

# Ammonia and Its Effects Relative to Nicotine, Free Nicotine, and pH Across Cigar Subcategories

Ruth A. Ganunis, Kenneth M. Taylor\*; U.S. Food and Drug Administration, Center for Tobacco Products, Office of Science, Division of Product Science, 11785 Beltsville Drive, Calverton, MD 20705

Lavinia Mills-Herring, Christopher Hershberger, María Morel-Espinosa, Tameka Lawler, Megan McGuigan, Liza Valentín-Blasini, Clifford H. Watson; Centers for Disease Control and Prevention, National Center for Environmental Health, Division of Laboratory Sciences, Tobacco and Volatiles Branch, Atlanta, GA 30341



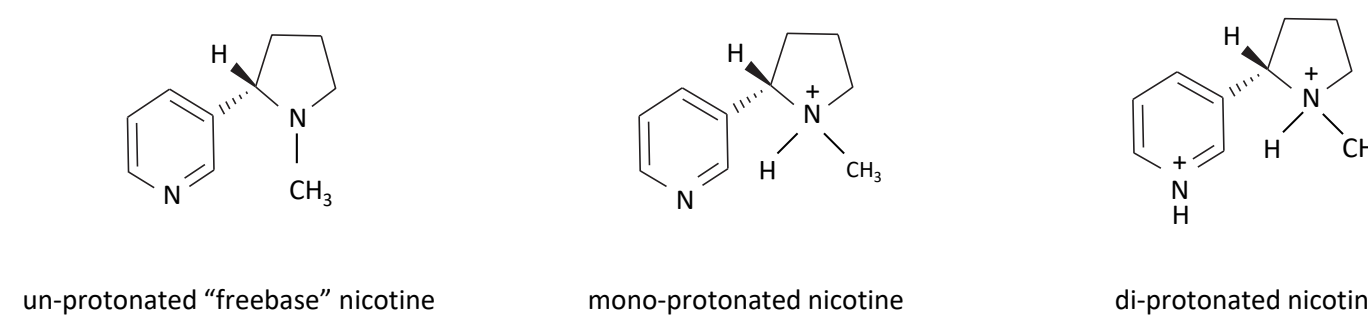
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## Abstract

