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QUANTITATIVE FOURIER TRANSFORM INFRARED ANALYSIS OF GAS PHASE CIGARETTE SMOKE AND OTHER GAS MIXTURES

KEY WORDS: FTIR, cigarette smoke, nitric oxide, nitrogen dioxide, free radical

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ABSTRACT

A new method for the analysis of selected components in complex gas mixtures has been developed utilizing a relatively inexpensive Fourier transform infrared spectrometer and a continuous flow gas cell. The method was used to monitor nitric oxide and nitrogen dioxide concentrations in cigarette smoke with time.

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Using multivariate least-square regression analysis, it is possible to simultaneously quantitate both NO and NO_2, even in the presence of overlapping peaks. Using this method, the oxidation of nitric oxide in the presence of isoprene in cigarette smoke and in a model system was followed with time. The method also can be applied to other compounds in smoke or to any other gaseous mixture.

INTRODUCTION

It has been known for many years that cigarette smoke contains free radicals, and it has often been assumed that these radicals are involved in smoking-induced diseases (e.g cancer[1,2,3], and emphysema[4,5]). The radicals in gas-phase cigarette smoke are very reactive and short lifetimes are expected. However, these radicals appear to survive even if smoke is aged for 5-10 minutes.[6,7] Even more surprisingly, the concentration of radicals actually increases in smoke as it ages, reaching a maximum in about 1-2 minutes.[8,9] Previous reports from this group suggest that the radicals in smoke are continuously produced in a steady-state mechanism that depends in NOx.[6,7] In this mechanism, nitric oxide (NO), which is relatively unreactive toward organic molecules, serves

as the radical reservoir. The mechanism postulates that NO slowly oxidizes to the reactive nitrogen dioxide (NO_2) (eq 1), which adds to unsaturated compounds present in the smoke (e.g. isoprene), producing alkyl radicals (eq 2) that rapidly add oxygen to form peroxyl radicals (eq 3).[6,7] These peroxyl radicals then rapidly react with another NO to form alkoxyl radicals and NO_2.

$$NO + 1/2\ O_2 \xrightarrow{\text{Slow}} NO_2 \qquad (1)$$

$$NO_2 + \text{>C=C<} \longrightarrow NO_2\text{-C-C}^{\bullet}\ (R^{\bullet}) \qquad (2)$$

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet} \qquad (3)$$

$$RO_2^{\bullet} + NO \longrightarrow RO^{\bullet} + NO_2 \qquad (4)$$

It is important to know the kinetic behavior of NO and NO_2 in both cigarette smoke and model systems in order to confirm this mechanism. Vilcins and Lephardt[10] have published a preliminary analysis of NO and NO_2 in cigarette smoke using FTIR; however, their results are of limited utility since they use only relative absorbances for their studies. Borland et al.[11] reported the time course for the disappearance of NO both in whole smoke and in filtered gas-phase smoke using a chemiluminescence method that does not permit continuous monitoring of concentrations. They remark on the importance

of a method to monitor the change in NO concentration continuously.

We here report a method that allows the simultaneous determination of NO, NO_2, and isoprene in gas phase cigarette smoke and in a model system, using continuous flow gas phase Fourier transform spectrometry. The method can be applied to multicomponent analysis of other gaseous mixtures as well.

MATERIALS AND EQUIPMENT:

Commercial NO (Matheson) was used for the model systems. Matheson's certified standards of NO (554 ppm) in helium, and NO_2 (520 ppm) in helium were used for calibration. Isoprene (Aldrich "gold label"), and hexatriacontane (Sigma) were used without further purification.

Research cigarettes (1R1) were obtained from the University of Kentucky, Tobacco and Health Research Institute. They were conditioned by storing in a desiccator over a saturated aqueous solution of ammonium nitrate (12% relative humidity) for at least 48 hours.

