.\textsuperscript{81} was tried, but found unsatisfactory because the paraffin wax used contains unsaturated bonds that react with NO\textsubscript{2}. It was found that hexatriacontane, which can be obtained inexpensively and in high purity, can be used instead. The coating procedure consists of gently warming the windows with a thin layer of the powdery hexatriacontane on a hotplate until the hydrocarbon starts to melt; the pool is then spread uniformly on the window by rolling a hot glass rod across the window; the excess wax is wiped off the rod.
Figure 1. Diagram of the gas cell used for the different FTIR experiments.
and the procedure is repeated until a very thin uniform film is obtained. This relatively simple method gives a uniform thin film that lasts throughout several experiments for concentrations of NO₂ up to 800 ppm.

Figure 2 shows the FTIR spectrum of the gas cell, with unprotected NaCl windows, after being exposed to 520 ppm of NO₂ for 20 minutes. The band at 1360 cm⁻¹ corresponds to NaNO₃, which is one of the reaction products of nitrogen dioxide with sodium chloride⁸⁰-⁸² (the other product is NOCl). This NaNO₃ band starts appearing almost as soon as NO₂ is introduced in the cell, and grows up very fast.

Figure 3 shows the FTIR spectrum of n-hexatriacontane. The regions used for the analysis of NO (1905 cm⁻¹), and NO₂ (1628 cm⁻¹) are free of absorptions. The coating on the windows is very thin and very stable; for most purposes the region between 2800 and 600 cm⁻¹ is free of interferences.

GAS MIXTURES

During the development of the method the apparatus used to prepare the gas mixtures was modified several times; it went from a stopcock and flowmeter system, with tygon tubing connections, to the final design (Figure 4), that uses mass flow controllers, check-valves, and ground glass joints to allow a more precise metering of the mixtures and a more inert system.
Figure 2. FTIR spectrum of the gas cell with unprotected NaCl windows, after being exposed to 520 ppm of NO$_2$ for 20 minutes. The band at 1360 cm$^{-1}$ corresponds to NaNO$_3$. The other bands correspond to NO$_2$. 
Figure 3. FTIR spectrum of n-hexatriacontane.
Figure 4. Apparatus used to mix nitric oxide with air and different vapor organic compounds.
Nitric oxide: The nitric oxide, controlled by a mass flow controller, is first passed through a 30% solution of potassium hydroxide saturated with thymol blue in order to remove any traces of nitrogen dioxide (Figure 4). Then the NO is passed through a cold trap at -78 °C (dry ice/acetone) to remove possible traces of nitrous oxide and water. Next the NO goes through a capillary, and is diluted with either air or nitrogen. A check valve between the traps and the capillary prevents any other gases or vapors from backing into the traps.

Organic components (isoprene, acrolein, acetaldehyde, or methanol): The organic components for the different mixtures can be metered in, either by controlling the temperature of the bath in which the vial containing the organic components is immersed or by adjusting the flow rates of the carrier gas (Figure 4). For different components and different concentrations, different cooling solutions were used. One or two components can be placed in the vial at the same time, or a third branch can be added to the system for more complex mixtures.

In a similar way to the nitric oxide, there is a capillary and a check valve to provide better control of the flow rate and prevent contaminations from gases backing into the system.
Mixing: The mixing of the different components occurs at the end of the "Y" shaped tube ending in two capillaries (Figure 4). The total flow rate for every experiment was set at 250 ml/minute.

Ageing: Ageing of the mixtures is accomplished by a "stop flow" system: after the gases are mixed and constant concentrations are achieved, the gas cell is closed and data collection is started. The dead volume of the system including the volume of the cell gives an initial dead time of 13 seconds.

An alternate method that uses variable lengths of tubing between the mixing and the gas cell was tried. This method has several disadvantages: the number of data points is limited to the number of different lengths of tubing; very long pieces of tubing are needed for long residence times; and in some instances the presence of laminar flow causes inconsistencies in the obtained data. Some experiments were attempted with this method but the results did not compare favorably to those obtained with the "stop flow" method.

CALIBRATION

The calibrations for NO and NO₂ were made using standards from Matheson; lower concentrations were obtained
by dilution with helium. Total flow rates were 250 ml/minute. 100 scan spectra were collected for each standard.

Isoprene, acrolein, acetaldehyde and methanol were calibrated indirectly using gas chromatography (GC); 100 scan FTIR spectra were measured, and then samples of 5 ml were taken from the cell with a gas-tight syringe and injected into the gas chromatograph to determine the concentration. GC standards were made following the procedure described by Cotabish et al. The calibration data for NO, NO₂, and isoprene were used to build a multicomponent calibration method, which was then used for all the calculations in the kinetic runs. The data for acetaldehyde, methanol, and acrolein were used for the calibration of the flow system to get similar concentrations of these components to those found in cigarette smoke.

