Rapid and Sensitive Determination of Airborne N-Nitrosamines Using the Agilent Capillary Trap Sampler, Thermal Separation Probe, and an Agilent 5975T LTM GC/MS

Application Note

Environmental

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Abstract

A method for determination of N-nitrosamines in ambient air was developed using the innovative Agilent Capillary Trap Sampler (CTS), Thermal Sample Probe (TSP) and the Agilent 5975T LTM GC/MS. Gas sampling was accomplished in seconds to minutes in the field, and the nitrosamines captured by the capillary trapping columns were desorbed directly in the GC/MS inlet using the TSP. The calibration range was 48 to 1,600 ng, and the presumed method detect limitation (MDL) was as low as 1 ng.

Introduction

The carcinogenic effects of nitrosamines have been clearly demonstrated in animals, and they are suspected of being carcinogenic to humans by several organizations, including the International Agency for Research on Cancer, Health Canada, and the National Toxicology Program (NTP) of theUnited States.

These compounds may be present in ambient air as a result of direct emission or from atmospheric reactions between secondary or tertiary amines. The highest concentrations of nitrosamines in the human environment have been measured in the rubber industry; they can also be found in tobacco smoke.

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The National Institute for Occupational Safety and Health (NIOSH) in the US has developed method 2522 for the collection and analysis of airborne nitrosamines. However, the air sampler used in this method requires a large sample volume and a long sampling time, and the nitrosamines must be re-extracted with solvents, making the method slow and tedious. Gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) are often used to detect nitrosamines. However the nitrosamines tend to be thermally labile and the sensitivity of detection can be limited by the high temperature of the GC injector.

This application note describes a sensitive method for the detection of airborne nitrosamines that has been developed using the innovative Agilent Capillary Trap Sampler (CTS), thermal sample probe (TSP) and the Agilent 5975T LTM GC/MS. The method is fast, economical, and easy to use, enabling a presumed method detection limit (MDL) of less than 1 ng, due to its ability to capture analyte from a large volume of air.

Experimental

Reagents and Standards

Nitrosamine standards were obtained from Supelco, EPA8270 Nitrosamines Mix, 2,000 ng/µL (Cat.No. 48489), and six nitrosamines were tested (Table 1).

Table 1. Nitrosamine Analyzed Using this Method

Name	CAS	MW	R.T (min)
N-nitrosoethylmethylamine (NEMA)	595-95-6	88	5.01
N-nitrosodiethylamine (NDEA)	55-18-5	102	5.88
N-nitrosomorpholine (NMOR)	59-89-2	116	9.26
N-nitrosopyrrolidine (NPYR)	930-55-2	100	9.52
N-nitrosopiperidine (NPIP)	100-75-4	114	10.22
N-nitrosodi-n-butylamine (NDBA)	924-16-3	158	13.29

Instruments

This method was developed on the Agilent 5975T GC/MS system using a split/splitless inlet, the CTS (p/n G1181A) for airborne sample collection, and the TSP (p/n G4381A) installed on the split/splitless injector for sample desorption. Table 2 shows the instrument conditions used.

Table 2. CTS and GC/MS Run Conditions

Capillary Trap Sampler (CTS)	
Trapping columns	6 PoraPLOT Q, 530 µm id, 20-µm film thickness
Sampling pump rate	100 mL/min
GC run conditions	
Guard column	0.5 m column with same phase as analytical column, connected to the injector
Analytical column	VOC analysis: DB-624 LTM module with a 20 m × 0.18 mm, 1.0 µm column (p/n G3900-63010)
Injection volume	1 µL
Inlet temperature	Isothermal at 220 °C
Injection mode	Split, 5:1, using the TSP
LTM temperature gradient	2.5 minute hold at 60 °C 60 °C to 120 °C at 6 °C/min, hold for 2.5 minutes 120 °C to 160 °C at 40 °C/min, hold for 2.5 minutes 160 °C to 200 °C at 40 °C/min, hold for 2.667 minutes
Isothermal temperature	220 °C
Carrier gas	Helium, constant flow at 1.8 mL/min
Transfer line temperature	230 °C
MS conditions	
Ion source temperature	230 °C
Quadrupole temperature	150 °C
Ionization	EI mode
Scan mode	Full scan, *m/z* 40–250
EMV mode	Gain factor
Gain factor	5.00
Resulting EM voltage	1,400 V
Solvent delay	0.2 minutes