FTIR spectra were obtained using an IBM IR/32 FTIR spectrometer equipped with a DTGS detector, a 20 cm gas cell with hexatriacontane-coated NaCl windows, and a IBM 9000 data system. Some of the experiments were carried out using

the upgraded IBM IR/44, which uses an IBM-AT computer. Typical experiments were performed using 4 cm^{-1} resolution, 5-10 scans, Happ-Genzel apodization, and automatic correlation. Interferograms were collected, fast Fourier transform executed, baseline corrected, and water subtracted in some cases. For the multiple component quantitative analysis, the QUANT software package from IBM Instruments, was used. This software uses multivariate least-square regression analysis making it possible to simultaneously quantitate several components, even in the presence of overlapping peaks.

Preparation of NO/air and NO/air/isoprene Mixtures

Mixtures of NO (600 to 800 ppm) and isoprene (about 700 ppm) in air were prepared using the apparatus shown in Figure 1. This is an improvement on a similar apparatus we have already described;[7] we have added mass-flow controllers and check-valves, to allow a more precise metering of the gas mixtures. Total flow rates of 250 mL/min were used in all the experiments.

Coating of Gas-cell Windows

It has been reported[12,13] that NO_2 reacts with the NaCl of the gas-cell windows, producing NOCl (1790 cm^{-1}), and nitrate (1340 and 840 cm^{-1}). To avoid this problem, the procedure of coating windows with commercial paraffin reported by Carlson

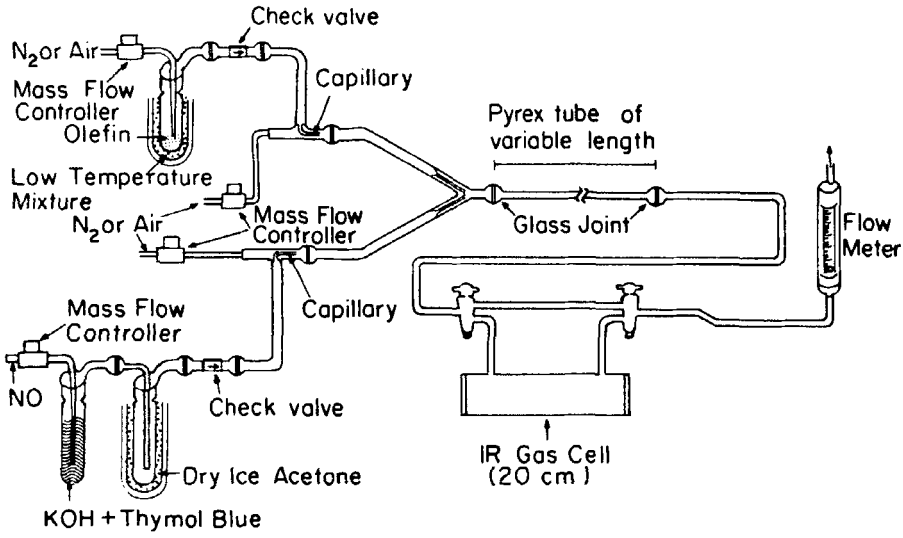

FIGURE 1.
Apparatus used to mix NO with air and isoprene.

et al.[13] was tried. However, it was found to be unsatisfactory, apparently because the paraffin wax contains unsaturated bonds that react with NO_2. We found that hexatriacontane, which can be obtained inexpensively and in high purity, can be used. The coating procedure involves gently warming the windows with a thin layer of the powdery hexatriacontane on a hotplate until the hydrocarbon melts; the pool is then spread uniformly on the window by rolling a hot glass rod across it. This simple method gives a uniform thin film that lasts throughout several experiments for concentrations of NO_2 up to 800 ppm.

Calibration

The calibration for NO and NO_2 was made using the standards, diluting with helium for lower concentrations. Isoprene was calibrated indirectly by gas chromatography (GC); infrared absorptions were measured using the gas cell, and then 5 ml samples were taken and injected into the GC to determine the concentration. GC standards were made using the procedure described by Cotabish et al.[14]

Procedure for Smoking Cigarettes

Cigarettes were smoked using two different protocols:

i) A puff protocol: puffs (35 cm^3) 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: The smoke stream was pulled through the cigarette and through a Cambridge filter, using a water aspirator, and finally through the gas cell at a flow rate of 250 ml per minute. The cell was closed 90 sec after the cigarette was lit, and collection of data was started.

