

Supplementary Information

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Contents

Table S1: Analytical relative recoveries of four TSNA compounds with different types of sampling filters (CFP and QW) for the analysis of EC aerosol samples.

Table S2: Concentration of spiked samples according to each experiment stage

Table S3: Basic information on the six types of commercial EC liquid solutions examined in this study.

Table S4: Basic information on the four tobacco-specific nitrosamine (TSNA) compounds investigated in this study.

Figure S1: Schematics of two analytical methods (Type 1 and Type 2) for the analysis of aerosol samples that were compared in this study.

Figure S2: Five-point calibration curve of four TSNA

Figure S3: Comparison of relative recovery (RR) of the four TSNA for different dilution factors using 100 mM ammonium acetate (AA) and Acetonitrile (ACN). $RR (\%) = (\text{Concentration of spiked sample detected by LC-MS/MS system}) / (\text{theoretical concentration of spiked sample}) \times 100$.

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Table S1. Analytical relative recoveries of four TSNA compounds with different types of sampling filters (CFP and QW) for the analysis of EC aerosol samples.

| Order | Sample code ^{a]} | Δ EC | Δ Filter | Sample | Theoretical concentration of | | | | Measured concentration of TSNAS | | | | Method recovery (%) | | | |
|-------|---------------------------|--------------------|----------------------|-------------------|---|------|------|------|--------------------------------------|------|------|------|---------------------|------|------|------|
| | | weight | weight ^{c]} | recovery | TSNA (ng mL ⁻¹) ^{e]} | | | | (ng mL ⁻¹) ^{e]} | | | | | | | |
| | | ^{b]} (mg) | (mg) | ^{d]} (%) | NNN | NNK | NAT | NAB | NNN | NNK | NAT | NAB | NNN | NNK | NAT | NAB |
| 1 | A-CFP-2 | 28.5 | 26.1 | 91.7 | 508 | 508 | 508 | 508 | 391 | 306 | 250 | 243 | 76.9 | 60.2 | 49.2 | 47.8 |
| 2 | A-CFP-5 | 33.2 | 32.1 | 96.6 | 1263 | 1263 | 1262 | 1263 | 997 | 804 | 658 | 670 | 78.9 | 63.6 | 52.2 | 53.0 |
| 3 | A-CFP-10 | 29.7 | 28.1 | 94.6 | 2511 | 2511 | 2509 | 2511 | 1977 | 1662 | 1337 | 1274 | 78.7 | 66.2 | 53.3 | 50.7 |
| | Mean | 29.3 | 27.6 | 94.6 | | | | | | | | | 78.2 | 63.3 | 51.6 | 50.0 |
| | SD ^{g]} | 2.90 | 3.10 | 2.61 | | | | | | | | | 3.82 | 6.16 | 4.06 | 4.92 |
| 1 | A-QW-2 | 33.4 | 32.6 | 97.7 | 104 | 104 | 103 | 104 | 95.5 | 81.0 | 85.6 | 105 | 92.2 | 82.4 | 82.7 | 101 |
| 2 | A-QW-10 | 36.0 | 34.5 | 95.8 | 501 | 501 | 500 | 501 | 421 | 358 | 378 | 460 | 83.3 | 71.5 | 75.5 | 91.8 |
| 3 | A-QW-20 | 33.4 | 32.3 | 96.8 | 1001 | 1001 | 1000 | 1001 | 781 | 662 | 661 | 820 | 77.5 | 66.2 | 67.7 | 88.5 |
| | Mean | 34.3 | 33.1 | 96.7 | | | | | | | | | 84.3 | 73.3 | 75.3 | 93.8 |
| | SD ^{g]} | 2.72 | 2.65 | 1.63 | | | | | | | | | 13.7 | 10.9 | 16.3 | 12.3 |

^aSample code was assigned by analytical condition of EC aerosol with sampling filter (Cambridge filter pad [CFP] or Quartz wool filter [QW]), and the final concentration (ng mL⁻¹) of spiked samples extracted with 100 mM AA.

^bEC solution consumed when generating an aerosol using E-cigarette automatic capture device.

^cAerosol generated by the E-cigarette automatic capture device captured on the filter (CFP or QW).