PROCEDURE FOR SMOKING CIGARETTES

Cigarettes were smoked using two different protocols:

1) A puff protocol: puffs (35 cm³) of 2 sec duration were pulled from the cigarette (using a syringe) at one minute intervals and passed through a Cambridge filter. The third puff was introduced into the evacuated gas cell.
ii) A continuous flow system (Figure 5): The smoke stream was pulled through the cigarette, a Cambridge filter, and finally the gas cell, using a water aspirator set at a flow rate of 250 ml per minute. The cell was closed 90 sec after the cigarette was lit, and data collection was started at this time.

KINETIC RUNS

**Preliminary operations:** Before each kinetic run using a known gas mixture or cigarette smoke, the gas cell, glass tubing, and connections were rinsed with acetone, and the coating on the windows examined. Sometimes part of the paraffin wax coating flaked after the acetone rinse and had to be replaced. Next the gas cell was evacuated and checked for leaks; when leaks were found, the cell was tightened until the leak stopped. This has to be done very carefully, or the cell windows will crack. Next the cell was introduced in the FTIR, and both the FTIR and the gas mixing system (including the cell) were purged with dry air for several minutes. Finally a background spectrum was collected (30 scans).

**Gas mixtures:** The flow through the reservoirs containing the different components was started and spectra were collected until stable readings, with the correct initial concentrations for each component (Table 1), were
Figure 5. Apparatus used for the generation of cigarette smoke in the continuous flow system.
obtained. At this point the cell was closed, and data collection started. Typical runs lasted 20 minutes. Each experiment was repeated at least five times.

Cigarette smoke: After the background spectrum was collected, the cigarette was lit. After 90 seconds the cell was closed and data collection started; typical runs lasted 20 minutes; each experiment was repeated at least five times. Data were processed as described in the FTIR conditions section.

Kinetic calculations: For the calculations of the rate constants the kinetic fitting routine SI-FIT from OLIS (Online Instrument Systems, Inc, Jefferson GA) was used. SI-FIT uses a successive integration method that solves its kinetics cases by fitting the Y value against one or more integrations of Y with respect to time. SI-FIT differs from other non-linear fitting methods in that it obtains very good starting values which are then improved very slightly, requiring very few iterations to obtain convergence.
RESULTS

SELECTION OF FTIR CONDITIONS

Resolution: The FTIR instrument used is capable of resolutions ranging from 1 to 16 cm$^{-1}$. Figure 6 shows the five scan spectra of a mixture of NO and NO$_2$ taken at 1, 2, 4, and 8 cm$^{-1}$ resolution. When the resolution is decreased, the signal to noise ratio increases, while the time for one scan decreases$^{48,78}$. Each time the resolution is increased, the number of data points doubles, increasing the time of data processing, and the disk and memory storage space. Also at a resolution of 8 cm$^{-1}$ the spectral features start disappearing. Based on the previous observations the resolution selected for the different experiments was 4 cm$^{-1}$.

Number of scans: Considering that the signal to noise ratio increases with the square root of the number of scans$^{48,78}$, a large number of scans is needed to obtain a significant increase in the signal to noise ratio. Figure 7 shows the spectra of a mixture of NO and NO$_2$ at 4 cm$^{-1}$ resolution with accumulation of one to five scans. After four scans, very small differences are noticed in the improvement of the signal to noise ratio, unless several scans are added. Therefore a value of 5 scans was selected for most of the experiments.
Figure 6. Five scan spectra of a mixture of NO and NO₂ taken at 1, 2, 4, and 8 cm⁻¹ resolution.
Figure 7. Spectra of a mixture of NO and NO$_2$ at 4 cm$^{-1}$ resolution with accumulation of one to five scans.
With 5 scans, a resolution of 4 cm⁻¹, and the conditions described in the experimental section, the average time between measurements (using the IBM-AT computer) was 7.5 seconds.

CALIBRATION

Selection of frequencies: The two main components used for the quantitative analysis were NO and NO₂, though isoprene was quantitated on some occasions. The strongest bands, and if possible the most free of overlap were chosen for the quantitative analysis.

The FTIR spectrum of NO (Figure 8) shows the strongest absorption bands at 1905, 1873, and 1850 cm⁻¹. The band selected for quantitative analysis was the one located at 1905 cm⁻¹.

The FTIR spectrum of NO₂ (Figure 9) shows the strongest bands at 1628, and 1601 cm⁻¹. The band selected for quantitative analysis was the one located at 1628 cm⁻¹.

The FTIR spectrum of isoprene (Figure 10) shows the strongest bands at 991, 906, and 893 cm⁻¹. The band selected for quantitative analysis was the one located at 893 cm⁻¹.

Figure 11 shows the FTIR spectrum of: a) a mixture of NO/air/isoprene aged 15 seconds; b) 1R1 cigarette smoke aged 13 seconds, (water subtracted); c) the same smoke from (b), 120 seconds later. It can be seen that the frequencies
Figure 8. FTIR spectrum of nitric oxide taken with 5 scans, at 4 cm\(^{-1}\) resolution. The strongest absorption bands are at 1905, 1873, and 1850 cm\(^{-1}\).
Figure 9. FTIR spectrum of nitrogen dioxide taken with 5 scans, at 4 cm\(^{-1}\) resolution. The strongest absorption bands are at 1628, and 1601 cm\(^{-1}\).
Figure 10. FTIR spectrum of isoprene taken with 5 scans, at 4 cm\(^{-1}\) resolution. The strongest absorption bands are at 991, 906, and 893 cm\(^{-1}\).
Figure 11. A: FTIR spectrum of a mixture of NO (700 ppm), air, and isoprene (450 ppm), aged 15 seconds. B: FTIR spectrum of 1R1 cigarette smoke aged 13 seconds. C: FTIR spectrum of 1R1 cigarette smoke aged 133 seconds.

