# Characterization of cigarette smoke using chemical ionization time-of-flight mass spectrometry

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## INTRODUCTION

The adverse health effects associated with cigarette smoking, combined with its widespread usage, has motivated a large number of chemical, toxicological, and epidemiological studies of the subject of cigarette smoke over many decades. Although the chemicals that comprise tobacco smoke had already been identified by the 1950's, research activity on the subject has only increased since then. The largest subset of these studies focuses on understanding the biological effects of specific chemical components. Another subset focuses on understanding the fundamental chemistry associated with the formation and evolution of specific chemical components. Yet another aims to quantify the mass of cigarette smoke components in indoor and outdoor urban environments. At least the latter two subsets define a need for instrumentation that can determine the chemical properties of cigarette smoke in real time.

In the present study, we apply proton transfer ionization and time-of-flight mass spectrometry (TOF-MS) to the real-time analysis of cigarette smoke. The objective of the study is to explore the potential of this relatively soft ionization technique in rapidly identifying chemical differences among cigarette types, smoke streams (mainstream or sidestream), and phase (gas or particle).

## EXPERIMENTAL SECTION

Cigarette smoke aerosol is generated using a Walton smoke machine, which was designed to produce mainstream and sidestream smoke in a highly reproducible manner. Mainstream smoke samples are obtained by drawing air through the cigarettes in 2-second puffs every 60 seconds.

Each puff consists of 35 mL of flow per cigarette. The collected mainstream smoke is diluted by an 84 mL/s flow of clean air, yielding a dilution ratio of 140 for one cigarette. The flow is then passed through a 27 L residence chamber where the mixing time is approximately 2 minutes. The chemical analyzer samples from the residence chamber at a flow rate 0.8 L/min. Sidestream smoke samples are obtained during an identical puff protocol, but the sample aerosol is collected using a funnel placed roughly 10 cm from the ends of the smoldering cigarettes and aspirating a flow of 13.5 L/min. The sidestream sample flow is diluted by air entrained into the funnel along with the smoke, during which the dilution ratio is estimated to be on the order of 2200, based on cigarette plume calculations. The entrained sample is further diluted by a 120 L/min flow, resulting in total dilution ration of 22000. The collected sidestream aerosol sample is also held in the 27 L residence chamber prior to introduction into the CIMS.

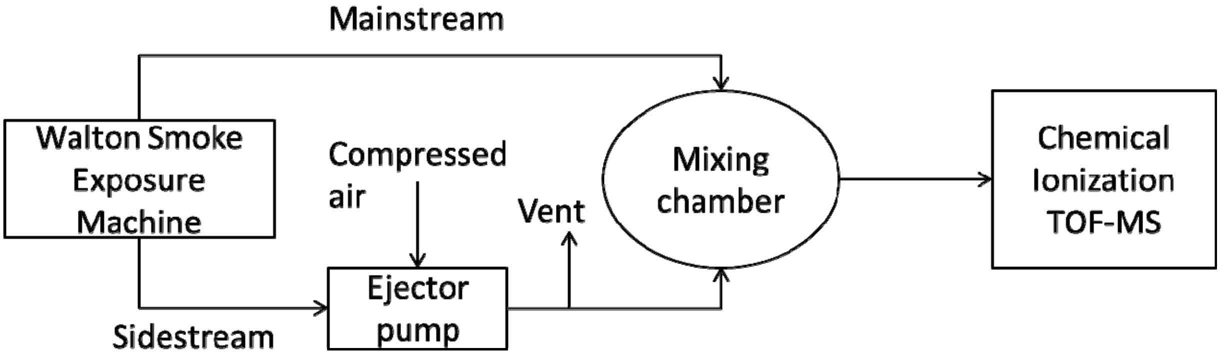

Figure 1. Schematic diagram of the experimental setup.

Two standard cigarette types developed at the University of Kentucky were analyzed. These include the 3R4F low nicotine standard (0.73 mg Nicotine per cigarette, 9.40 mg tar per cigarette), and the 1R5F ultralow nicotine standard (0.17 mg Nicotine per cigarette, 1.67 mg tar per cigarette). Mainstream and sidestream samples were analyzed for both standards. Since the mainstream was an intermittent source (i.e. sample generated only during puffs), three cigarettes were consumed at a time. Sidestream samples included one cigarette at a time.