^dSample recovery (%) = $(\Delta\text{Filter weight (mg)}) / (\Delta\text{EC weight (mg)}) * 100$

^eThe values in the table were expressed as mean values

^fMeasured concentration of TSNA in the aerosol (ng mL⁻¹) = (detected concentration of TSNA after extraction with 100 mM AA by LC-MS/MS) * (extraction factor (in case of CFP: 365 ± 40.02, in case of QW: 50.8 ± 1.41))

^gStandard deviation

Table S2. Concentration of spiked samples according to each experiment stage

| Order | Sample phase | Sample code | Concentration of spiked sample before dilution | | | | Final concentration of spiked sample diluted with | | | | Dilution Factor |
|-------|---------------|-------------|--|------|------|------|---|-------|-------|-------|-----------------|
| | | | (ng mL ⁻¹) | | | | solvent (ng mL ⁻¹) | | | | |
| | | | NNN | NNK | NAT | NAB | NNN | NNK | NAT | NAB | |
| 1 | Liquid (L-S1) | L-AA-100 | 103 | 103 | 101 | 103 | 1.03 | 1.03 | 1.01 | 1.03 | 100 |
| 2 | | L-AA-50 | 103 | 103 | 101 | 103 | 2.07 | 2.07 | 2.03 | 2.07 | 50 |
| 3 | | L-AA-20 | 103 | 103 | 101 | 103 | 5.17 | 5.17 | 5.07 | 5.17 | 20 |
| 4 | | L-ACN-100 | 103 | 103 | 101 | 103 | 1.03 | 1.03 | 1.01 | 1.03 | 100 |
| 5 | | L-ACN-50 | 103 | 103 | 101 | 103 | 2.07 | 2.07 | 2.03 | 2.07 | 50 |
| 6 | | L-ACN-20 | 103 | 103 | 101 | 103 | 5.17 | 5.17 | 5.07 | 5.17 | 20 |
| 7 | Liquid (L-S2) | L-AA-1 | 53.0 | 53.0 | 51.9 | 53.0 | 1.06 | 1.06 | 1.038 | 1.06 | 50 |
| 8 | | L-AA-5 | 256 | 256 | 251 | 256 | 5.127 | 5.127 | 5.021 | 5.127 | 50 |
| 9 | | L-AA-10 | 516 | 516 | 505 | 516 | 10.32 | 10.32 | 10.11 | 10.32 | 50 |
| 10 | | L-ACN-1 | 53.0 | 53.0 | 51.9 | 53.0 | 1.06 | 1.06 | 1.038 | 1.06 | 50 |
| 11 | | L-ACN-5 | 256 | 256 | 251 | 256 | 5.127 | 5.127 | 5.021 | 5.127 | 50 |
| 12 | | L-ACN-10 | 516 | 516 | 505 | 516 | 10.32 | 10.32 | 10.11 | 10.32 | 50 |
| 13 | Aerosol | A-CFP-2 | 508 | 508 | 508 | 508 | 1.32 | 1.32 | 1.32 | 1.32 | 384 |

| | | | | | | | | | | |
|----|----------|------|------|------|------|------|------|------|------|------|
| 14 | A-CFP-5 | 1263 | 1263 | 1262 | 1263 | 4.04 | 4.04 | 4.04 | 4.04 | 313 |
| 15 | A-CFP-10 | 2511 | 2511 | 2509 | 2511 | 7.05 | 7.05 | 7.04 | 7.05 | 356 |
| 16 | A-QW-2 | 104 | 104 | 103 | 104 | 2.05 | 2.05 | 2.04 | 2.05 | 50.7 |
| 17 | A-QW-10 | 501 | 501 | 500 | 501 | 9.83 | 9.83 | 9.82 | 9.83 | 51.0 |
| 18 | A-QW-20 | 1001 | 1001 | 1000 | 1001 | 19.7 | 19.7 | 19.7 | 19.7 | 50.8 |

Table S3. Basic information on the six types of commercial EC liquid solutions examined in this study.

| Sample code | Type of sample | Flavor | Nicotine content | Volume (mL) | Puff number | Puff volume (mL) |
|-------------|----------------|-------------------|-------------------------------|-------------|-------------|------------------|
| A | | Brown cigar | 6 mg ^{a]} | 30 | | |
| B | | Cowboy | 0.95% ^{b]} | 30 | | |
| C | Liquid | Red berry | 3 mg | 30 | 10 | 33.3 mL |
| D | | Raspberry | Less than 0.05% ^{c]} | 30 | | |
| E | | Strawbana edition | 0.97% ^{b]} | 30 | | |

^{a]}Natural nicotine

^{b]}Based on chemical synthetic nicotine (CSN).

^{c]}This product contains stem nicotine extracted from the stem rather than the tobacco leaf.