Bands are marked as follows: 1=NO, 1905 cm\(^{-1}\); 2=NO\(_2\), 1628 cm\(^{-1}\); 3=isoprene, 893 cm\(^{-1}\). Water was subtracted from the cigarette smoke spectra.
selected for each component (1=NO, 2=NO₂, and 3=isoprene) are relatively free of overlap in the systems studied, which makes the calibration simpler, and the quantitation process faster.

**Calibration method:** Before using the multicomponent analysis software, individual linear regression analyses were run for NO, NO₂, and isoprene. Figure 12 shows the calibration curves, with the fitted lines for NO, isoprene, and NO₂. In the range of concentrations used (Table 2), the absorbance is linear for all three components, with correlation coefficients of 0.999 for all three components.

For the multicomponent analysis, three methods were tested: the P-matrix method⁵¹-⁵², ⁵⁵, ⁵⁶, the K-matrix method⁵¹-⁵⁴, and the PLS method⁵³, ⁵⁷-⁶⁰. The K-matrix method did not give very reproducible results. The P-matrix method is the most commonly used in commercial quantitative FTIR software, and it was found very adequate for the systems studied. The PLS gave similar results to those obtained using the P-matrix method but required additional data processing and used more time for each analysis. Therefore the P-matrix method using the Quant software package from Nicolet was selected for the multicomponent analysis.

A quantitative method was developed using eight mixtures of standards of NO, NO₂, and isoprene. Several frequency ranges were tried for each component; Table 2
Table 2. Concentrations and frequencies used for the calibration of NO, NO\textsubscript{2}, and isoprene

<table>
<thead>
<tr>
<th></th>
<th>NO</th>
<th>NO\textsubscript{2}</th>
<th>Isoprene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start freq. (cm\textsuperscript{-1})</td>
<td>1945</td>
<td>1645</td>
<td>897</td>
</tr>
<tr>
<td>End freq. (cm\textsuperscript{-1})</td>
<td>1880</td>
<td>1615</td>
<td>886</td>
</tr>
<tr>
<td>Standard 1 (ppm)</td>
<td>138</td>
<td>52</td>
<td>0</td>
</tr>
<tr>
<td>Standard 2 (ppm)</td>
<td>249</td>
<td>130</td>
<td>136</td>
</tr>
<tr>
<td>Standard 3 (ppm)</td>
<td>360</td>
<td>234</td>
<td>220</td>
</tr>
<tr>
<td>Standard 4 (ppm)</td>
<td>471</td>
<td>338</td>
<td>369</td>
</tr>
<tr>
<td>Standard 5 (ppm)</td>
<td>526</td>
<td>442</td>
<td>641</td>
</tr>
<tr>
<td>Standard 6 (ppm)</td>
<td>554</td>
<td>520</td>
<td>863</td>
</tr>
<tr>
<td>Standard 7 (ppm)</td>
<td>0</td>
<td>328</td>
<td>220</td>
</tr>
<tr>
<td>Standard 8 (ppm)</td>
<td>249</td>
<td>0</td>
<td>136</td>
</tr>
</tbody>
</table>
Figure 12. Calibration curve, with the fitted lines for NO (triangles), isoprene (squares), and NO₂ (circles).

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shows the optimal frequency ranges found for each component, and the concentrations used for the different mixtures for the calibration method used for all the analyses.

The calibration method was tested with the spectra of standard mixtures, and with the spectra of individual components, of known concentrations, giving results within a 5% margin of error, the expected error range for this type of analysis.

**Extinction coefficients for NO and NO₂:** The extinction coefficients (base $\varepsilon$, ppm$^{-1}$ x cm$^{-1}$) for NO and NO$_2$ for the selected frequencies were calculated using the data from the calibration curves. This resulted in the following values:

- NO: $\varepsilon = 4.80 \times 10^{-7}$ ppm$^{-1}$ cm$^{-1}$ at 1905 cm$^{-1}$
- NO$_2$: $\varepsilon = 1.23 \times 10^{-3}$ ppm$^{-1}$ cm$^{-1}$ at 1628 cm$^{-1}$

Infrared extinction coefficients for NO and NO$_2$ are reported infrequently; however, the reported values were measured at different frequencies, and in some cases under completely different experimental conditions, so it was not desirable to make a comparison.