Sampling the gas-phase or the particle-phase from cigarette smoke is far from trivial due to the interaction between the two phases that generally results in partitioning of semi-volatile compounds. In the present study, the particle/gas interaction is maintained by analyzing the gas phase while simultaneously collecting particles onto a Nichrome filament. Particles that enter the instrument are either collected by diffusion onto the filament or removed by coarse pumping of the system. The collected particles are then analyzed by thermal desorption at 500$^o$C immediately after the gas-phase signal dropped below background. Mainstream particles were sampled during the consumption of 9 cigarettes, and sidestream particles were sampled during the consumption of 3 cigarettes.

## RESULTS

### *Mass spectra of gas-phase samples*

The most notable difference between the mass spectra obtained from the low-nicotine (3R4F) and the ultralow-nicotine (1R5F) cigarette standards is the size of the nicotine peak for both sidestream and mainstream samples. For the gas-phase sidestream samples, there is surprisingly little difference in the mass spectra between the cigarette types (see Figure 2) other than the size of the nicotine peak. Other prevalent compounds in both sidestream spectra include isoprene, benzene, pyridine, 2-methylfuran, toluene, 3-ethenylpyridine, xylene, indole, naphthalene, isoquinoline, myosmine, and nicotyrine, where identification of the peaks was aided by comparison with previous studies.

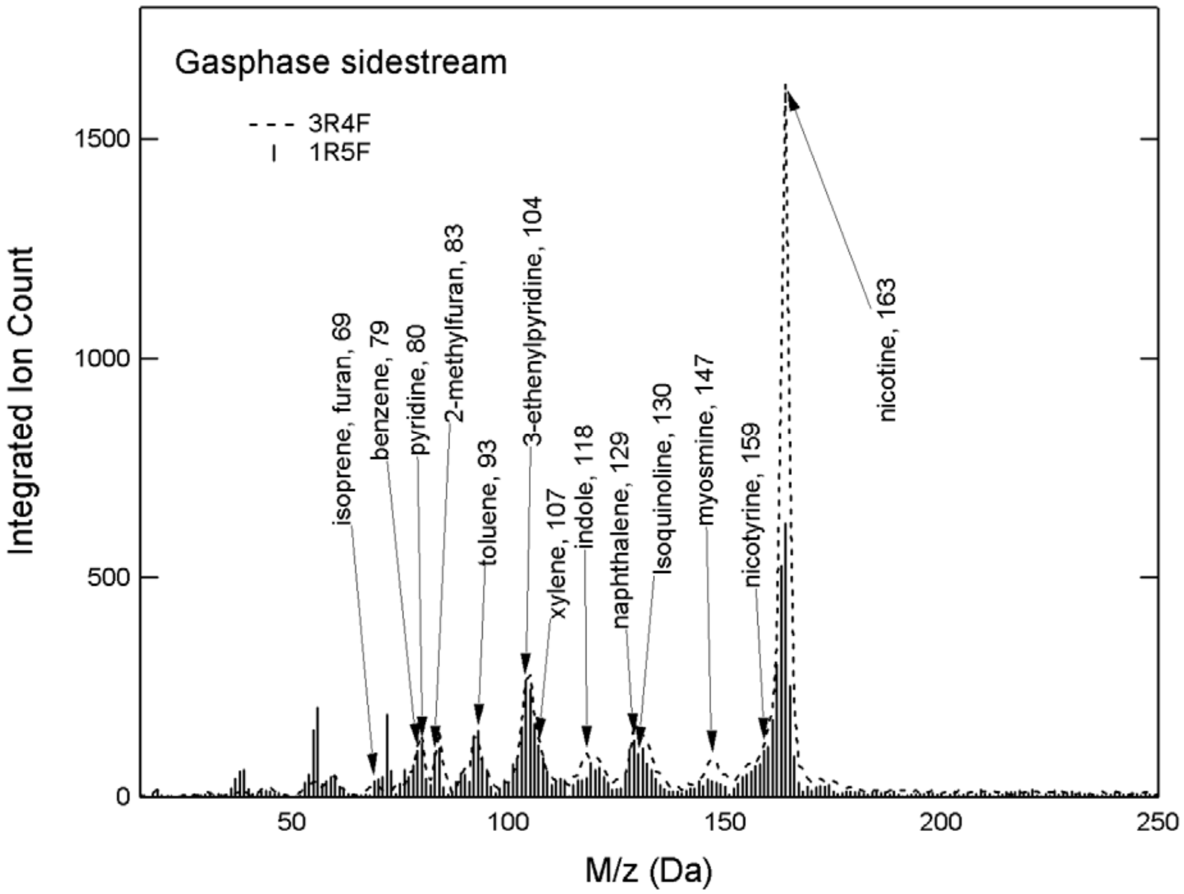

Figure 2. CIMS-TOF mass spectra of gas-phase sidestream samples from both cigarette types.