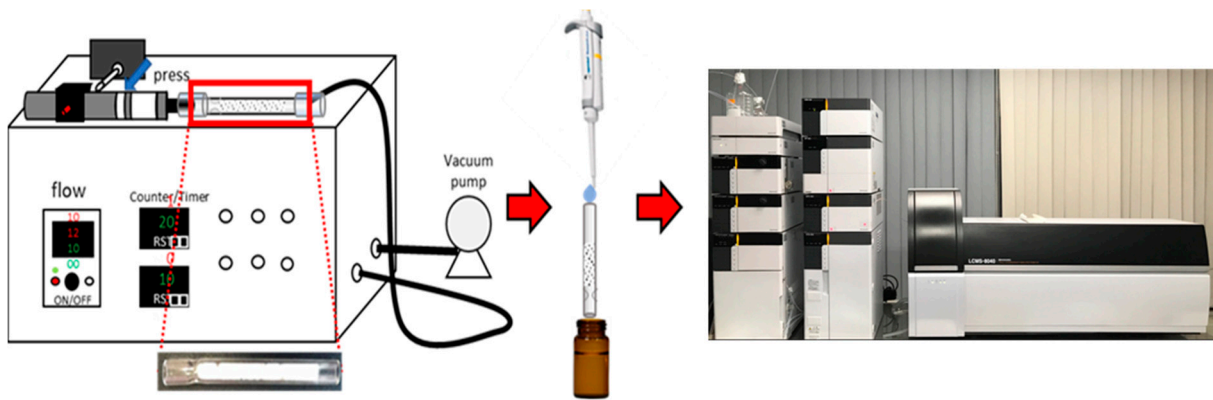
Table S4. Basic information on the four tobacco-specific nitrosamine (TSNA) compounds investigated in this study.

| | 4- | | | |
|-----------------------|---|---|--|--|
| Full Name | (±)-N'-nitrosonornicotine | (Methylnitrosamino)-1-(3-pyridyl)-1-butanone | N'-nitrosoanatabine | N-nitrosoanabasine |
| Short Name | NNN* | NNK* | NAT | NAB* |
| Formula | C ₉ H ₁₁ N ₃ O | C ₁₀ H ₁₃ N ₃ O ₂ | C ₁₀ H ₁₁ N ₃ O | C ₁₀ H ₁₃ N ₃ O |
| MW (g/mole) | 177 | 207 | 189 | 191 |
| Boiling point (°C) | 154 | 376 | 368 | 380.2 ± 3.5 |
| Vapor pressure (mmHg) | 0.20 | 6.8E-05 | - | 0.0 ± 0.8 |
| CAS No. | 80508-23-2 | 64091-91-4 | 71267-22-6 | 37620-20-5 |

*NNN, NNK, and NAB is 1 mg mL⁻¹ in 1 mL of methanol



(a) Type 1: Sampling the aerosol using Cambridge filter pad (CFP)



(b) Type 2: Sampling the aerosol using Quartz wool (QW) filter

Figure S1. Schematics of two analytical methods (Type 1 and Type 2) for the analysis of aerosol samples that were compared in this study.