**CALCULATION OF CONCENTRATIONS IN CIGARETTE SMOKE**

**Concentration units:** The concentration units for most of the gas phase experiments are given in parts per million.
by volume (ppm, or micromoles of gas per mole of gas). For cigarette smoke the results are expressed in micrograms per cigarette. The conversion from ppm is made by first calculating the concentration of the component in the gas phase:

$$\text{Concentration(\mu g/l)} = \frac{C \times \text{Wt.} \times 298 \times P}{24.45 \times T \times 760}$$

where

- $C$ = concentration in ppm
- Wt. = Molecular weight of substance
- $P$ = Absolute pressure in torr of the sample stream
- $T$ = Absolute temperature

Then total delivery ($\mu g/cigarette$) equals the total volume of smoke (flow rate(l/minute) multiplied by the burning time(minutes)), multiplied by the concentration ($\mu g/l$).

Concentrations of NO<sub>2</sub> in cigarette smoke: The concentrations of NO, NO<sub>2</sub>, and isoprene in gas phase cigarette smoke of several commercial, and some research cigarettes were calculated. For these experiments the cigarette was lit and a minute later scanning in the FTIR was started. The data collection was stopped when the flame reached the first mark in research cigarettes, or 5 mm before the filter in commercial cigarettes. At least 10
measurements were made for each type of cigarette. Table 3 shows the concentrations measured for NO and NO₂, and the reported values for nitric oxide⁴. NO₂ was found in cigarette smoke, because the smoke is at least 13 seconds old by the time the FTIR measurement is started, and as a result some NO has already been converted to NO₂.

The concentration values for nitrogen oxides in cigarette smoke reported in this dissertation are 2.2 times higher than the reported literature values⁴, because the values reported here were obtained using the continuous flow protocol, while the literature values use the puff protocol. The continuous flow protocol accounts for all the smoke generated by burning one cigarette (average burning time 3.08 minutes at 250 ml/min); the puff protocol accounts only for the volume of smoke inhaled by the smoker (350 ml)²⁴.⁷⁰ 

\[ \frac{3.08 \text{ min} \times 250 \text{ ml/min}}{350 \text{ ml}} = 2.2 \]

**FTIR STUDY OF CIGARETTE SMOKE**

**Differential spectral kinetic profiles:** A detailed study of the ageing of cigarette smoke was made using differential spectral kinetic profiles. The differential spectra exhibit only the bands of those compounds which have changed concentration over the time interval between collection of spectra. Compounds that increase in concentration show bands similar to the normal transmittance
Table 3. Calculated concentrations of NO and NO₂ for examined commercial and research cigarettes.

<table>
<thead>
<tr>
<th>Cigarette</th>
<th>NO (μg/Cigarette)</th>
<th>NO₂ (μg/Cigarette)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exp.*</td>
<td>Rpt.*</td>
</tr>
<tr>
<td>Winston</td>
<td>671 ± 41</td>
<td>712</td>
</tr>
<tr>
<td>Winston Light</td>
<td>638 ± 13</td>
<td>646</td>
</tr>
<tr>
<td>Marlboro</td>
<td>767 ± 36</td>
<td>726</td>
</tr>
<tr>
<td>Marlboro Light</td>
<td>716 ± 59</td>
<td>686</td>
</tr>
<tr>
<td>Camel</td>
<td>733 ± 86</td>
<td>1029</td>
</tr>
<tr>
<td>Camel Light</td>
<td>944 ± 90</td>
<td></td>
</tr>
<tr>
<td>Kent</td>
<td>759 ± 41</td>
<td>706</td>
</tr>
<tr>
<td>Kent Light</td>
<td>739 ± 30</td>
<td>83 ± 7</td>
</tr>
<tr>
<td>Barclay</td>
<td>333 ± 118</td>
<td>61</td>
</tr>
<tr>
<td>1R1</td>
<td>743 ± 25</td>
<td>733</td>
</tr>
<tr>
<td>2R1F</td>
<td>923 ± 27</td>
<td>925</td>
</tr>
<tr>
<td>1R3</td>
<td>771 ± 80</td>
<td></td>
</tr>
<tr>
<td>1R3F</td>
<td>768 ± 73</td>
<td>98 ± 9</td>
</tr>
<tr>
<td>1R4F</td>
<td>720 ± 88</td>
<td>748</td>
</tr>
<tr>
<td>2A1</td>
<td>766 ± 139</td>
<td>150 ± 3</td>
</tr>
</tbody>
</table>

* Experimental value
† Reported value*(adjusted by a factor of 2.2).
spectra, while compounds that decrease in concentration show inverted bands. The differential format allows one to observe very small changes with time more clearly. Most interfering components do not change over time, and therefore they do not appear in the modified spectra.

Figure 13 shows a sample of the changes found in the ageing of 1R1 gas phase cigarette smoke between 0.0 seconds and 7 minutes. The most important feature is the appearance of absorption bands at 800 and 822 cm⁻¹. These bands correspond to methyl nitrite⁸⁸–⁹¹, which is the product of the reaction of methanol with nitrogen dioxide⁹²–⁹³. This finding was the main reason behind the addition of methanol to the model system. In Figure 13 we can also see very clearly the appearance of NO₂ (1580–1660 cm⁻¹), and the disappearance of NO (1820–1940 cm⁻¹), NO₂ (1580–1660 cm⁻¹), and isoprene (860–1000 cm⁻¹). A similar study of a NO/air/isoprene/methanol system (Figure 14) gave similar results.