*Mass spectra of particle-phase samples*

The mass spectra of the particle-phase for both cigarette standards and both sample streams are shown in Figure 3. Once again, the most common ion is nicotine and, as expected, the condensed phase contains an almost continuous range of ion masses heavier than nicotine. Also prevalent in all of the particle-phase spectra are nicotyrine, myosmine, isoquinoline, naphthalene, indole, and 3-ethenylpyridine, thereby demonstrating the gas/particle partitioning potential of these lower molecular weight compounds. A notable feature of Figure 3 is the difference in nicotine content between the low and ultralow cigarettes, which is only apparent in the mainstream samples. Sidestream particle-phase nicotine content is comparable between cigarette types. This is in direct contrast to the gas-phase sidestream spectra, which exhibit significantly higher nicotine content in the 4F cigarette.

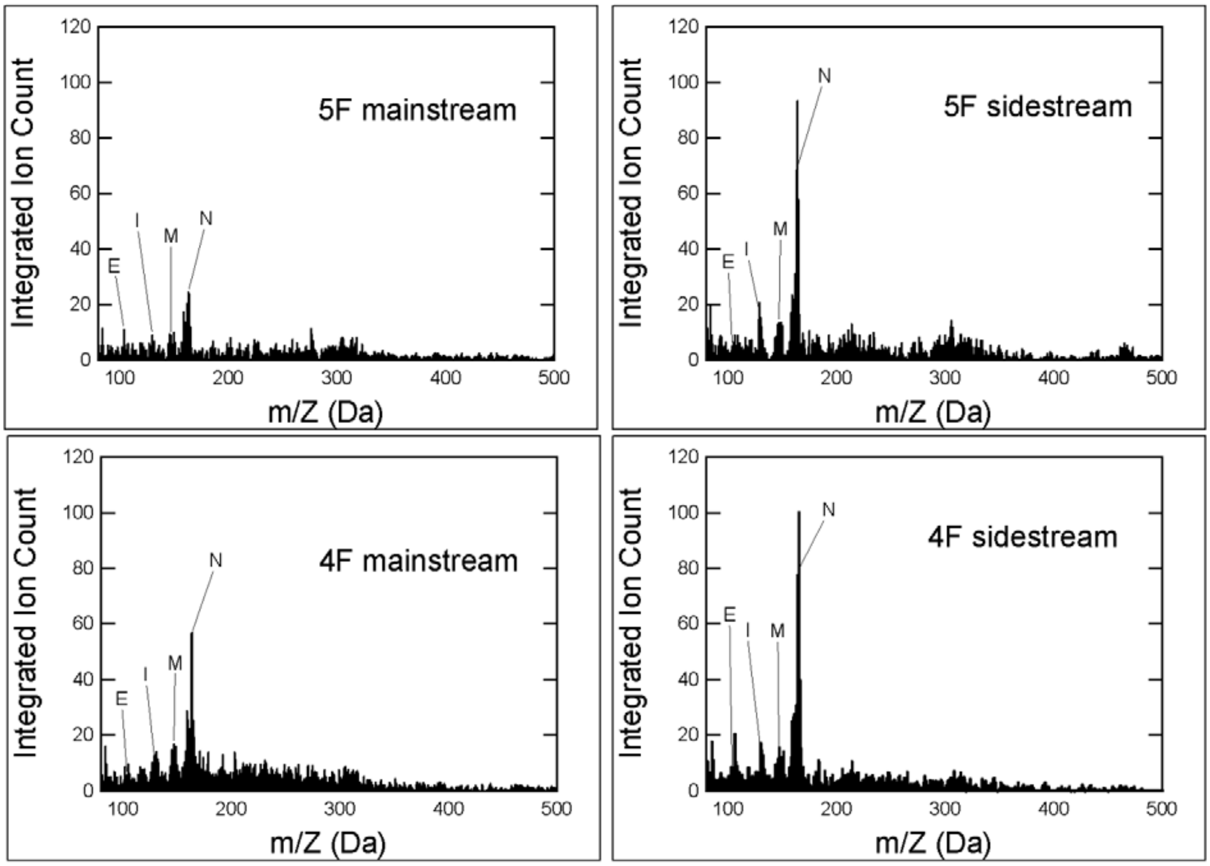

Figure 3. CIMS-TOF spectra of thermally desorbed particles from mainstream and sidestream smoke for both cigarette types. The labeled prominent peaks are 3-ethenylpyridine (E), isoquinoline (I), myosmine (M), and nicotine (N).

## CONCLUSIONS

Chemical ionization TOF-MS was applied to the analysis of mainstream and sidestream cigarette smoke samples generated from a Walton smoke machine for University of Kentucky 3R4F and 1R5F cigarette standards. The gas phase was analyzed in real-time during collection of the particle phase onto a nichrome filament. The particle phase was thermally desorbed for analysis immediately after the gas-phase analysis was complete. The expected differences in nicotine content between the low and ultralow nicotine cigarette standards were resolved in both phases. In addition to nicotine, gas-phase species detected in significant amounts in the sidestream samples include benzene, toluene, isoprene, pyridine, 3-ethenylpyridine, xylene, naphthalene, isoquinoline, myosmine, and nicotyrine. Mainstream gas samples exhibited different signatures, dominated by acetaldehyde, acetone, pyrrole, pyrroline, pyrrolidine, and