RESULTS AND DISCUSSION:

Figure 2A shows the FTIR spectrum of a mixture of NO/air/isoprene. The different bands used for the quantitation

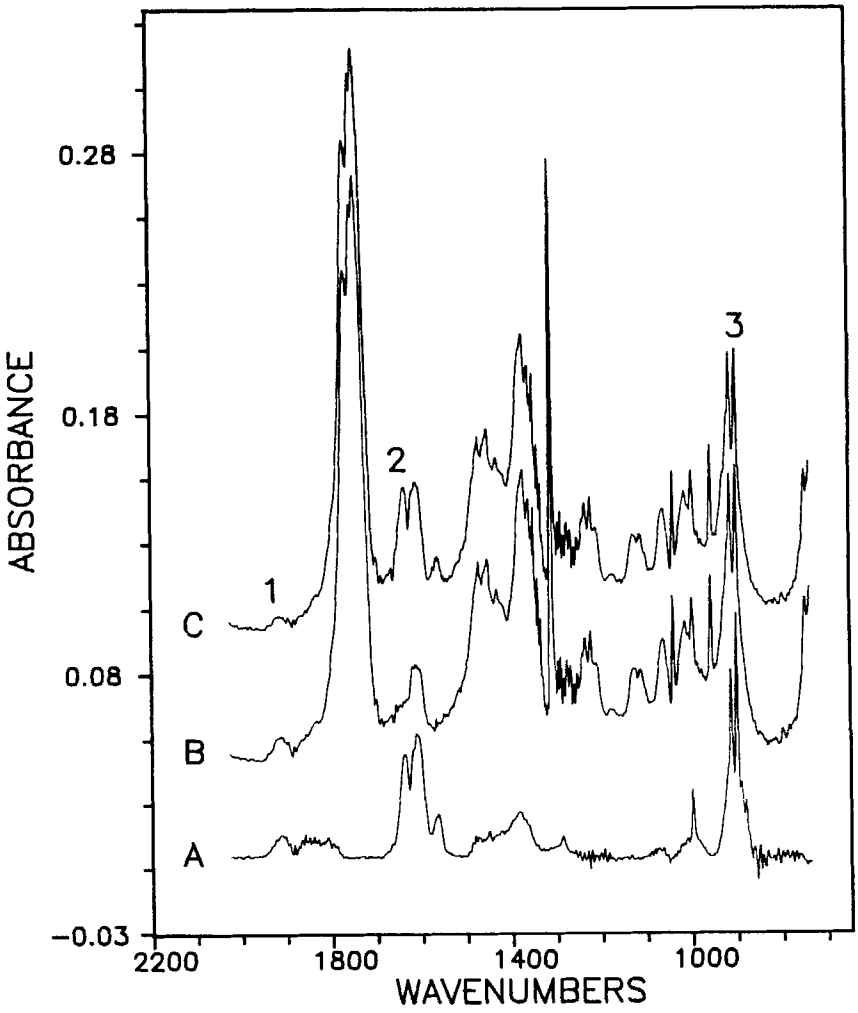

FIGURE 2.

A: FTIR spectrum of a mixture of NO(700 ppm), air, and isoprene(450 ppm), aged 15 sec.
B: FTIR spectrum of 1R1 cigarette smoke aged 13 sec.
C: FTIR spectrum of 1R1 cigarette smoke aged 133 sec.
Bands shown are: 1=NO, 1905 cm^{-1}; 2=NO_2, 1628 cm^{-1}; 3=isoprene, 893 cm^{-1}. Water was subtracted from the cigarette smoke spectra.

are marked: band 1, 1905 cm^{-1} for NO; band 2, 1628 cm^{-1} for NO_2, and band 3, 893 cm^{-1} for isoprene. These are characteristic frequencies for each component, and relatively free of overlapping in the systems studied.

