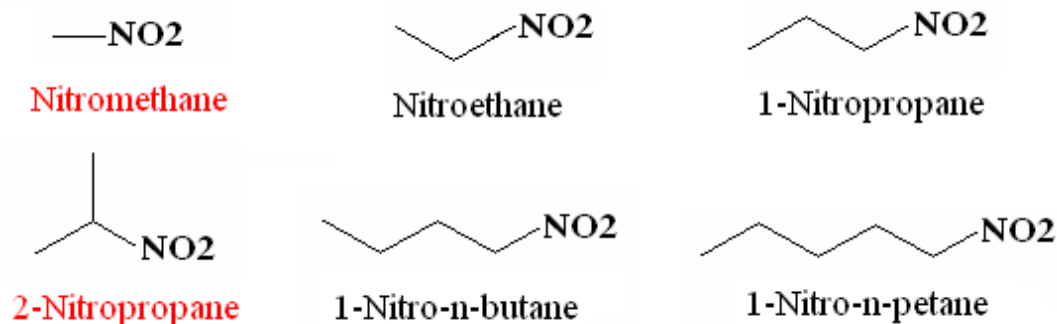# DETERMINATION OF NITROALKANES IN CIGARETTE MAINSTREAM SMOKE WITH HEART-CUT TWO-DIMENSIONAL GC/MS METHOD

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Nitroalkanes In Mainstream Smoke(MSS)

- Nitroalkanes were detected from MSS by Hoffmann and Rathkamp in 1968.

- Among of these nitroalkanes, nitromethane and 2-nitro-propane are IARC Group 2B carcinogens.

Multidimensional chromatography

- Hoffmann's method includes one steam distillation and two Liquid-Liquid extraction steps for sample preparation. It's some labourious.

- Multidimensional chromatography using columns in series with different stationary phases have shown much greater separating power than normal chromatography.

- With multidimentional chromatography ,one can obtain better results while simplify the sample preparation. It has been used in the analysis of complex sample, such as petrol, flavor.
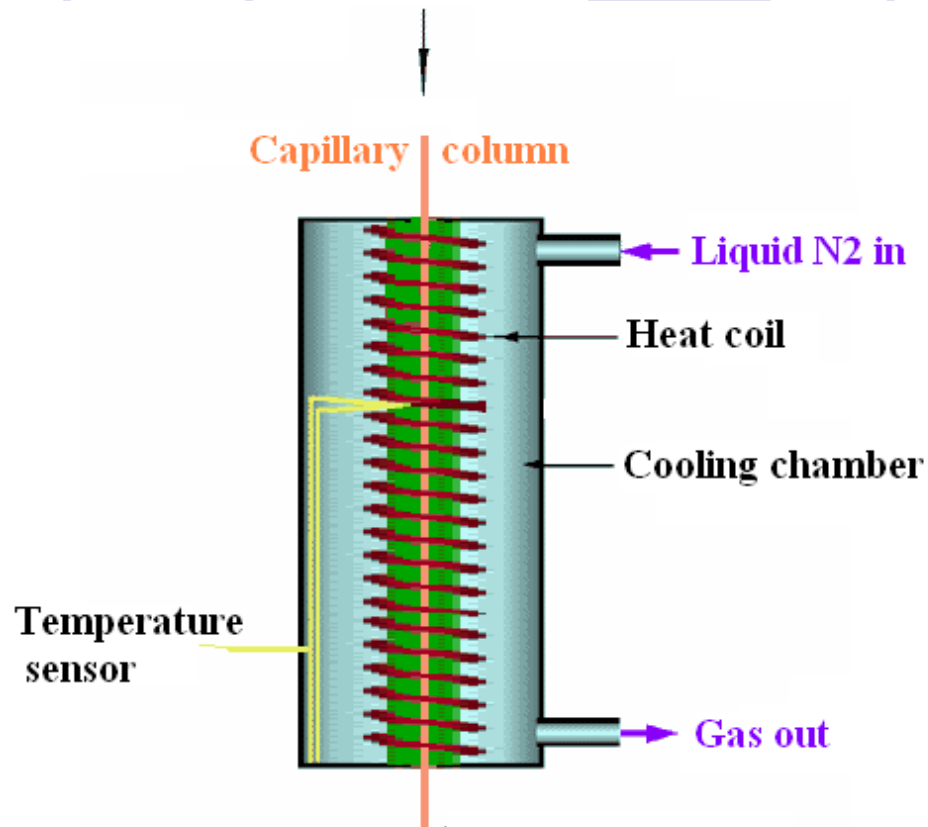
- Here, we fabricated a heart-cut two-dimensional GC/MS (GC-GC/MS) system, and with which, a method for analysis of nitroalkanes in MSS was developed.