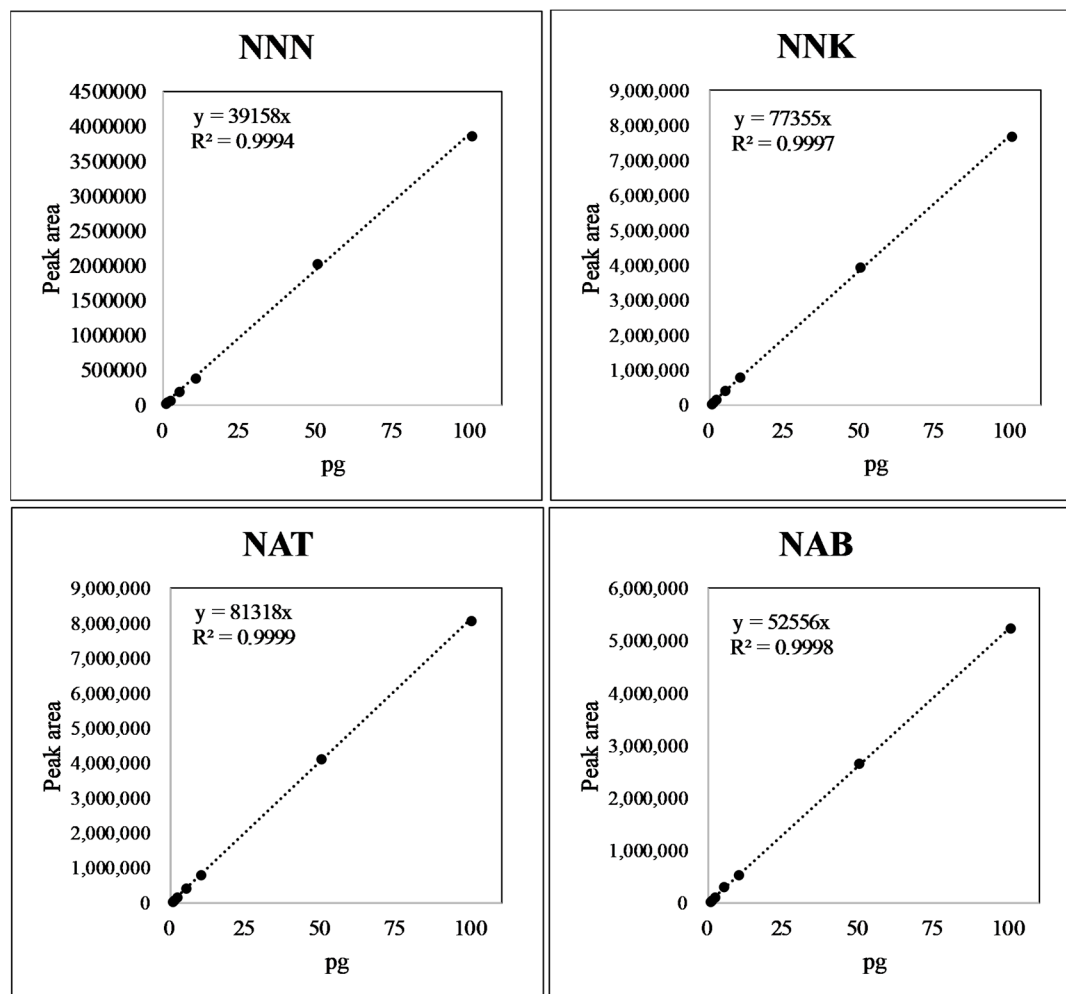


Figure S2. Five-point calibration curve of four TSNAs

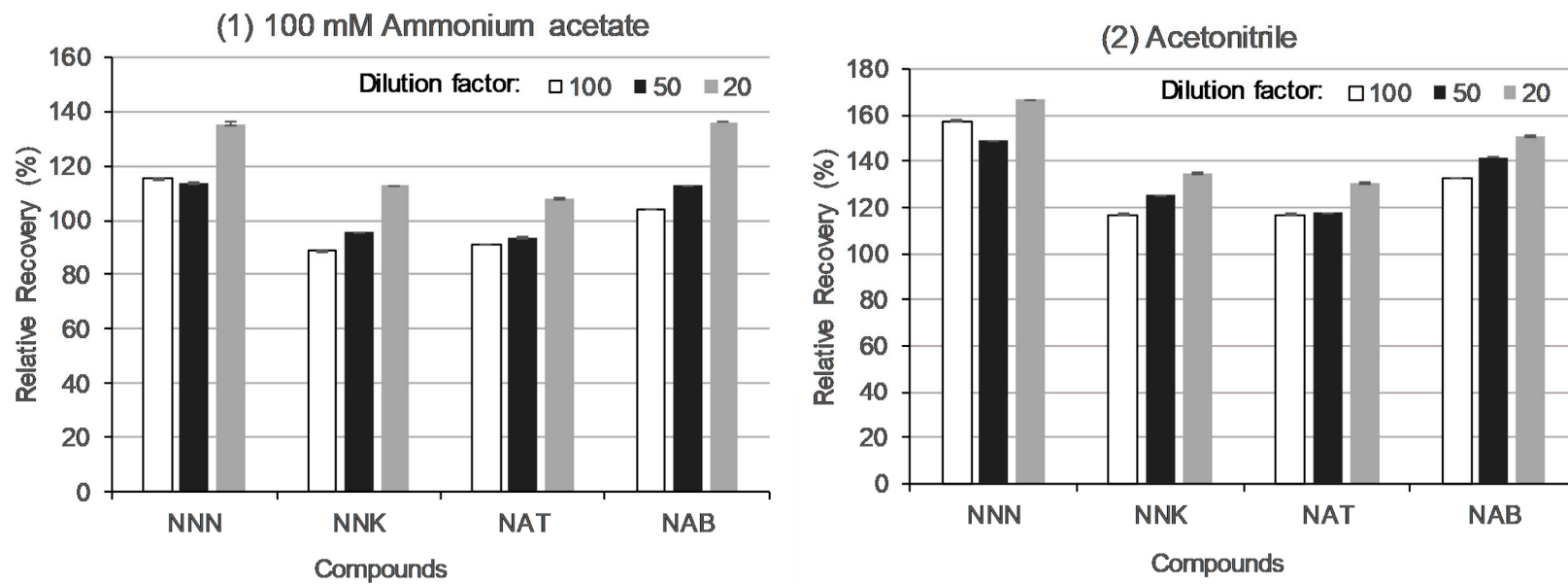


Figure S3. Comparison of relative recovery (RR) of the four TSNAs for different dilution factors using 100 mM ammonium acetate (AA) and Acetonitrile (ACN). $RR (\%) = (\text{Concentration of spiked sample detected by LC-MS/MS system}) / (\text{theoretical concentration of spiked sample}) \times 100$