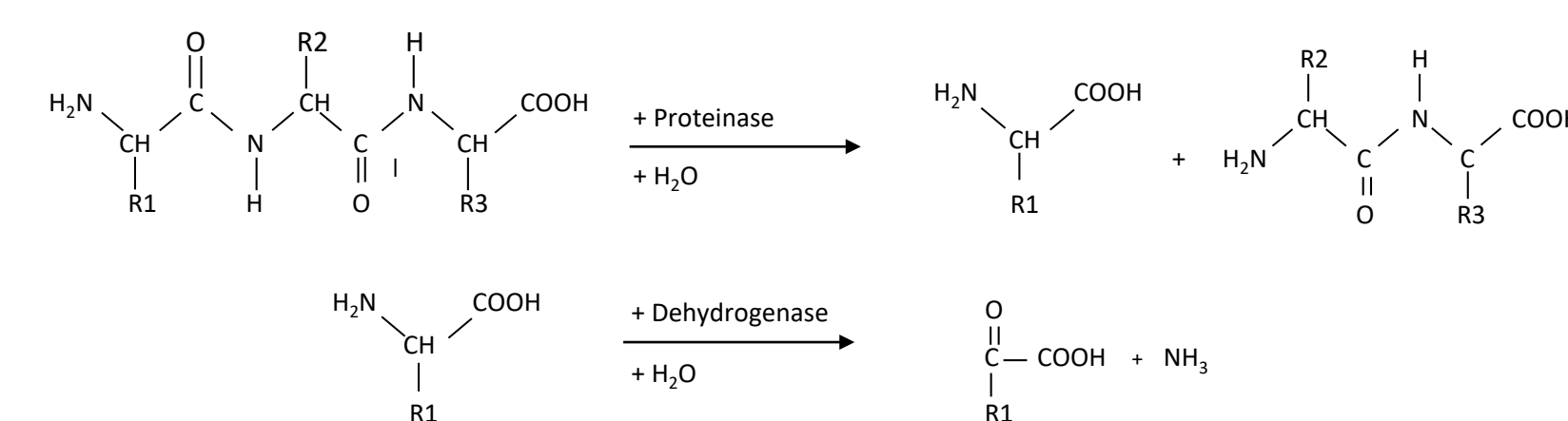
**Background.** Cigars vary in size, shape, tobacco blend, and manufacturing process. Although terminology varies, cigars are often subcategorized or labelled as cigarillos, little cigars, or large cigars. Nicotine, the addictive chemical, is present in cigars at varying levels. However, a smoker's actual exposure may not be reflected by the mean nicotine content due to the effect of pH on nicotine absorption. Nicotine in cigars exists in both the monoprotonated salt form and the unprotonated or "free" form. As the pH of the mainstream smoke becomes more alkaline, a larger fraction of the total nicotine is present in the unprotonated free nicotine form, which is more readily absorbed through the mucous membranes. Purpose. Studying the chemistry that differentiates cigar subcategories may allow for better understanding of the addictive potential of cigars. Methodology. Tobacco filler from fifty unburned cigars (7 little cigars, 19 large cigars, 16 cigarillos, and 8 pipe tobacco cigarillos) was analyzed using validated in-house methods for nicotine, ammonia, and pH. Results. The mean nicotine content is higher for pipe tobacco cigarillos (14.5 mg/g) and large cigars (13.2 mg/g) than for little cigars (11.6 mg/g) and cigarillos (11.5 mg/g). Increases in the mean ammonia content correlate with increases in mean pH across the product subcategories of pipe tobacco cigarillos (1.4 mg/g; 5.2), little cigars (2.2 mg/g; 6.3), cigarillos (3.1 mg/g; 6.3), and large cigars (3.5 mg/g; 6.7). Although the mean nicotine content of pipe tobacco cigarillos and large cigars are comparably high, due to their relatively lower ammonia content and pH, pipe tobacco cigarillos have the lowest calculated mean free nicotine content (0.02 mg/g). The mean free nicotine content increases across the other product subcategories of little cigars (0.22 mg/g), cigarillos (0.28 mg/g) and large cigars (0.75 mg/g), which corresponds to increases in mean ammonia content and mean pH. Conclusion. Our results suggest that ammonia levels, pH, and the calculated free nicotine content in the tobacco filler content all have potential utility for helping better define cigar subcategories and related addictive characteristics.

## Introduction

- Nicotine can exist in one of three forms. Under very acidic conditions it exists as a di-protonated form. In tobacco lamina, nicotine is usually present in a mono-protonated salt form, and under alkaline conditions it exists in the un-protonated "freebase" form.



- Differentiating the forms of nicotine is important in terms of addictive potential. In combustible tobacco products, nicotine in the freebase form is more readily absorbed for pharmacological activity in comparison to the other nicotine forms in the oral cavity.<sup>1</sup>
- Mainstream cigar smoke is more alkaline and contains a higher fraction of freebase nicotine than cigarette smoke.<sup>2</sup>
- Ammonia is present naturally in cigar tobacco. During the air-curing and fermentation processes, proteolysis produces amino acids which subsequently undergo oxidative deamination to generate ammonia.<sup>3</sup>



**Figure 1.** A common way to differentiate cigar subcategories is by weight.

## Materials and Methods

The cigar products included a variety of types (i.e., machine manufactured, hand rolled, with and without tips), manufacturers, flavors, and sizes (i.e., blunt, corona). For the purposes of this study, the products were subcategorized by the product labeling as a little cigar, large cigar, pipe tobacco cigar (often similar in size to cigarillos but contain tobacco that is used in pipes), or cigarillo. Cigar filler was analyzed in septuplicate (N=7).