Scheme of the GC-GC/MS system

Inlet FID EPC Cold trap

Transfer line

1st D GC   2nd D GC   MS
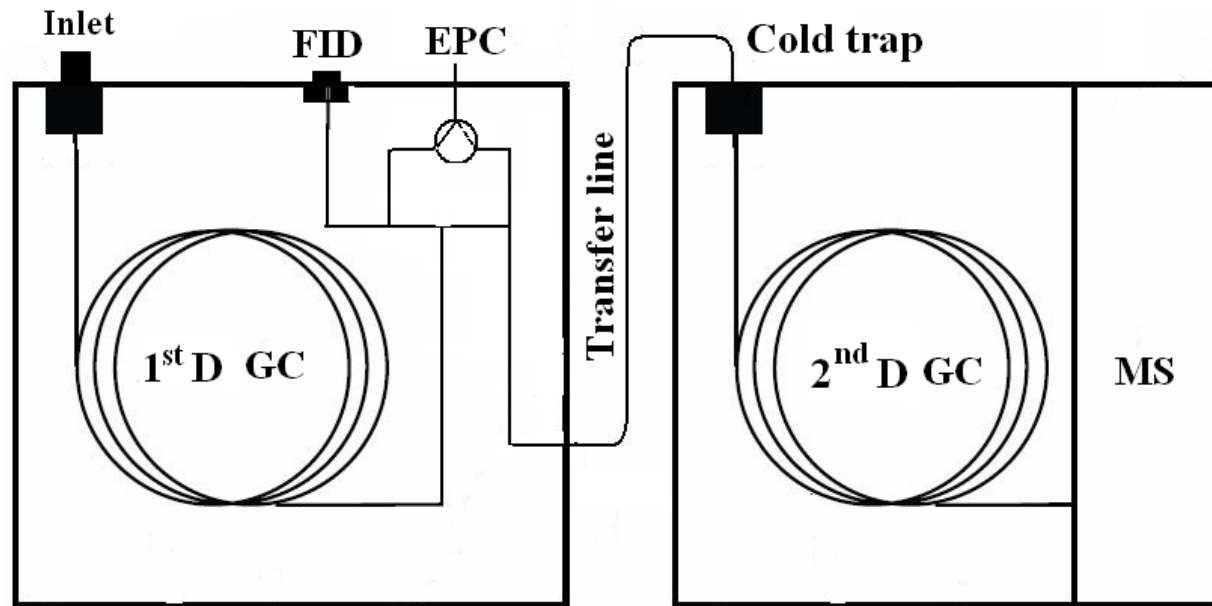
The cold trap was used to cryofocus and remobilze the "cuts".