Figure 2B shows the FTIR spectrum of 1R1 cigarette smoke (13 seconds old, water subtracted); the NO and isoprene bands can be clearly identified. Figure 2C shows the same smoke 120 seconds later. The decrease in intensity of the NO band at 1905 cm^{-1} and the appearance of the band for NO_2 at 1628 cm^{-1} can be seen.

Figure 3 shows the profiles for the appearance of NO_2 and the disappearance of NO in NO/air, NO/air/isoprene, and in 1R1 cigarette smoke. The NO/isoprene/air system and the NO/air system have been studied and explained by Glasson and Tuesday[15] who reported that "in the presence of the diene, the nitric oxide oxidation rate increases with time indicating that the reaction is autocatalytic". A comparison of the NO_2 profiles shows a much faster consumption of NO_2 in cigarette smoke than in the NO/air/isoprene model system. This may be due to the reaction of NO_2 with other components found in cigarette smoke in addition to isoprene. For example, the reaction between NO_2 and methanol is reported to give methyl nitrite by Vilcins and Lephardt.[10]

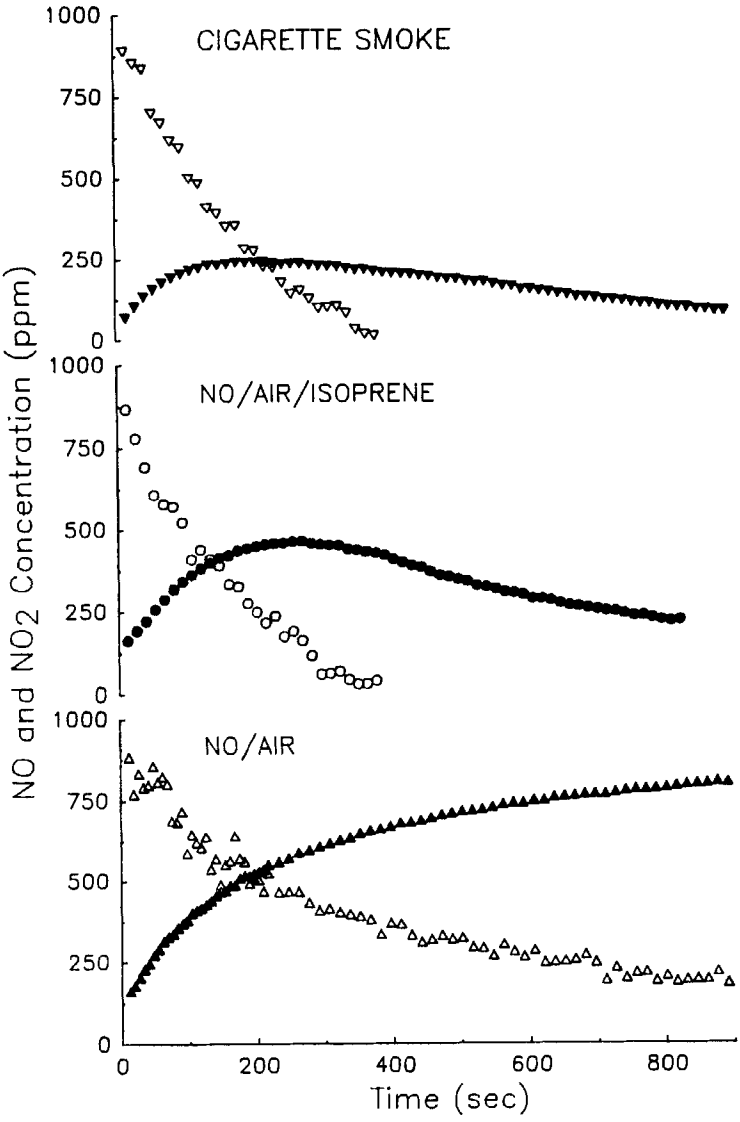

FIGURE 3.
Profiles for the appearance of NO_2 and disappearance of NO, for NO/air and NO/air/isoprene mixtures, and 1R1 cigarette smoke. Filled points correspond to NO_2, and open points to NO.