**Nicotine.** Total nicotine concentration was measured by gas chromatography-mass spectrometry (GC-MS) using selected ion monitoring (SIM) mode as previously described.<sup>6</sup>

**Free Nicotine.** The unprotonated or free nicotine fraction of the tobacco filler was calculated with the Henderson-Hasselbalch equation, using the pKa of the pyrrolic nitrogen of nicotine (pKa = 8.02) and the experimentally determined pH and total nicotine content of the respective cigar products.<sup>7</sup>

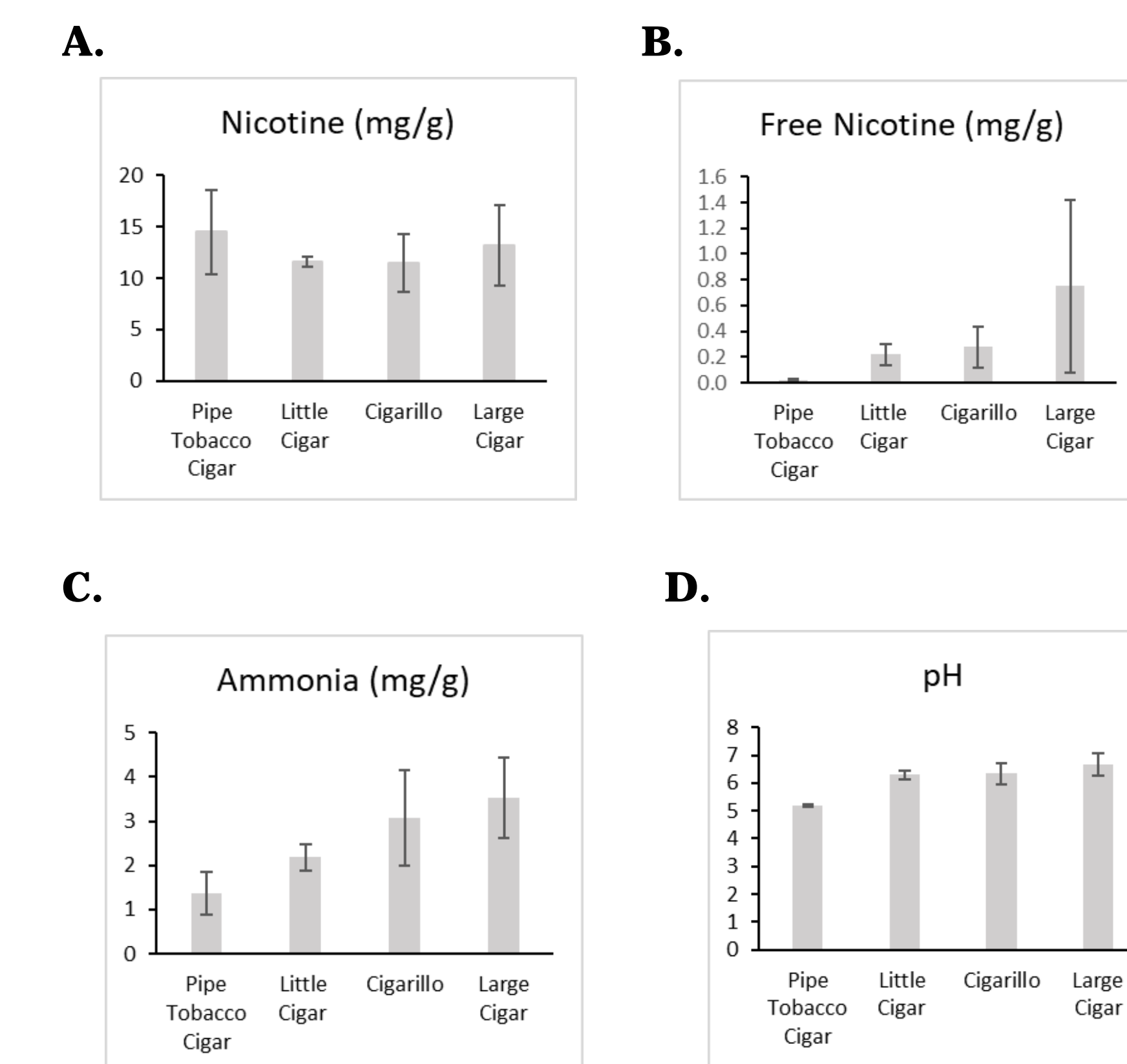
**pH.** pH was determined using a MANTECH pH meter (ManSci Inc., Orlando, Florida) as previously described.<sup>8</sup>