Structure of the cold trap

Capillary column

← Liquid N2 in

Heat coil

Cooling chamber

Temperature sensor

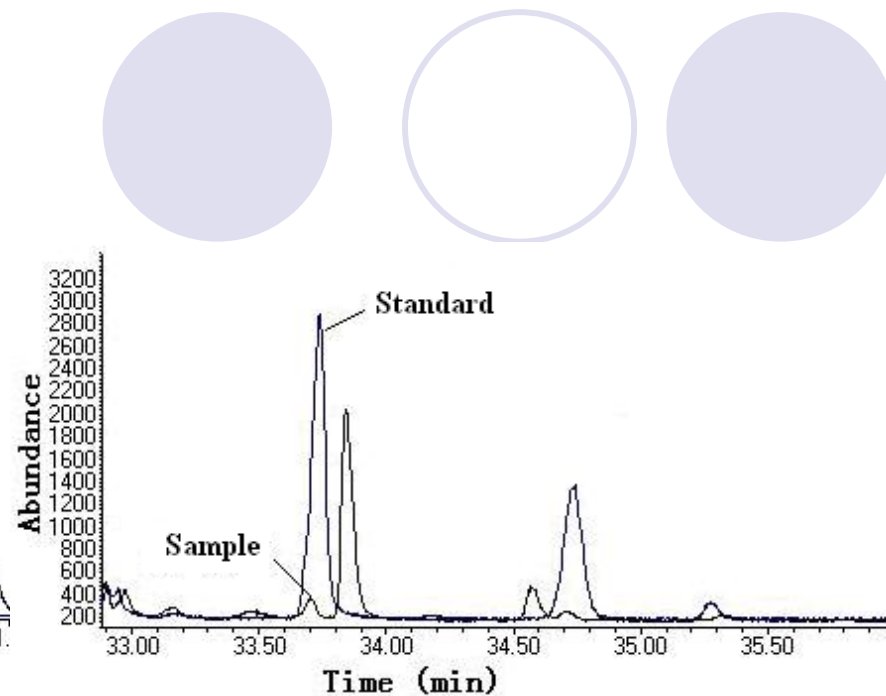Gas out

A programmed temperature vaporization (PTV) inlet was reconstructed as the cold trap. The cuts from 1st GC was focused in capillary column.
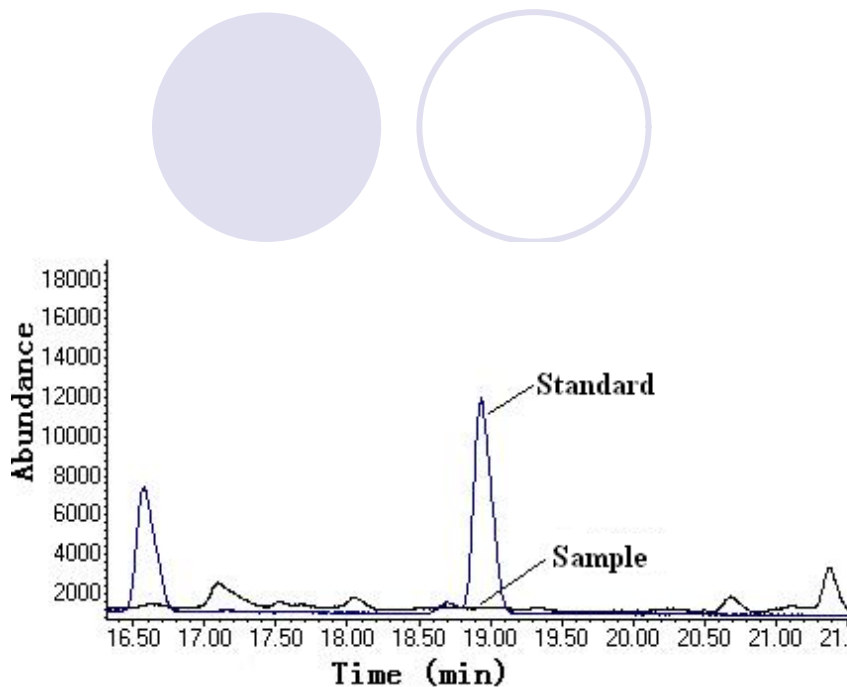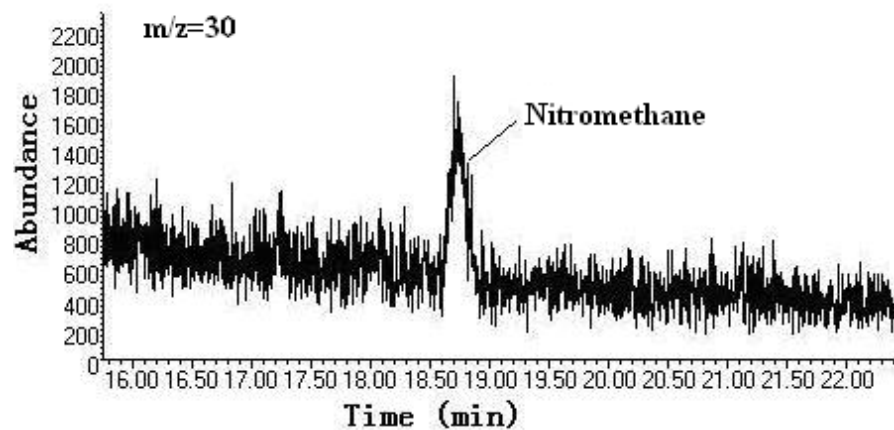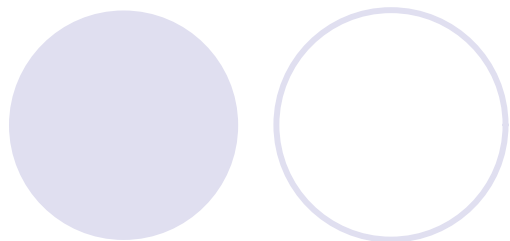
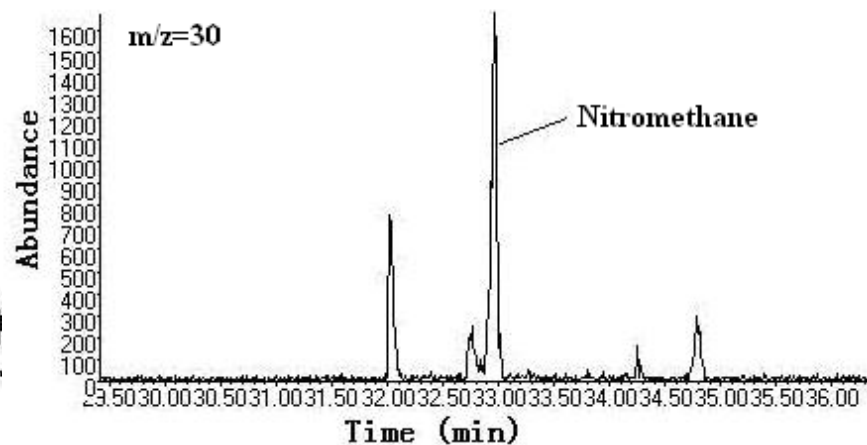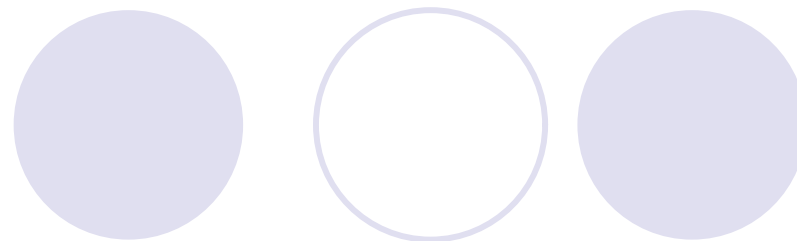**1D GC/MS** chromatograph of nitroethane standard and smoke sample.

2D GC/MS chromatograph of nitroethane standard and smoke sample.

GC-GC/MS has **better resolution ability** than 1D GC/MS.

1D GC/MS chromatograph of smoke sample

2D GC/MS chromatograph of smoke sample.

GC-GC/MS gets **better S/N** than 1D GC/MS.

Sample preparation for MSS

- **Gaseous matter** ： trapped by ethyl acetate in dry Ice-isopropyl alcohol .

- **Particulate matter** ： the particulate matter on cambridge filter was extracted by ethyl acetate.

- 2-Methyl-2-nitropropane was used as **Internal standard**.

Main chromatography condition

- **Column:**

  HP-INNOWAX（1st column）+ DB-17（2nd column）.

- **Carrier gas flow:**

  1st：1mL/min；**2nd**：2mL/min.