phenolics. Concentrations of the gas-phase compounds in the mainstream were in good agreement with previous studies. Spectra obtained for the particle-phase contain a complex mixture of high-molecular weight compounds, and lower molecular weight semi-volatile compounds, such as nicotyrine, myosmine, isoquinoline, naphthalene, indole, and 3-ethenylpyridine. These compounds are present in the particle-phase and the gas-phase.

# In-situ analysis of the gas- and particle-phase in cigarette smoke by chemical ionization TOF-MS

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## Introduction

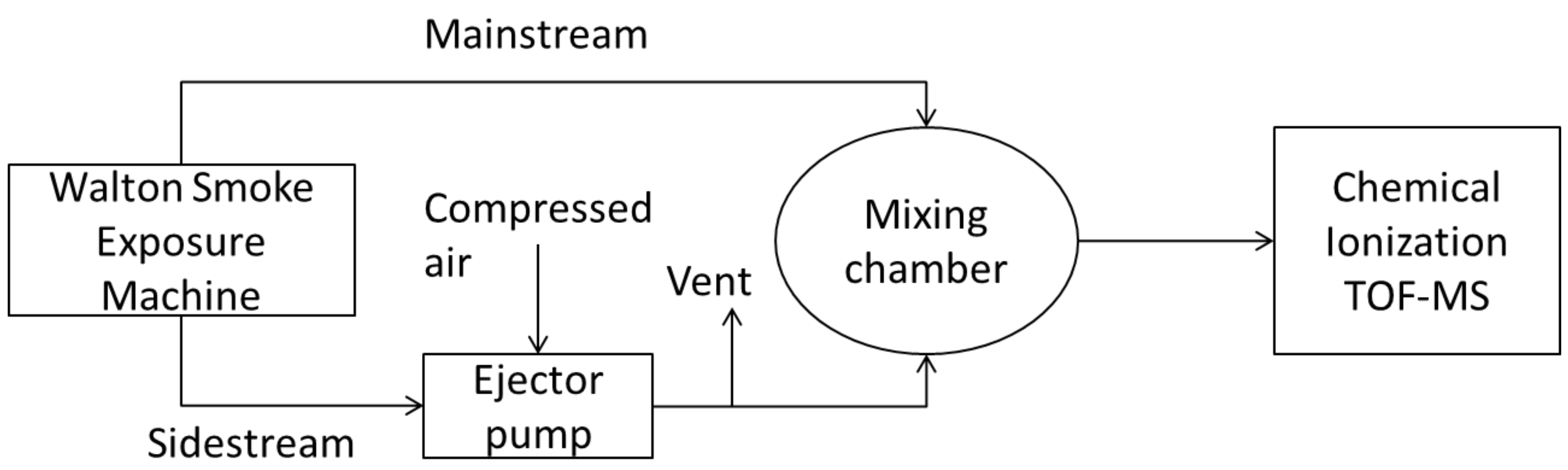
- The adverse health effects associated with cigarette smoking, combined with its widespread usage, has motivated a large number of chemical, toxicological, and epidemiological studies of the subject of cigarette smoke over many decades.
- Although the chemicals that comprise tobacco smoke had already been identified by the 1950's [1], research activity on the subject has only increased since then.
  - ✓ The largest subset of these studies focuses on understanding the biological effects of specific chemical components.
  - ✓ Another subset focuses on understanding the fundamental chemistry associated with the formation and evolution of specific chemical components.
  - ✓ Yet another aims to quantify the mass of cigarette smoke components in indoor and outdoor urban environments.
  - ✓ At least the latter two subsets define a need for instrumentation that can determine the chemical properties of cigarette smoke in real time.
- From a fundamental chemistry standpoint, recent studies have focused on the formation of persistent free radicals during pyrolysis of tobacco components [2]. Such species are stable in the atmosphere, but have damaging biological effects upon inhalation. On-line analysis techniques are required for tracking these relatively short-lived species.
- From an environmental measurement standpoint, real-time analysis not only minimizes the risk of sample modification prior to measurement, but it also allows for enhanced temporal resolution.