Comparison of continuous flow and puff protocols:
Figure 15 shows the kinetic profiles for the appearance and disappearance of NO₂ and the disappearance of NO in 1R1 cigarette smoke using both protocols. It was found that the continuous flow system, if the cell is clean, gives comparable results (for the compounds studied) to the puff system, and it is easier to use. In addition, larger volumes of smoke go into the cell when using the continuous
Figure 13. Differential spectral kinetic profiles of 1R1 gas phase cigarette smoke between 20 seconds and 7 minutes.
Figure 14. Differential spectral kinetic profiles of NO/air/methanol/isoprene between 20 seconds and 7 minutes.
Figure 15. Comparison of the profiles for the appearance and disappearance of NO₂, and the disappearance of NO in 1R1 cigarette smoke using the puff protocol and the continuous flow systems.
flow (50.6 ml for continuous flow, 35 ml for puff method), increasing the sensitivity. Therefore, the continuous flow system was used for most of the experiments.

It is also important to emphasize the importance of cleaning the gas cell before each determination, especially when using cigarette smoke. Figure 16 shows the dramatic change in the results, when the cell has not been cleaned compared with the data from a "clean" run. These changes are mainly due to deposits of tar on the gas cell walls (the Cambridge filter is not 100% efficient in trapping the cigarette tar). Tar deposits can quench some of the radicals formed, and reduce the rate of oxidation of NO. The results obtained with a dirty cell are similar to those obtained by Borland et al. using whole smoke.

KINETIC DATA

Kinetic profiles: For each of the systems studied (cigarette smoke, or model systems) profiles showing the appearance and disappearance of NO\textsubscript{2}, and the disappearance of NO were plotted; rate constants were calculated, and the fitted equations were used to draw lines through the data points.

Figure 17-21 show representative plots for the different systems studied. The LR1 cigarette smoke system (Figure 17) and the NO/air system (Figure 18) were the basis for the comparison of the kinetic trends of NO and NO\textsubscript{2}. The
Figure 16. Profiles for the appearance and disappearance of NO\textsubscript{2} (filled symbols), and the disappearance of NO (open symbols) in 1R1 cigarette smoke. Crosses represent measurements made with a clean cell; triangles represent measurements made with a "dirty" cell.
Figure 17. Profiles for the appearance of NO$_2$ (open circles), and disappearance of NO (filled circles) in 1R1 gas phase cigarette smoke. The lines through the symbols correspond to the fitted equation used for the calculation of the rate constants.
Figure 18. Profiles for the appearance of NO$_2$ (open circles), and disappearance of NO (filled circles) for the NO/air system. The lines through the symbols correspond to the fitted equation used for the calculation of the rate constants.
main differences between the two systems are: 1) The faster rate of oxidation of NO in cigarette smoke compared to NO/air, and 2) small concentrations of NO₂ present in cigarette smoke compared to NO/air.

The NO/air/isoprene system (Figure 19) was the original model for cigarette smoke⁸, and was the first system to be studied. The rate of oxidation of NO is closer to that found in cigarette smoke, but the profile for NO₂ is somewhere in between the NO/air system and cigarette smoke. With methanol substituted for isoprene (Figure 20) NO disappears at a slower rate, and concentrations of NO₂ are a little higher. When methanol is added to the NO/air/isoprene system, profiles very similar to those of cigarette smoke were obtained (Figure 21).

Other systems: Kinetic studies for the NO/acetaldehyde/air (Figure 22), NO/acrolein/air (Figure 23), NO/acetaldehyde/isoprene/air (Figure 24), and NO/acrolein/isoprene/air (figure 25) systems were also made. No differences were found for the first two systems compared to the NO/air system, or for the latter two systems compared to NO/air/isoprene.

The kinetic profiles of NO and NO₂ for the different research and commercial cigarettes were also studied. The only difference found compared to the 1R1 profiles was that
Figure 19. Profiles for the appearance and disappearance of NO$_2$ (open circles) and the disappearance of NO (filled circles) in the NO/air/isoprene system. The lines through the symbols correspond to the fitted equation used for the calculation of the rate constants.
Figure 20. Profiles for the appearance and disappearance of NO\textsubscript{2} (open circles) and the disappearance of NO (filled circles) in the NO/air/methanol model. The lines through the symbols correspond to the fitted equation used for the calculation of the rate constants.
Figure 21. Profiles for the appearance and disappearance of NO\textsubscript{2} (open circles) and the disappearance of NO (filled circles) in the NO/air/methanol/isoprene model. The lines through the symbols correspond to the fitted equation used for the calculation of the rate constants.

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Figure 22. Profiles for the appearance of NO₂ (open circles), and disappearance of NO (filled circles) for the NO/air/acetaldehyde system.
Figure 23. Profiles for the appearance of NO₂ (open circles), and disappearance of NO (filled circles) for the NO/air/acrolein system.
Figure 24. Profiles for the appearance of NO$_2$ (open circles), and disappearance of NO (filled circles) for the NO/air/acetaldehyde/isoprene system.
Figure 25. Profiles for the appearance of NO₂ (open circles), and disappearance of NO (filled circles) for the NO/air/acrolein/isoprene system.