**Ammonia.** Ammonia concentration was measured using a validated in-house ion chromatography – conductivity detection (IC-CD) method.<sup>9</sup>

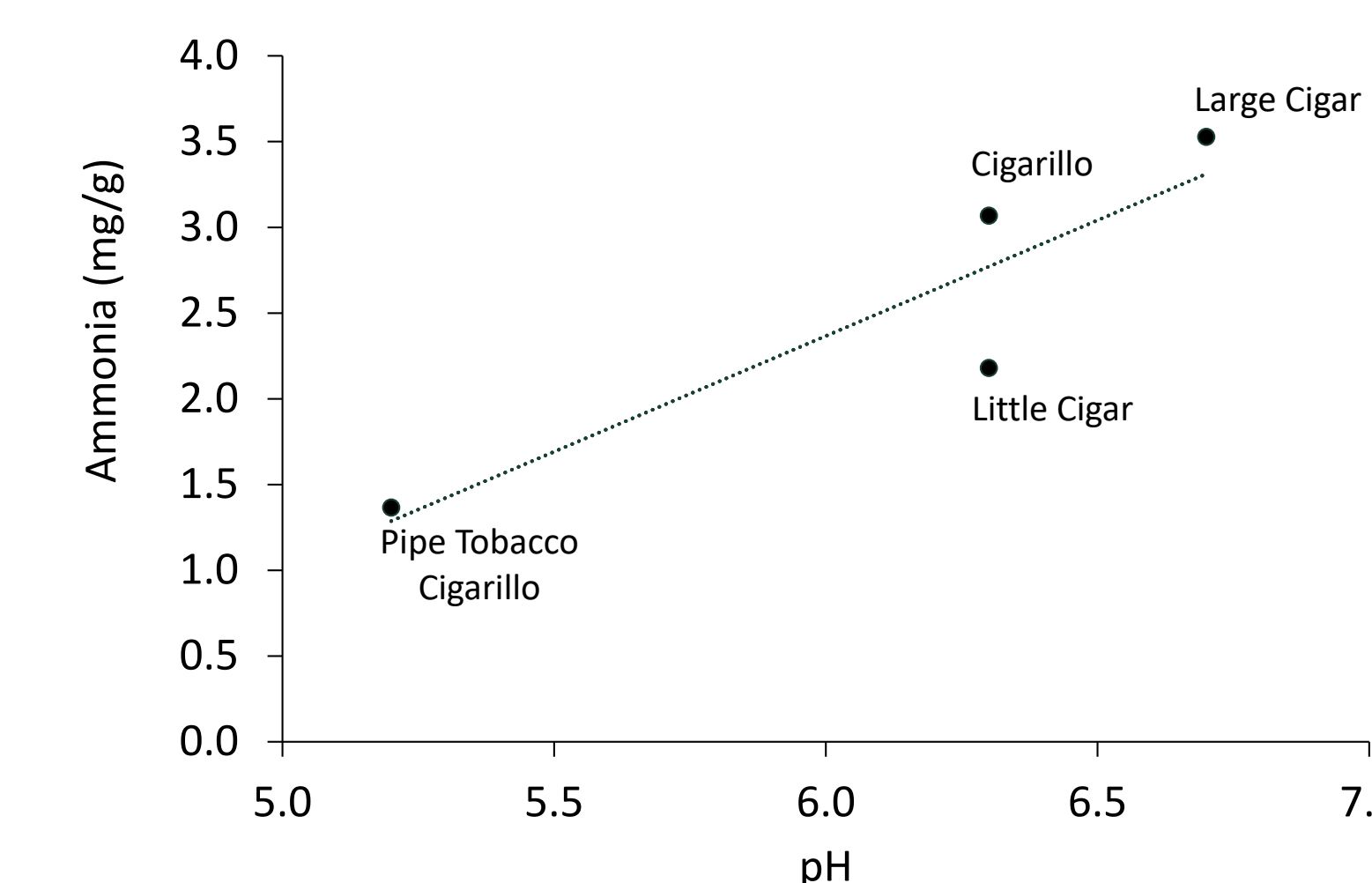
## Results and Discussion

Cigar Subcategory		Nicotine (mg/g)	Free Nicotine (mg/g)	Ammonia (mg/g)	pH
Pipe Tobacco Cigar	Mean	14.5	0.02	1.4	5.2
	Range	9.2 - 19.5	0.01 - 0.04	0.7 - 2.2	5.2 - 5.3
Little Cigar	Mean	11.6	0.22	2.2	6.3
	Range	10.5 - 12.2	0.13 - 0.34	1.8 - 2.6	6.1 - 6.5
Cigarillo	Mean	11.5	0.28	3.1	6.3
	Range	7.7 - 17.2	0.03 - 0.61	1.2 - 5.5	5.2 - 6.8
Large Cigar	Mean	13.2	0.75	3.5	6.7
	Range	7.5 - 23.7	0.18 - 2.34	1.9 - 5.6	6.2 - 7.4

**Table 1.** Comparison of nicotine, free nicotine, ammonia, and pH across cigar subcategories. Graphical comparisons of this data are provided in Figures 2 and 3.



**Figure 2.** A comparison of mean nicotine (A), free nicotine (B), ammonia (C), and pH (D), across product subcategories.



**Figure 3.** Comparison of Ammonia and pH Across Cigar Subcategories.

### Figure 2 and 3 Observations

- A wide range of nicotine and ammonia content and pH were determined for the products analyzed.
- Due to their relatively higher ammonia content and pH, large cigars have the highest calculated mean free nicotine content of the subcategories tested.
- Due to their relatively lower ammonia content and pH, pipe tobacco cigars have the lowest calculated mean free nicotine content of the subcategories tested.
- The mean free nicotine content, mean ammonia content, and mean pH concomitantly increase across the product subcategories of pipe tobacco cigars, little cigars, cigarillos, and large cigars.
- The ammonia levels of the little cigars and pipe tobacco cigarillos are similar to the levels reported in the literature for cigarettes<sup>9</sup> whereas the ammonia levels of some of the cigarillos and large cigars are higher than those of cigarettes

## Conclusion

- The wide variability in cigar size, shape, tobacco blend, and manufacturing process gives rise to a wide range of levels of nicotine, ammonia, and pH.
- When the diverse cigar types are grouped according to physical properties (size, weight, diameter) based on product labeling, this variability is reduced such that comparisons of the product subcategories are more meaningful.
- Products labeled as large cigars had the highest free nicotine filler content while pipe tobacco cigars had the lowest, with cigarillos and little cigars falling between these two extremes.
- Our results suggest that ammonia levels, pH, and the calculated free nicotine content in the tobacco filler content all have potential utility for helping better define cigar subcategories and related addictive characteristics.

## Significance

- Smoking topology may be a factor in cigar composition. Since large cigars are less likely to be inhaled, the relatively higher free nicotine content suggests the greater addiction potential of large cigars may rely more on absorption through the oral cavity than other types of cigars. Little cigars and cigarillos have a relatively lower free nicotine content, suggesting the addiction potential of little cigars and cigarillos may involve both the lungs and oral cavity.

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