Sample Preparation

The standards were diluted in air using the static dilution bottle technique in 5-L glass bottles which were first purged for 5 minutes with pure nitrogen gas. After placing 10 µL of the 2,000 ng/µL nitrosamine mixture into the bottle, the sample was equilibrated at 4 hours at room temperature to efficiently vaporize the nitrosamine, with a resulting concentration of 4,000 ng/L. Dilutions were made from this stock by taking 2, 60, 100, and 200 mL of vapor respectively into different 1-L bottles to prepare working standards of 8.0, 240, 400, and 800 ng/L respectively

Results and Discussion

CTS Operation

The CTS consisted of an air pump with a 10 to 300 mL/min flow range, one handheld sampling head and one adaptor. The head can accommodate six trapping columns of the same or different types. This method used six PoraPLOT Q 530-µm id columns. The TSP was used to directly desorb the sample collected using the CTS. Each collection capillary was placed into a disposable micro-vial, which was then placed in the TSP. The TSP was then inserted into a heated split/splitless inlet in the 5975T LTM GC/MS. The trapping column was then quickly and effectively desorbed into the GC injector.

Sampling was performed by inserting the CTS head directly into the bottle mouth, and the columns pierced the sealing film without allowing external air to enter the bottle. The calibration standards were prepared by using the CTS to pump 200 mL each from the 240, 400, and 800 ng/L working standard bottles respectively. In addition, 100, 200, and 400 mL volumes were pumped through the CTS from the 4,000 ng/L working standard to prepare three separate samples. As a result, calibration levels of 48, 80, 160, 400, 800, and 1,600 ng of the nitrosamine standard mixture were prepared for analysis by GC/MS.

CTS Performance

Analysis of a 400 ng nitrosamine standard sample collected using the CTS reveals sharp peaks, with no major components other than the nitrosamines, demonstrating the ability of the CTS to concentrate and quantitatively transfer the nitrosamines without introducing contaminants or artifacts (Figure 1). This is a notable result, given the high activity of nitrosamine compounds that can generate interactions during sample preparation.

Accuracy of Quantitation

The calibration samples prepared using the CTS were used to construct calibration curves for the six nitrosamines in the standard mix. All of the correlation coefficients (R^2) for the six nitrosamine compounds were ≥ 0.990 for the range of 48 to 1,600 ng (Table 3). Figure 2 shows the calibration curves for all six compounds. The calibration curves are not linear above 2,000 ng nor below 48 ng.

Table 3. Correlation Coefficients (R^2) for a Calibration Curve from 48 to 1,600 ng of the Nitrosamine Standards Mix

Name	Quantifier ion (*m/z*)	R^2
N-nitrosoethylmethylamine (NEMA)	88	0.997
N-nitrosodiethylamine (NDEA)	102	0.999
N-nitrosomorpholine (NMOR)	116	0.998
N-nitrosodi-n-butylamine (NDBA)	84	0.990
N-nitrosopiperidine (NPIP)	114	0.999
N-nitrosopyrrolidine (NPYR)	100	0.996