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the initial concentrations of NO and NO\textsubscript{2} were different, but all cigarettes showed the same kinetic trends.

\textbf{Rate constants:} Rate constants were calculated for all the systems studied, using the kinetic software package from OLIS. For each mixture at least five kinetic runs were collected, and the rate constants calculated.

The rate of oxidation of nitric oxide is third order, and when oxygen is greatly in excess it becomes (pseudo) second order\textsuperscript{11,19,94}:

\[-\frac{d[\text{NO}]}{dt} = 2k\ [\text{O}_2][\text{NO}]^2 \quad .\]

The calculated third order rate constant for the NO air system was 4.0 \times 10^{3} \text{ l}^{2}\text{mol}^{-2}\text{min}^{-1} which compares very well with the reported value (4.4 \times 10^{3} \text{ l}^{2}\text{mol}^{-2}\text{min}^{-1})\textsuperscript{11}.

Since the disappearance of NO in gas phase cigarette smoke is best fitted by a logarithmic decay curve (Figure 17), first order kinetics were assumed following the guidelines given by Glasson and Tuesday\textsuperscript{39}, and Borland \textit{et al.}\textsuperscript{12}:

\[-\frac{d[\text{NO}]}{dt} = k[\text{NO}] \quad .\]

These researchers attribute the first order oxidation of nitric oxide in gas phase cigarette smoke to the rapid reaction of peroxy radicals with nitric oxide (eq. 4, in the introduction).
Table 4 shows the average first order rate constants obtained for the different systems that were studied and the reported values for cigarette smoke. First order rate constants were calculated for all the systems for comparison purposes. Only the NO/air/isoprene, NO/air/isoprene/methanol, and cigarette smoke systems exhibit first order kinetics. Rate constants for cigarettes other than 1R1 were also calculated, and in all cases, the values measured were not significantly different from the rate constants found for 1R1 cigarettes.

PRODUCT ANALYSIS

Approximately 3900 compounds have been identified in cigarette smoke\textsuperscript{24,81,86}, of which about 450 occur in the gas phase\textsuperscript{87}. It was not the purpose of this dissertation to do any work in product analysis. However, some product analysis was done in the NO/air/isoprene system: after the kinetic data collection was finished, a light yellow liquid was observed on the inside walls of the gas cell. Figure 26 shows the FTIR spectrum of these products. The main absorptions with their assignments\textsuperscript{88,88} are: 1636 cm\textsuperscript{-1} (alkyl nitrate), 1557 cm\textsuperscript{-1} (primary and/or secondary nitroalkane), 1427 cm\textsuperscript{-1} (primary nitro compound), 1377 cm\textsuperscript{-1} (nitroalkane), 1281 cm\textsuperscript{-1} (alkyl nitrate), and 860 cm\textsuperscript{-1} (alkyl nitrate).
Table 4. Rate constants for oxidation of NO, and appearance ($k_1$) and disappearance ($k_2$) of NO$_2$.
All rates s$^{-1} \times 10^3$

<table>
<thead>
<tr>
<th></th>
<th>NO</th>
<th>NO$_2$</th>
<th>NO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>($k_1$)</td>
<td>($k_2$)</td>
<td></td>
</tr>
<tr>
<td>NO in air</td>
<td>2.9 ± 0.6</td>
<td>3.2 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>1R1 Cig. Smoke</td>
<td>5.7 ± 0.7</td>
<td>7.3 ± 1.4</td>
<td>3.3 ± 0.6</td>
</tr>
<tr>
<td>NO/Isoprene/air</td>
<td>3.8 ± 0.7</td>
<td>5.7 ± 0.8</td>
<td>1.1 ± 0.1</td>
</tr>
<tr>
<td>NO/MeOH/air</td>
<td>3.0 ± 0.3</td>
<td>11.1 ± 0.4</td>
<td>3.0 ± 0.3</td>
</tr>
<tr>
<td>NO/MeOH/Isop./air</td>
<td>5.1 ± 0.3</td>
<td>14.2 ± 0.8</td>
<td>0.8 ± 0.4</td>
</tr>
<tr>
<td>NO/acrolein/air</td>
<td>2.9 ± 0.7</td>
<td>3.1 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>NO/acetaldehyde/air</td>
<td>2.8 ± 0.7</td>
<td>3.1 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>NO/acrolein/isop./air</td>
<td>3.7 ± 0.9</td>
<td>5.8 ± 1.0</td>
<td>1.2 ± 0.3</td>
</tr>
<tr>
<td>NO/acetaldehyde/isop./air</td>
<td>3.9 ± 0.8</td>
<td>5.8 ± 1.1</td>
<td>1.3 ± 0.4</td>
</tr>
<tr>
<td>Borland et al$^{39}$</td>
<td>2.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(cigarette smoke)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vilecins &amp; Lephardt$^{46*}$</td>
<td>7.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(cigarette smoke)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Calculated by Borland et al$^{39}$
Figure 26. FTIR spectrum of liquid products from the NO/air/isoprene system.
These are all predicted products from the proposed steady-state mechanism and confirm results reported by other research groups for the reaction of NO$_2$ with isoprene.$^{12, 98, 99}$
DISCUSSION

GAS MIXTURES

The final design of the gas mixing system (Figure 4) is a great improvement over any of the systems used before. The use of mass flow controllers significantly reduced the variation between replications of experiments, decreased the setup time for the experiments, and allowed the preparation of mixtures of very precise concentrations. The use of a "stop flow" system for the kinetic experiments speeded the acquisition of data and allowed for a much higher number of data points to be collected per kinetic run.