- **Temperature programme:**

1st GC：50℃（5min）—2℃/min→ 140℃ —30℃/min→ 170℃（5 min）

2nd GC：40℃（36min）—2℃/min→ 70℃ —30℃/min→ 230℃（10min）

Cold trap：50℃（4min）—100℃/min→ -140℃（25min）—700℃/min→ 250℃（2 min）

Retention time and heart-cut time of nitroalkanes

Compounds	1D R.T. (min)	Heart-cut time (min)
2-Methyl-2-nitropropane （Internal standard）	11.64	11.45～11.85
Nitromethane	14.01	13.80～14. 70
Nitroethane	14.43	13.80～14. 70
2-Nitropropane	12.46	12.20～12.70
1-Nitropropane	17.08	16.80～17.40
1-Nitro-n-butane	22.07	21.80～22.40
1-Nitro-n-pentane	28.27	28.00～28.50

1D chromatograph of MSS particulate sample after heart-cut
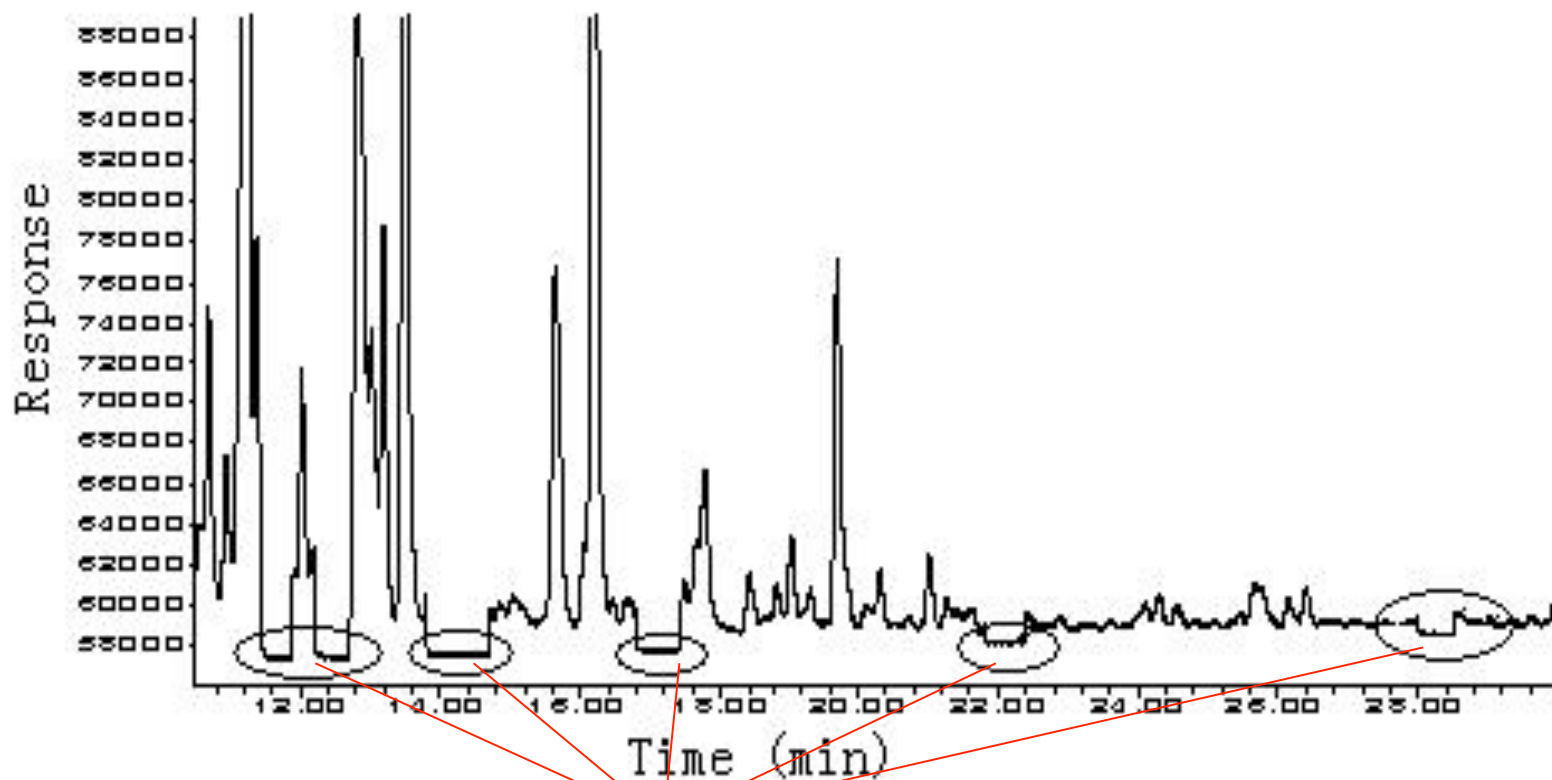
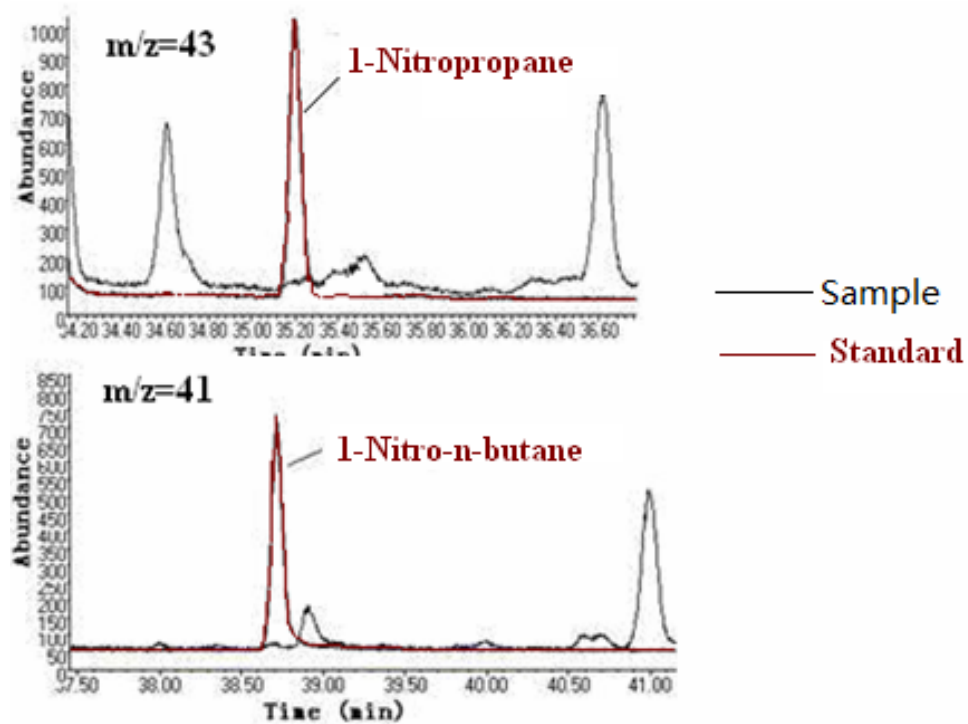Six cuts were executed in one injection.