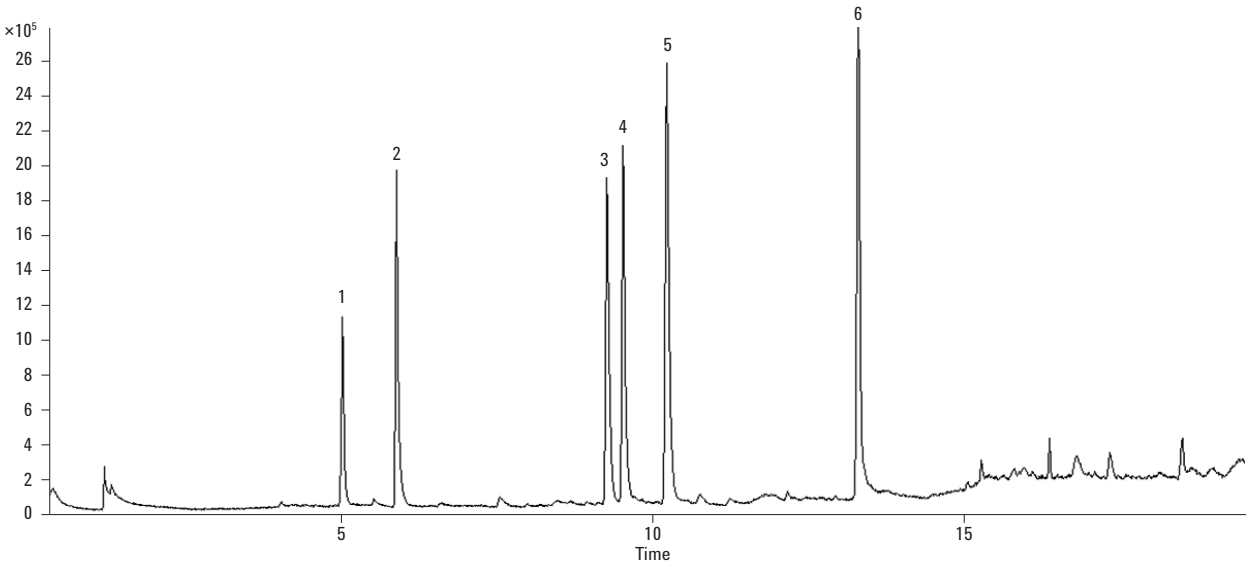

*Figure 1. Total ion current (TIC) of a 400-ng sample of the nitrosamine standard mix collected using the CTS. **1** NEMA; **2** NDEA; **3** NMOR; **4** NDBA; **5** NPIP; **6** NPYP.*

