Are Available Test Methods for the Determination of Ammonia in Mainstream Cigarette Smoke Fit for the Analysis of Cigars? -Part 2

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Background

- FDA regulation over Cigars went into effect on 8/8/2016
- FDA has requested reporting for HPHCs in Cigars by 11/8/19 (but did not provide the HPHC list for cigars)
- Ammonia is one of the HPHCs Listed for Cigarette Filler, Smokeless Tobacco and Cigarette Smoke



Background (Cont.)

 CRM No. 83 reported issue related to Dark Air Cured Tobacco (DAC) in cigarettes:

Results of the CS demonstrated equivalency of data obtained by using both trapping systems. From the results of CS, it was observed that the method was not fit for purpose for mainstream smoke generated from dark air-cured sample due to the high ammonia variation observed for both trapping systems.

- Significantly higher amount of Ammonia in Cigar Smoke compared to cigarettes.
- Many cigars contain DAC Tobacco

Is CRM No. 83 for Ammonia in Mainstream Cigarette Smoke fit for purpose for analysis of cigar smoke?



Cigar Smoke Collection



Vapor Phase Smoke Constituents pass through the Cambridge Filter (CF) Pad and are transferred to the trailing impinger train immediately behind.

Puffing Conditions According to CRM No. 64: 20 cc Volume, 1.5 sec Duration, 40 sec Interval



Impinger Set up for Cigar Smoke Collection



Modifications made to CRM No. 83:

- Special Adaptor for Cigars
- 3 impingers instead of 2
- 30 mL in each impinger instead of 15 mL
- 0.1N H₂SO₄ instead of 0.01M (=0.02N)
- Ice Water Bath for Chilled Impinger Trains (not specified in method)
- Narrow Capillary Impingers (not specified in method)

For Trapping Evaluation:

- CF Pad was extracted in 30 mL of 0.1N H₂SO₄, filtered, and analyzed separately
- Each impinger was analyzed separately



Comparison of Products



CRM No. 83 is not suitable for measuring ammonia in all cigar types

* Previously presented at CORESTA 2017



Goals

• To understand the source of ammonia increase in subsequent impingers for DAC Tobacco containing cigars

 To develop an accurate and reliable analytical method that can provide consistent data for measuring ammonia in smoke in all types of cigars



Physical Phenomena

Chemical Phenomena

Volume of Trapping Solution



Impact of Volume on Trapping Efficiency for Cigar Smoke

Evaluate the impact of trapping solution volume for cigar smoke



 No observable difference between 30 mL and 60 mL with cigar smoke (using high % DAC cigar)

Physical Phenomena

- **X** Volume of Trapping Solution
 - Trapping of Ammonia Gas



Evaluate Trapping Efficiency of Ammonia Gas

Cerulean SM-410RH (SMK 65) 10-Port Linear Smoking Machine



Certified Concentration of Ammonia Gas Concentration of Ammonia Gas

- 50 ppm & 600 ppm
- <u>Trapping Conditions</u> Pad + Three (3) impingers
 - Trapping Solution: Water vs 0.1N H₂SO₄
 - Temperature: Room Temperature vs Ice Bath
 - Volume in Impinger: 30 mL vs 60 mL
- Collection Details
 - Tedlar Bag was filled with ammonia gas from tank
 - Smoke Machine was used to puff directly from bag

Tedlar Bag filled with Ammonia Gas from the Tank



Trapping Efficiency Evaluation from Ammonia Gas Bag

| | <u>% From Total Ammonia</u> | | | |
|-----------------|-----------------------------|---|--|--|
| | 50 ppm | 50 ppm | 50 ppm | 600 ppm |
| | Ammonia | Ammonia | Ammonia | Ammonia |
| Condition | H₂O, Ice Bath | 0.01N H ₂ SO _{4,} Ice bath | 0.1N H ₂ SO _{4,} Ice Bath | 0.1N H ₂ SO _{4,} Ice Bath |
| CF Pad | 5.27 | 24.0 | 21.6 | 3.88 |
| Impinger 1 | 72.2 | 76.0 | 70.3 | 96.1 |
| Impinger 2 | 22.5 | 0 | 3.61 | 0 |
| Impinger 3 | 0 | 0 | 4.44 | 0 |
| Impinger volume | 30 mL | 30 mL | 30 mL | 30 mL |

• No breakthrough was observed for 600 ppm ammonia gas in 2^{nd} and 3^{rd} Impinger with 30 mL of 0.1N H₂SO₄ using Ice Bath

Note: approximate amount of ammonia in cigar gas phase is 1 ppm

Altria Client Services

Physical Phenomena

- X Volume of Trapping Solution
- X Trapping of Ammonia Gas
 - Dependency of Number of Puffs



Trapping Dependency on Number of Puffs



- As number of puffs increases the trapping profile changes
- The amount of ammonia trapped in the impingers does not linearly increase with number of puffs