CONCENTRATION VALUES IN CIGARETTE SMOKE

The concentration values calculated for nitrogen oxides (Table 3) are 2.2 times higher than the reported values because the experiments described here were done using a continuous flow system, which uses all the smoke generated by a cigarette, while previously reported values are calculated based on a puff protocol, which uses only the volume of smoke that would be inhaled by the smoker. The values obtained for the concentration of NO in research cigarettes are in close agreement with those reported in the literature (after adjustment), which shows the validity of the data obtained by the FTIR method developed in this study. For a few commercial cigarettes the calculated
concentration values do not match the reported concentration values (Table 3). These changes may be due to changes in the composition and treatment of the tobacco in the different brands since 1981 (the year the reported values were measured).

The FTIR method developed here has several advantages over the method most frequently used in the literature (chemiluminescence). The most distinct advantage is that the FTIR method is a real time analysis. In addition, several components can be determined simultaneously, even in the presence of overlapping bands, and the FTIR method is free of the interferences found in the chemiluminescence method. Another advantage is that use of the FTIR method can differentiate between NO and NO₂, and other components if desired, while the chemiluminescence method cannot.

KINETIC STUDIES

**Study of profiles for NO disappearance, and NO₂ appearance and disappearance:** The comparison of the profiles for the disappearance of NO and the appearance and disappearance of NO₂ in the different systems studied was the most important application of the method developed in this dissertation. All the systems studied were compared to gas phase cigarette smoke (Figure 17). In general the results obtained for NO₂ are of a better quality, because of the much higher extinction coefficients for NO₂ compared to
NO (at least one order of magnitude). This is especially apparent when looking at the data with concentrations of NO below 120 ppm.

**NO in air:** First, we may compare cigarette smoke (Figure 17) and the NO/air system (Figure 18); the disappearance of nitric oxide in cigarette smoke is faster compared to the NO/air system. There is no consumption of nitrogen dioxide in the NO/air system, which is the expected result since at concentrations below 1000 ppm the equilibrium of NO$_2$ with N$_2$O$_4$ is insignificant. The profile obtained for the oxidation of NO in air (Figure 18) is similar to the ones reported in the literature$^{11,38,94}$, and the calculated third order rate constant ($4.0 \times 10^5$ l$^2$mol$^{-2}$min$^{-1}$) is similar to the reported value ($4.4 \times 10^5$ l$^2$mol$^{-2}$min$^{-1}$)$^{11}$.

The differences between the NO/air system and the cigarette smoke system are in agreement with the steady state model$^8$ that predicts a faster oxidation of NO and consumption of NO$_2$ in cigarette smoke.

**NO/air/isoprene system:** The fact that reactive olefins increase the rate of oxidation of NO in air$^{12,99}$ and that the model for the continuous production of free radicals in gas phase cigarette smoke is based in NO/air/isoprene, made the NO/air/isoprene system the first one studied (Figure 19). In the NO/air/isoprene system the
rate of disappearance of nitric oxide is almost as fast as in cigarette smoke, but the rates of formation and consumption of nitrogen dioxide still differ from those for cigarette smoke. This was expected, because such a simple model can only mimic certain features of real cigarette smoke. The rate of disappearance of nitric oxide is close to that in cigarette smoke because, as predicted in the mechanism (eq 4, in the introduction), NO in addition to being consumed in the oxidation step, reacts with the peroxyl radicals formed in the reaction of isoprene with NO₂. The rate of disappearance of NO₂ in this system is slower than that for cigarette smoke, because NO₂ can react with several other components in cigarette smoke but not in this system.

**NO/air/methanol:** The formation of methyl nitrite in cigarette smoke, as shown in Figure 13, leads us to suggest that methanol could be an important contributor to the model. It is difficult to follow the formation of methyl nitrite, because it is present in low concentrations and the infrared absorption for this type of compound is relatively weak. A study of the NO/air/methanol system (Figure 19) shows almost the same rate of oxidation for NO as that of NO in air alone, which is the expected result (there is no formation of the reactive intermediate alkyl and peroxyl radicals). The behavior of the NO₂ in the
NO/air/methanol system is in between that found in the NO/air and the NO/air/isoprene systems. This also is expected, because the only reaction of NO\textsubscript{2} that can occur is with methanol to form methyl nitrite. In contrast, NO\textsubscript{2} can disappear by several reactions in the NO/air/isoprene system.