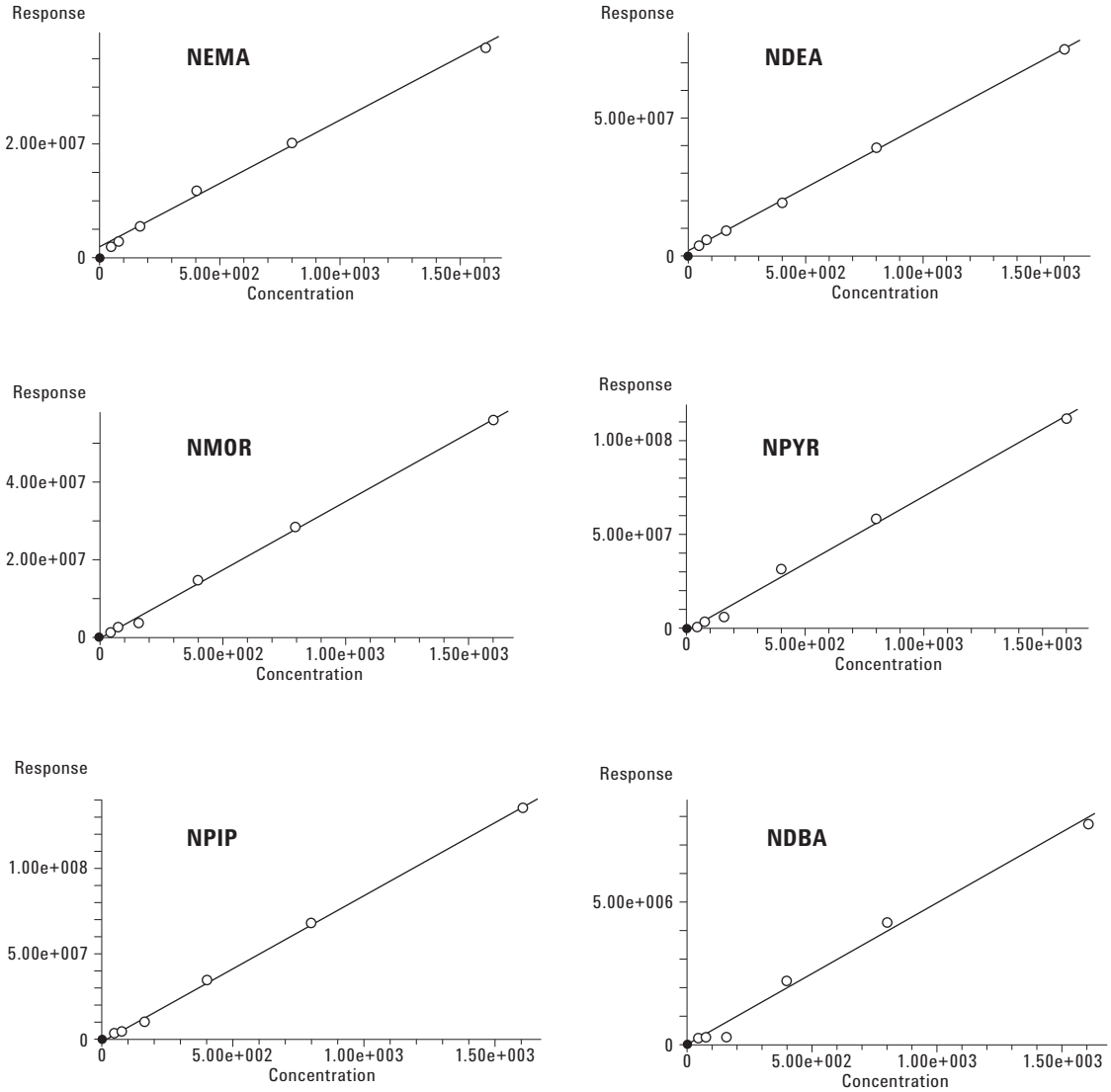

Figure 2. Calibration curves from 48 to 1,200 ng for the six nitrosamines contained in the standards mix.

Sensitivity and Selectivity

This method can be used to detect air concentrations as low as 8 ng/L by pumping 500 mL of the working standard to produce 4 ng of each nitrosamine for injection into the GC/MS. All the compounds exhibit good signal-to-noise, without significant interference (Figure 3). CTS sampling may impart selectivity to the analysis by removing some interferences in air.

The CTS was also used to collect 1.0 ng of the nitrosamine standards mix by pumping 125 mL of the 8 ng/L working standard through the CTS. The signal-to-noise ratios in the extracted ion current (EIC) traces of all of the compounds ranged from 3 to 9, making possible a MDL that may be below 1 ng. The CTS can be used to analyze trace levels of nitrosamines due to its efficient capture of the compounds from large sample volumes.

The recovery of the method was calibrated by liquid injection, and at 200-ng levels was as high as 100% for NDBA. Higher than 100% recoveries were obtained for the other five compounds because liquid injection with TSP causes a slight loss of higher volatility compounds due to instantaneous vaporization of the solvents. The recoveries for the other nitrosamines ranged from 105.0% to 125.5%.

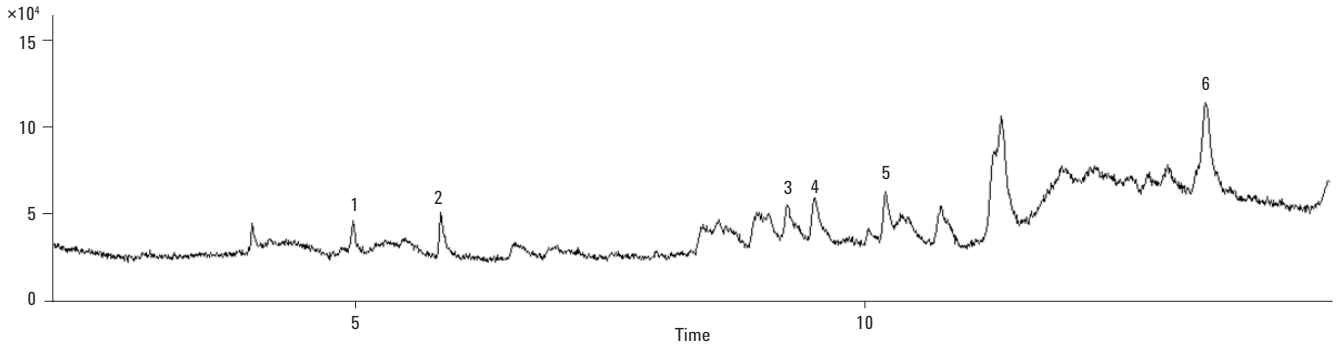

*Figure 3. TIC of 4 ng of the nitrosamine standard mix collected from 500 mL of the 8 ng/L working standard using the CTS. **1** NEMA; **2** NDEA; **3** NMOR; **4** NDBA; **5** NPIP; **6** NPYP*

Conclusions

The innovative Agilent Capillary Trap Sampler (CTS) can provide useful, cost-effective data for volatile nitrosamine screening, routine monitoring and quantitation over a broad concentration range. It is very easy to use and flexible, allowing sampling of low volumes for higher concentration air samples and high volumes for low concentration air samples. Field sampling can be conducted in seconds to minutes. Matching the CTS with the TSP and the transportable Agilent 5975T LTM GC/MS provides a sensitive analysis system for airborne compounds that is ideally suited for a variety of applications, ranging from producing rapid analytical results in screening investigations to accurate and precise data for quantitative studies.

For More Information

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