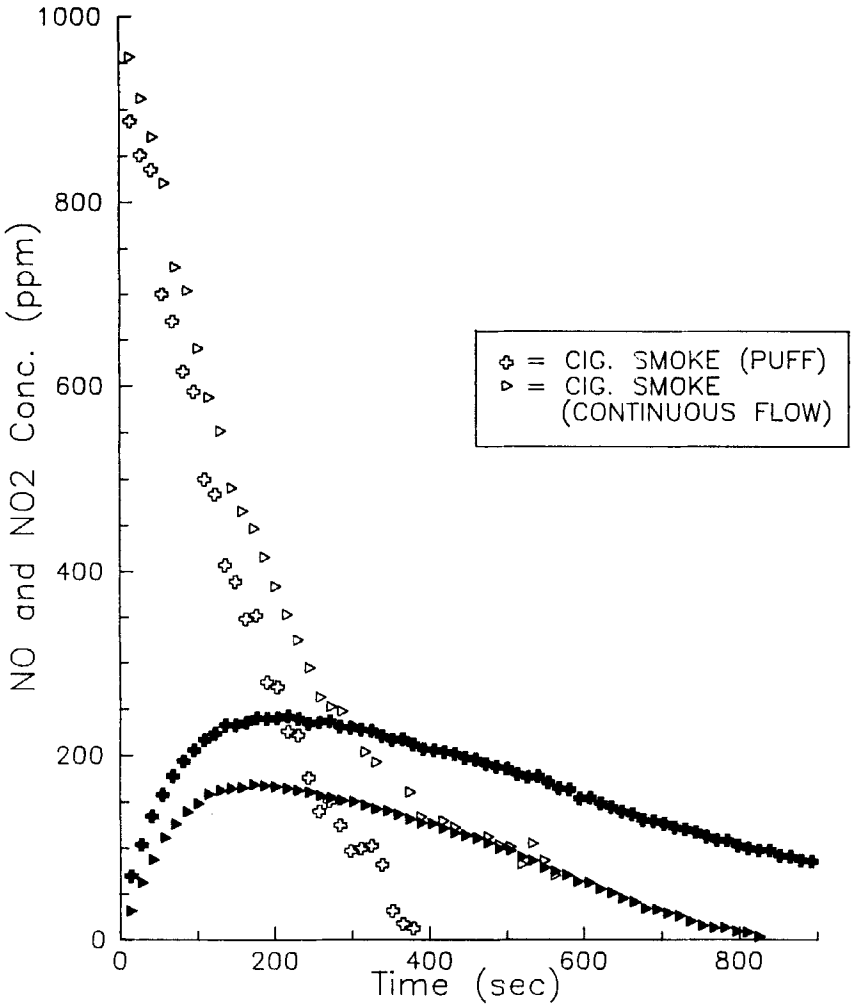

FIGURE 4.
Profiles for the appearance of NO_2 and disappearance of NO in cigarette smoke using the puff protocol and the continuous flow protocol. Filled points correspond to NO_2, and open points to NO.

Figure 4 shows the profiles for the disappearance of NO_2 and the appearance of NO in cigarette smoke, using both the puff and the continuous flow protocols. The difference in the results probably is due to deposits of tar on the gas cell when using the continuous flow system, which could quench some of the radicals formed and reduce the rate of oxidation of NO. These data are comparable to the results obtained by Borland et al.,[11] who found slower rates of disappearance of NO in whole cigarette smoke compared to gas phase smoke. When using the flow system with a very clean gas cell and very little flow through the cell, the data obtained are comparable to that collected using the puff protocol (data is not shown because it overlaps with data in figure 4).

CONCLUSION

This communication reports the development of a general FTIR method for following concentration changes in complex gas mixtures, and the application of the method both to cigarette smoke and to NO/isoprene model systems. Because the rates of appearance of NO_2 and disappearance of NO in cigarette smoke do not follow exactly those found in the NO/air/isoprene model, we are investigating other gas mixtures (e.g. methanol/isoprene/NO/air and isoprene/acrolein/NO/air) using the same method.

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