Qualitative analysis of nitroalkanes in MSS
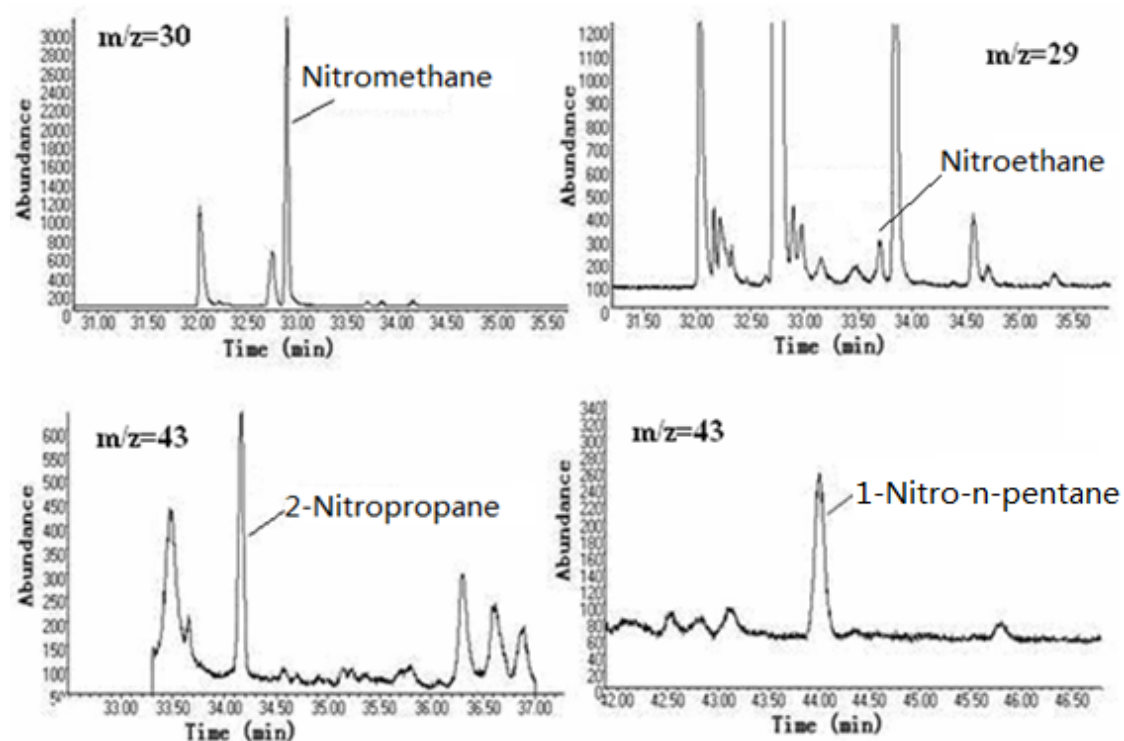
Extracted ion chromatographs of MSS sample