**NO/air/methanol/isoprene:** The preceding results led to the study of the NO/air/methanol/isoprene system (Figure 20). Of the different systems studied, the NO/air/methanol/isoprene system is the one that simulates most closely the NO\textsubscript{x} concentrations in cigarette smoke, especially with regard to the rate of disappearance of nitric oxide. The model is not a perfect fit for the data from cigarette smoke, but it is very similar, especially in consideration of the large number of components found in cigarette smoke that can react either with NO\textsubscript{2}, or with the intermediate radicals formed in the steady-state mechanism. This is a more realistic model for the NO\textsubscript{x} chemistry in cigarette smoke than the model proposed originally\(^8\).

It is remarkable that by using only four components (NO, oxygen, methanol, and isoprene) it is possible to get such a good model for a system as complicated as cigarette smoke.
Other models: Combinations of the systems described above with acetaldehyde and acrolein did not give any significant change in the results. This was not very surprising, because changes were not found comparing the NO/air system with the NO/air/acetaldehyde, or the NO/air/acrolein systems. Analyzing the differential spectral kinetic profiles of gas phase cigarette smoke (Figure 13), no major changes are observed in the region corresponding to the carbonyl absorption (1700 cm⁻¹), which indicates very low reactivity for any carbonyl-containing component found in the gas phase cigarette smoke.

Rate constants: The rate constants calculated for the different systems are difficult to analyze further (Table 4), because of the slow reaction rates and the fact that all the calculated values have the same order of magnitude.

The rates of oxidation of nitric oxide are easier to compare than those for the appearance and disappearance of nitrogen dioxide, because the reactions are very straightforward. Nitrogen dioxide, being a very reactive compound, has more routes to follow. Still we can observe the same trends in the numerical values (Table 4) as found by visual comparison of the data (Figures 17 to 25).

Only two values of rate constants for the oxidation of nitric oxide in cigarette smoke were found in the literature.
(Table 4): The value reported by Borland et al.\textsuperscript{39} 
(2.7 \times 10^{-3} \text{ sec}^{-1}) is very small (even smaller than the rate of oxidation of NO in air), and it was obtained using chemiluminescence. Chemiluminescence is a non-continuous method of analysis of NO, which the authors acknowledge as a problem. The second value is by the same group, based in the data published by Vilcins and Leppard\textsuperscript{46}. This value (7.0 \times 10^{-3} \text{ sec}^{-1}) is larger than any of the values for the rate constant found in the FTIR experiments, but this value was calculated from relative absorbances estimated from a printed plot\textsuperscript{39}.

\textbf{Comparison of kinetic profiles with original model:}

One of the most important features of the original ESR studies that led to the steady state model\textsuperscript{7,8} was that maximum spin adduct yields were not observed until the smoke was at least one minute old; the proposed mechanism suggested that most of the radicals formed arose from reactions from NO$_2$. The profiles of NO$_2$ in the different systems (Figures 15-25) show the time when the concentration of NO$_2$ reaches a maximum, and this value can be compared with the time for the maximum concentration of spin adducts (about 100 seconds)\textsuperscript{9,10}. Both the NO/air/isoprene and the NO/air/methanol systems (Figure 19-20) show maximum concentrations of NO$_2$ at about 400 seconds, which is more than three times the time of occurrence of the maximum
concentration of spin adducts, or NO\textsubscript{2} in cigarette smoke. In contrast, both cigarette smoke (Figure 17) and the NO/air/isoprene/methanol model (Figure 21) show maximum concentrations of NO\textsubscript{2} at about 120 seconds, closer to the time (100 scc) when the spin adduct concentrations are maximum. In addition, the profile for appearance and disappearance of NO\textsubscript{2} in both systems is very similar to the profile for the spin adduct concentrations against time\textsuperscript{a}. These two facts (similar time course, and similar maxima) give more evidence to support the steady state mechanism.
CONCLUSIONS

A FTIR method was developed for the simultaneous analysis of NO and NO\textsubscript{2} in cigarette smoke and in model systems. The method also allows the simultaneous determination of other components.

Using the developed method, the steady-state mechanism for the production of free radicals in gas phase cigarette smoke was substantiated. In addition a more realistic model, consisting of a mixture of NO/methanol/isoprene/air, was proposed. The concentrations of nitric oxide and nitrogen dioxide in the new proposed model follow time courses that duplicate very closely the ones found for the same components in gas phase cigarette smoke.
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VITA

Rafael Cueto

He was born in Bogota, Colombia, on July 18, 1955. He received high school diploma from Gimnasio Moderno, Bogota, Colombia, December 1973. He graduated with a degree in Chemistry from the Universidad Nacional de Colombia, Bogota, Colombia, in April 1981. He entered the Chemistry Department at Louisiana State University in the Fall of 1983. He is a member of the American Chemical Society, The Society for Applied Spectroscopy, and the Asociacion Colombiana de Quimicos.
Candidate: Rafael Cueto

Major Field: Chemistry

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Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Robert J. Gale

Andrew W. Warrack

Mary O. Jruley

May 16, 1990