## Objective

- Apply proton transfer ionization and time-of-flight (TOF) mass spectrometry (MS) to the real-time analysis of cigarette smoke.
- Explore the potential of this technique in rapidly identifying chemical differences among cigarette types, smoke streams (mainstream or sidestream), and phase (gas or particle).

## Experimental

### Setup



### Material

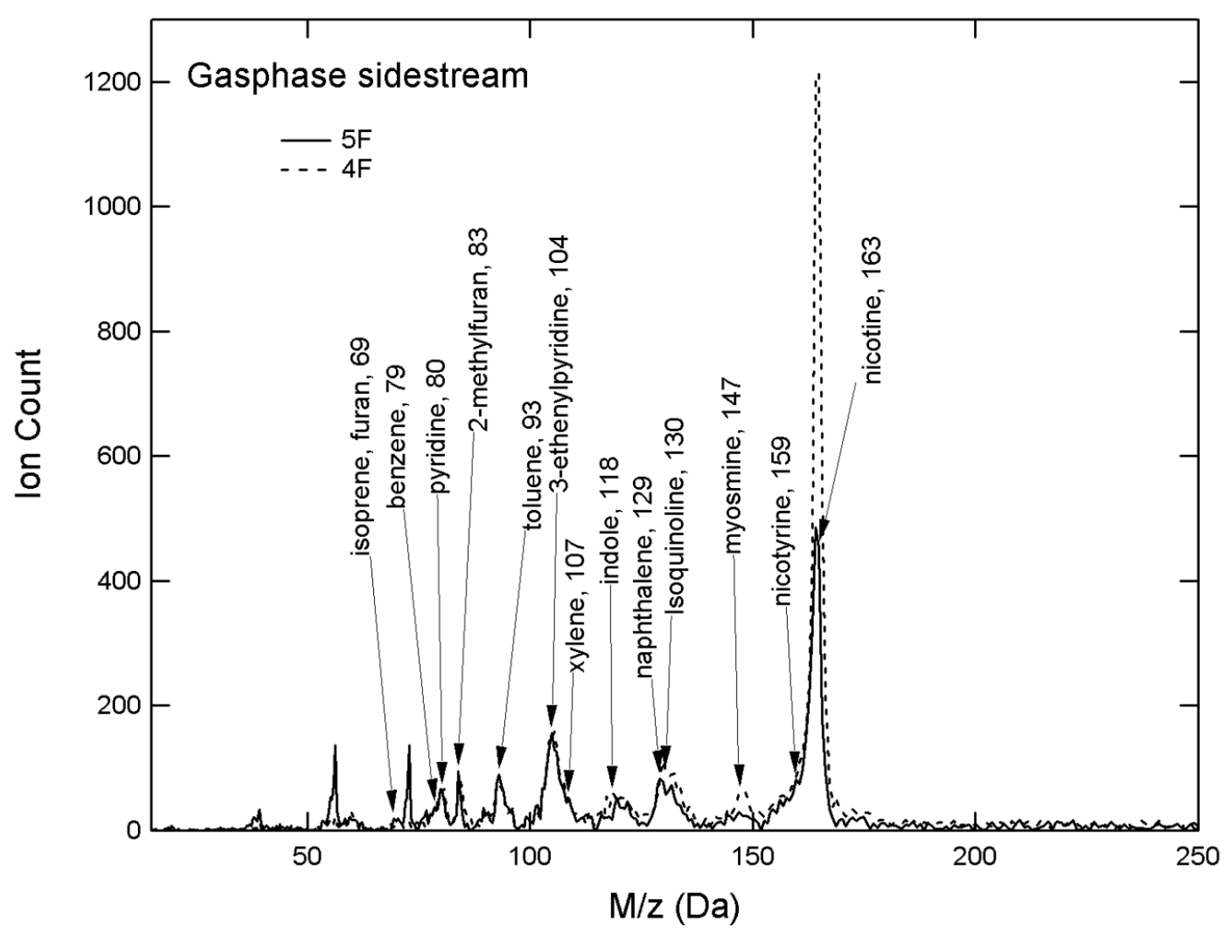
The cigarettes used in this study were research cigarettes purchased from University of Kentucky. Selected properties of the cigarettes used are summarized in the table shown below.