Trapping Dependency on Number of Puffs

Cigar "A" – 0% DAC Tobacco



- The trapping profiles are different from cigar "D" 90% DAC Tobacco
- The amount of ammonia trapped in the impingers appears to linearly increase with . number of puffs

Physical Phenomena

- X Volume of Trapping Solution
- X Trapping of Ammonia Gas
- Puffs
 Puffs
 - Evaluation of Sorbent Tubes



Evaluate Trapping with Sorbent Tubes Smoke Collection Set-up with Sorbent Tubes



Solid sorbent tube (sulfuric acid treated silica gel), 6 cm long, 6-mm OD, 4-mm ID, containing two sections of 20/40 mesh sulfuric acid treated silica gel (200 mg front/100 mg back) separated and held in place with plugs of silylated glass wool, SKC Cat. # 226-10-06

Contents of front and back of each sorbent tube were extracted -10 mL of H_2O , shake 45 min

Sorbent Tubes were added to impinger train to investigate if ammonia was breaking through impingers



Ammonia Results Using Sorbent Tubes

Cigar "D" – 90% DAC Tobacco



- Additional Ammonia was trapped in 2 sorbent tubes after 3 impingers
- More ammonia was observed in 2nd Sorbent tube compared to 1st

Altria Client Services

Physical Phenomena

- X Volume of Trapping Solution
- X Trapping of Ammonia Gas
- Pependency of Number of Puffs
- X Evaluation of Sorbent Tubes

- Type of Tobacco
 - Percentages of Dark Air Cured tobacco



Trapping Dependency: % DAC Tobacco in Cigar



Trapping profile changes depending on % of Dark Air Cured Tobacco



Physical Phenomena

- X Volume of Trapping Solution
- X Trapping of Ammonia Gas
- Pependency of Number of Puffs
- X Evaluation of Sorbent Tubes

- Type of Tobacco
- Percentages of Dark Air Cured tobacco
 - Changing Trapping Solution
 - Acid Strength & Storage Time
 - Addition of Organic Solvent



Amount of Ammonia: Acid Strength & Storage Time



The level of ammonia in smoke samples:

- Increases with increasing acid strength
- Increases over time when stored at RT

Note CRM 83 recommends using 0.02N H_2SO_4



Physical Phenomena

- **X** Volume of Trapping Solution
- X Trapping of Ammonia Gas
- Puffs
 Puffs
- X Evaluation of Sorbent Tubes

Chemical Phenomena

Type of Tobacco



- Percentages of Dark Air Cured tobacco
 - Changing Trapping Solution
- Acid Strength & Storage Time
 - Addition of Organic Solvent



Ammonia Results Using Alternative Solvents





Ammonia Results Using Alternative Solvents





Physical Phenomena

- X Volume of Trapping Solution
- X Trapping of Ammonia Gas
- Pependency of Number of Puffs
- X Evaluation of Sorbent Tubes

- Type of Tobacco
- \checkmark
 - Percentages of Dark Air Cured tobacco
 - Changing Trapping Solution
 - Acid Strength & Storage Time
 - Addition of Organic Solvent



Summary

- Based on our work there is a strong indication of chemical reactions that convert some precursors to ammonia
- 3 impingers with 0.1N H2SO4 may not be sufficient to accurately trap and quantify ammonia from all types of cigars

- Future plans:
- Evaluate role of organic solvent
- Investigate secondary method for analysis of Cigar smoke
- Evaluate "larger" cigars
- Validate method







Sample Extract Stability

| Cigar "D" | Imp.#1 with 0.1N H2SO4 | Imp.#1 with EtOH | Imp.#1 with ACN |
|---------------------|------------------------|------------------|-----------------|
| 90% DAC Tobacco | lmp. #1 | lmp. #2 | lmp. #2 |
| T0, Av. (n=3) | 3.14 | 9.77 | 7.57 |
| T ~88 HR, Av. (n=3) | 3.84 | 9.88 | 7.76 |
| % Diff. | 20.1 | 1.13 | 2.41 |
| | | | |
| | | | |
| | | | |
| Cigar "A" | Imp.#1 with 0.1N H2SO4 | Imp.#1 with EtOH | Imp.#1 with ACN |
| 0% DAC Tobacco | lmp. #1 | lmp. #2 | lmp. #2 |
| T0, Av. (n=3) | 4.31 | 3.84 | 2.41 |
| T ~60 HR, Av. (n=3) | 5.04 | 3.92 | 2.47 |
| % Diff. | 15.6 | 2.08 | 2.51 |



Amount of Ammonia: Acid Strength & Storage Time



The level of ammonia in smoke samples:

- Increases with increasing acid strength
- Increases over time when stored at RT

Note CRM 83 recommends using 0.02N H_2SO_4

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