PO-CON1254E

SHIMADZU
Excellence in Science

GC-MS Determination of 12 N-Nitrosamines in Rubber Teats

IMSC 2012 PWe-201

Peng Gao, Jun Fan, XiaoLi Deng, TaoHong Huang
Analytical Instruments Dept. Analytical Application Center, Shimadzu (CHINA) CO.,LTD, Shanghai 200052, China

GC-MS Determination of 12 N-Nitrosamines in Rubber Teats

Introduction

N-nitroso compounds and specially N-nitrosamines exhibit mutagenic, carcinogenic, and teratogenic activities. It is demonstrated that N-nitrosamines developed a carcinogenic effect in a wide range of animal species like fishes, reptiles, birds, and mammals, including five species of primates.

N-nitrosamines affect the human being in several ways. These substances can be found in foods, such as bacon, fish, cheese, beer, tobacco, water and also in rubber products. In rubber-based articles, vulcanization accelerators are the primary source of the secondary amines, which react with atmospheric or adsorbed nitrogen oxides to produce N-nitrosamines.

In 1985, FDA-USA established a maximum level of 10 ppb of total volatile N-nitrosamines for nipples and pacifiers. The EU directive for child use and care articles has imposed a maximum total concentration of N-nitrosamines at 10 µg/kg, and for nitrosatable compounds at 100 µg/kg as N-nitrosamines.

In this article, a GC/MS method was developed for determination of 12 N-nitrosamine in rubber teats. The release of N-nitrosamines from rubber teats were accomplished by microwave extraction and then purified by C18 SPE cartridges. The analyses were separate on Stabilwax capillary column and detected by EI ion source and selected ion mode.