| Type | TPM [mg per CIG] | Tar [mg per CIG] | Nicotine [mg per CIG] |
|---|---|---|---|
| 1R5F | 2.08 | 1.67 | 0.17 |
| 3R4F | 10.9 | 9.4 | 0.73 |

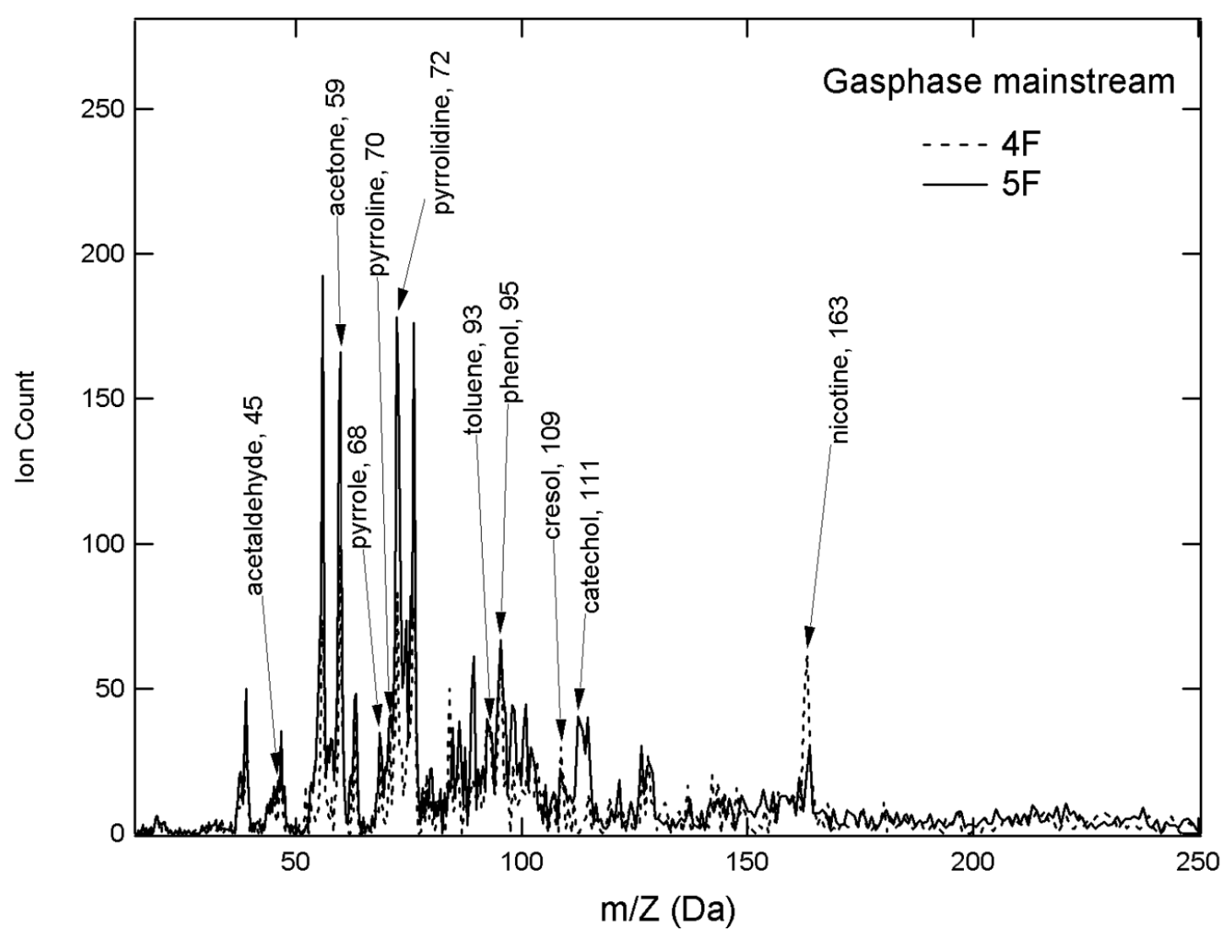
## Results

### Mass spectra of gas-phase samples

### Sidestream



### Mainstream



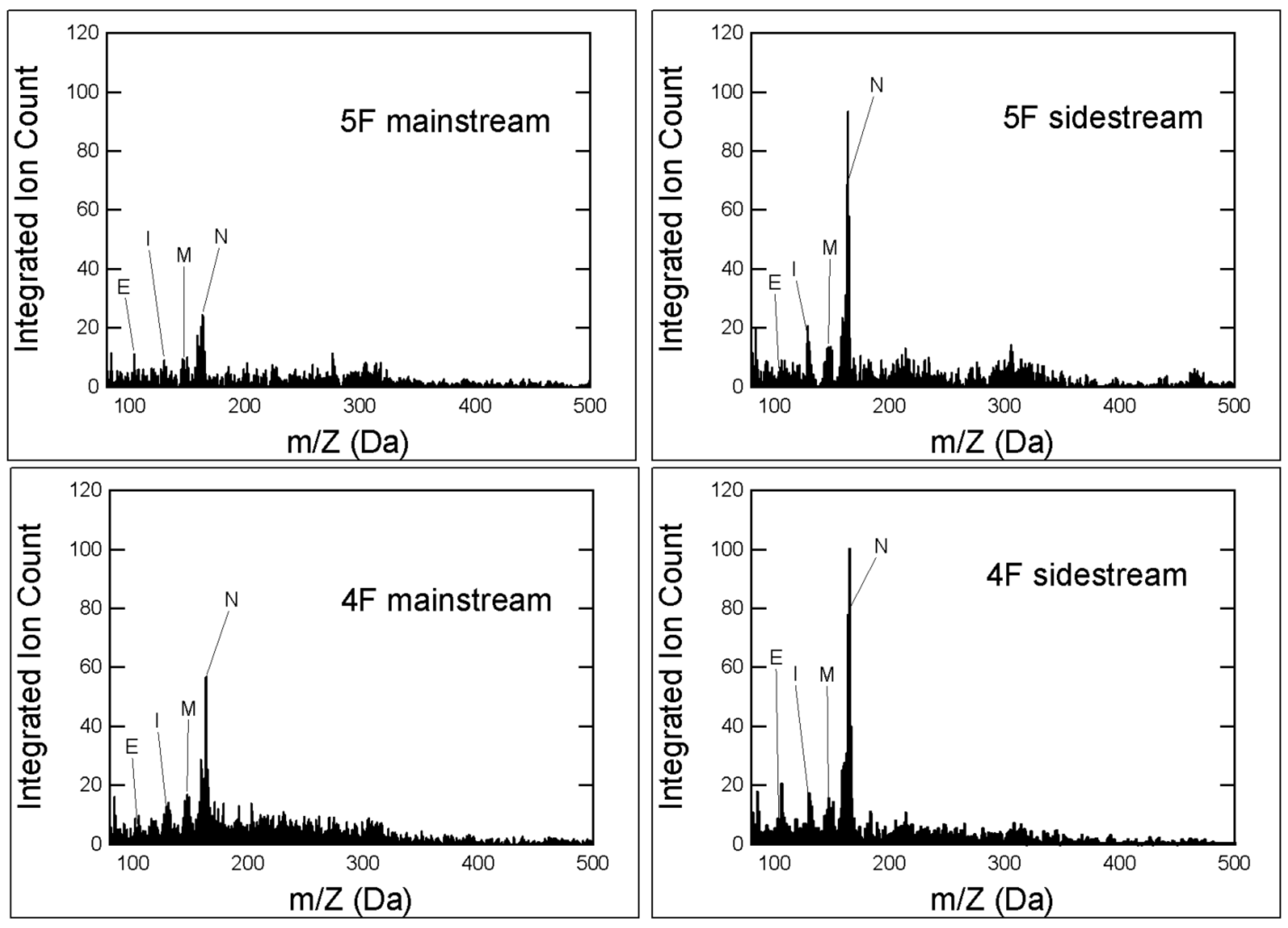
- For the gas-phase sidestream samples, there is surprisingly little difference in the mass spectra between the cigarette types other than the size of the nicotine peak.
- Due to their reduced proton affinities, small-chain alkanes that are known to be present in gas-phase cigarette smoke in comparably large concentrations [3], including methane, ethane, propane, and butane, do not react with protonated water [4] and are thus not detected in the present study.
- The mainstream samples are dominated by other N-ring compounds (pyrrole, pyrroline, and pyrrolidine), phenolics (phenol, cresol, and catechol), acetone, and acetaldehyde. These compounds may be indicative of the higher-temperature chemistry that exists during a puff.