After comparing with the mass spectrum of standards, nitromethane, nitroethane, 2-nitropropane and 1-nitro-n-butane was identified from MSS.

Qualitative analysis of nitroalkanes in MSS

Extracted ion chromatographs of MSS sample and nitroalkane standards.

1-Nitropropane and 1-nitro-n-butane was not detected from MSS.

Evaluation of quantification method

- **LOD:**

Range from 1.30 ng/cig （for nitromethane) to 9.80 ng/cig（1-nitro-n-butane）。

- **RSD（n=7）**

	Nitromethane	Nitroethane	2-Nitropropane	1-Nitro-n-pentane
Average (µg/cig)	2.67	0.150	0.660	0.180
RSD (%)	7.17	9.43	7.31	8.25

- **Recovery(%)**

Add level	Nitromethane	Nitroethane	1-Nitropropane	2-Nitropropane	1-Nitro-n-butane	1-Nitro-n-pentane
Low	109	110	97.6	90.3	94.0	95.0
High	104	101	104	90.2	98.2	87.1

Yields of nitroalkanes in MSS of different cigarettes

Compounds	Yields range (µg/cig)
Nitromethane	0.12–1.61
Nitroethane	0.07–0.16
2-Nitropropane	0.17–1.49
1-Nitro-n-pentane	0.12–0.26

Note: 13 brands of cigarettes were tested, inculding 7 blend and 6 virginia cigarettes.
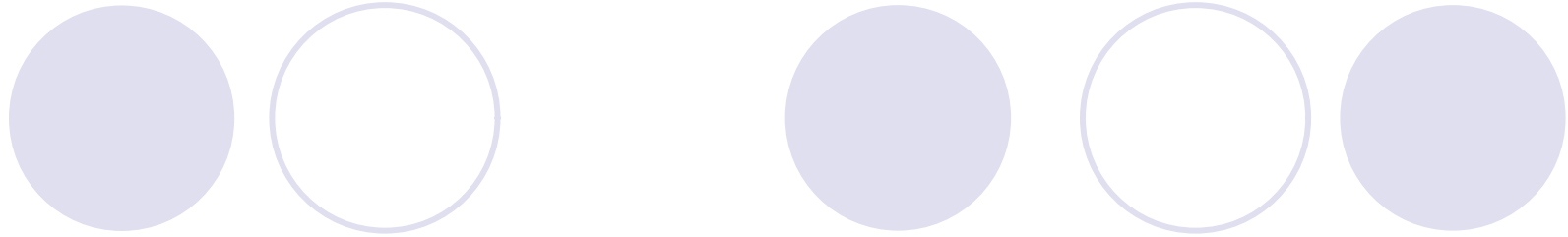
Thank you for your attention!

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