Fig. 1 Rubber teats

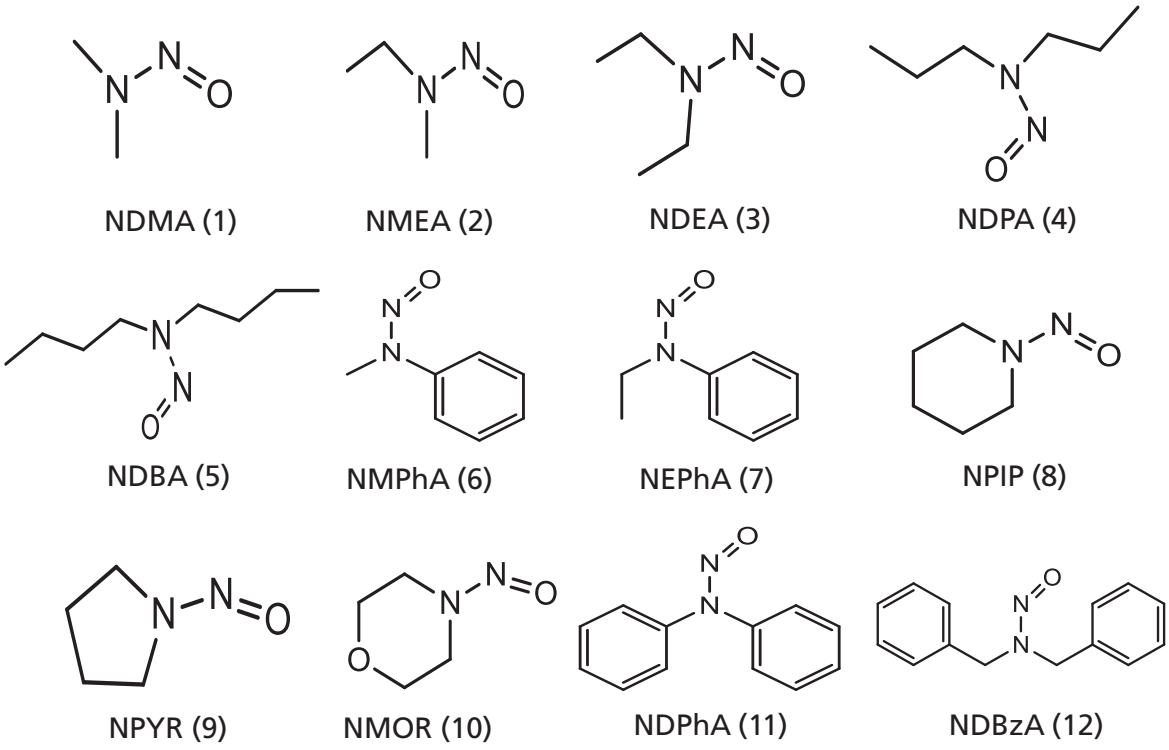


Fig. 2 Structures of 12 N-nitrosamines analyzed in this study

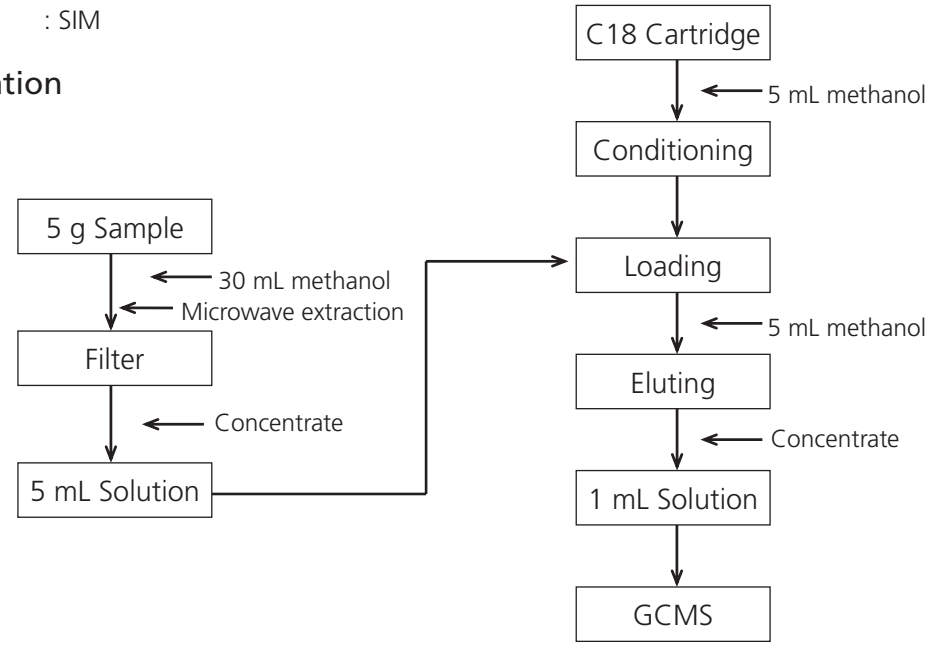
Experimental

Chromatographic conditions

The analysis were performed on a Shimadzu GCMS-QP2010 Ultra (Kyoto, Japan) equipped with AOC-20i+s auto sampler.

Column	: Stabilwax, 30 m × 0.25 mm × 0.25 µm
Constant linear velocity	: 40 cm/sec
Injector temperature	: 230°C
Injector mode	: Spitless
Oven temperature	: 50°C (2 min) - 6°C/min- 170°C (6 min) - 30°C/min- 245°C (10 min)
Injection volume	: 1 µL
Ionization mode	: Electron impact ionization
Ion source temperature	: 200°C
Interface temperature	: 240°C
Solvent Cut Time	: 4 min
Acquisition Mode	: SIM

Sample preparation



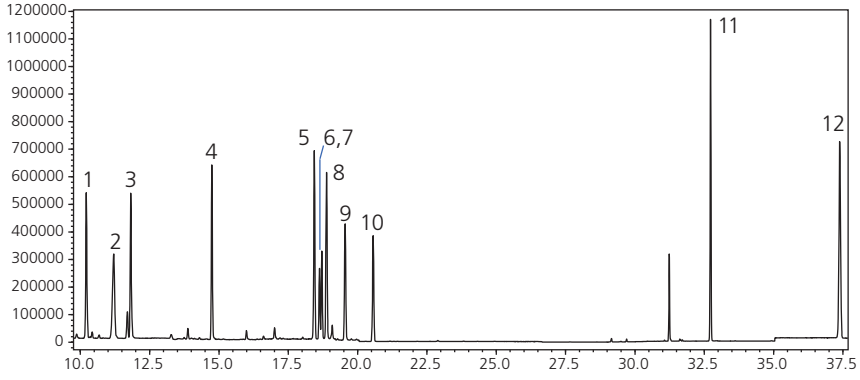


Fig. 3 TIC of 12 N-nitrosamines standard solution in SIM mode (1 ng injection^{-1})

Results and discussion

Linearity range, detection limits, repeatability and recoveries

Prepared 50, 100, 200, 500 and 1000 µg/L standard solutions. The calibration curves and correlation coefficients are shown in Fig. 3.
For 10 µg/mL standard solution, calculating the LODs by GCMSsolution software (S/N=3), LODs are shown in Table 1.

Spiked mixed standard solution into blank samples. The final concentration of spiked samples is 50 µg/kg. The average recoveries and relative standard deviations are shown in Table 1.

Table 1 Retention times, limits of detection (LODs, S/N≥3), average recoveries and the relative standard deviations (RSD, n=5) for N-nitrosamines

NO	Compounds	Linear equation	r	Rt (min)	Recoveries (%)	RSD (%, n=5)	LOD (µg/kg)
1	NDMA	y=798.63x-9418.23	0.9999	10.216	72.51	5.70	0.15
2	NMEA	y=685.28x-14639.68	0.9999	11.201	74.96	5.29	0.27
3	NDEA	y=739.42x-8082.61	0.9999	11.820	88.78	9.72	0.12
4	NDPA	y=246.12x-3436.02	0.9999	14.742	98.73	8.39	0.61
5	NDBA	y=1053.2x-25379.28	0.9999	18.441	82.61	0.86	0.48
6	NMPhA	y=2851.1x+23124.17	0.9991	18.625	103.02	3.66	0.19
7	NEPhA	y-=674.465x-1115.84	0.9991	18.708	101.52	8.51	0.91
8	NPIP	y=731.32x-12849.21	0.9998	18.878	101.71	7.69	0.28
9	NPYR	y=663.04x-12488.32	0.9997	19.551	104.69	7.75	0.36
10	NMOR	y=348.60x-5985.70	0.9998	20.558	97.56	7.42	0.51
11	NDPhA	y=1773.34x+433.94	0.9999	32.732	109.19	4.50	0.33
12	NDBzA	Y=3109.21x-45080.61	0.9996	37.383	104.61	4.44	0.23

Conclusion

A method of GCMS was developed for the determination of 12 N-nitrosamines in rubber teats. The release of N-nitrosamines from rubber teats were accomplished by microwave extraction and then purified by C18 SPE cartridges. The analyses were separated on Stabilwax capillary column and detected by EI ion source with selected ion mode. Good linearity of the calibration curve was obtained in the concentration ranged from 50 to 1000 µg/L for all compounds examined. Recoveries ranged from 70 to 110%, with RSD less than 10% (n=5). The limits of detection of 12 N-nitrosamines examined ranged from 0.15 to 0.61 µg/kg.

First Edition: September, 2012

Shimadzu Corporation
www.shimadzu.com/an/