### Mass emissions of selected gas-phase compounds in mainstream smoke

Values are estimated from the integrated ion count using the toluene calibration, and then corrected using the proton transfer reaction rate constant, k, reported by Zhao and Zhang (2004) [5]. Only compounds for which a reaction rate constant is available are listed.

| Compound | k [20] ($10^{-6}$ cm$^3$/s) | Puff Concentration (ppm) | Emission rate (mg/puff) |
|---|---|---|---|
| isoprene | 1.94 | 27.2 | 2.89 |
| benzene | 1.97 | 27.5 | 3.36 |
| toluene | 2.12 | 39.6 | 5.70 |
| xylene* | 2.3 | 9.6 | 1.60 |
| naphthalene | 2.59 | 17.5 | 3.50 |
| acetone | 3.00 | 51.2 | 4.64 |
| acetaldehyde | 3.36 | 9.9 | 0.68 |
| furan | 1.78 | 29.7 | 3.16 |
| phenol | 2.52 | 49.5 | 7.28 |
| cresol* | 2.5 | 27.6 | 4.67 |

### Mass spectra of particle-phase samples



- The most common ion is nicotine and, as expected, the condensed phase contains an almost continuous range of ion masses heavier than nicotine.
- Also prevalent in all of the particle-phase spectra are nicotyrine, myosmine, isoquinoline, naphthalene, indole, and 3-ethenylpyridine, thereby demonstrating the gas/particle partitioning potential of these lower molecular weight compounds.
- The difference in nicotine content between the low and ultralow cigarettes is only apparent in the mainstream samples.
- Sidestream particle-phase nicotine content is comparable between cigarette types. This is in direct contrast to the gas-phase sidestream spectra, which exhibit significantly higher nicotine content in the 4F cigarette.

## Conclusions and Discussion

- A benefit of the simultaneous analysis of the gas- and particle-phase in cigarette smoke is the enhanced ability to elucidate the gas/particle partitioning behavior of certain prevalent compounds in cigarette smoke, such as those determined in this study.
- The concentration of these compounds in the condensed phase may affect the toxicity of smoke particles and how they are absorbed into tissue.
- Gas-phase species present in significant amounts in the sidestream samples include benzene, toluene, isoprene, pyridine, 3-ethenylpyridine, xylene, naphthalene, isoquinoline, myosmine, and nicotyrine.
- Mainstream gas samples exhibited different signatures, dominated by acetaldehyde, acetone, pyrrole, pyrroline, pyrrolidine, and phenolics.

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[1] R. A. W. Johnstone and J. R. Plimmer, "The chemical constituents of tobacco and tobacco smoke," Chemical Reviews, vol. 59, pp. 885-936, 1959. Ingebrethsen, B. J.: Evolution of the Particle-Size Distribution of Mainstream Cigarette-Smoke during a Puff, Aerosol Sci Tech, 5, 423-433, 1986.
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**For questions, please contact heejung@engr.ucr.edu**