Ellutia
Chromatography Solutions

TEA Analysis of N-Nitrosamines and Nitrosatable Substance in Toys

As per BS EN 71-12:2013

Toy Testing of Nitrosamines

Nitrosamines are a group of carcinogenic and mutagenic compounds. Daily and prolonged contact with manufactured items including rubber products, such as toys, will lead to continual exposure of these compounds. Potentially any item containing nitrites/nitrates could contain nitrosamines and any process that uses secondary amines, where the manufacturing process results in an introduction of atmospheric nitrous oxide, could produce nitrosamines.

Concern over cumulative exposure has resulted in Ellutia developing an analysis solution, with specific focus on exposure to babies and young children under the scope of UK method ISO EN 71-12 (Safety of toys; N-nitrosamines and N-nitrosatable substances). This method utilises an Ellutia 200 GC for separation followed by an Ellutia 810 TEA (Thermal Energy Analyser) for detection. TEA is a well-established method for analysing compounds containing nitroso groups.

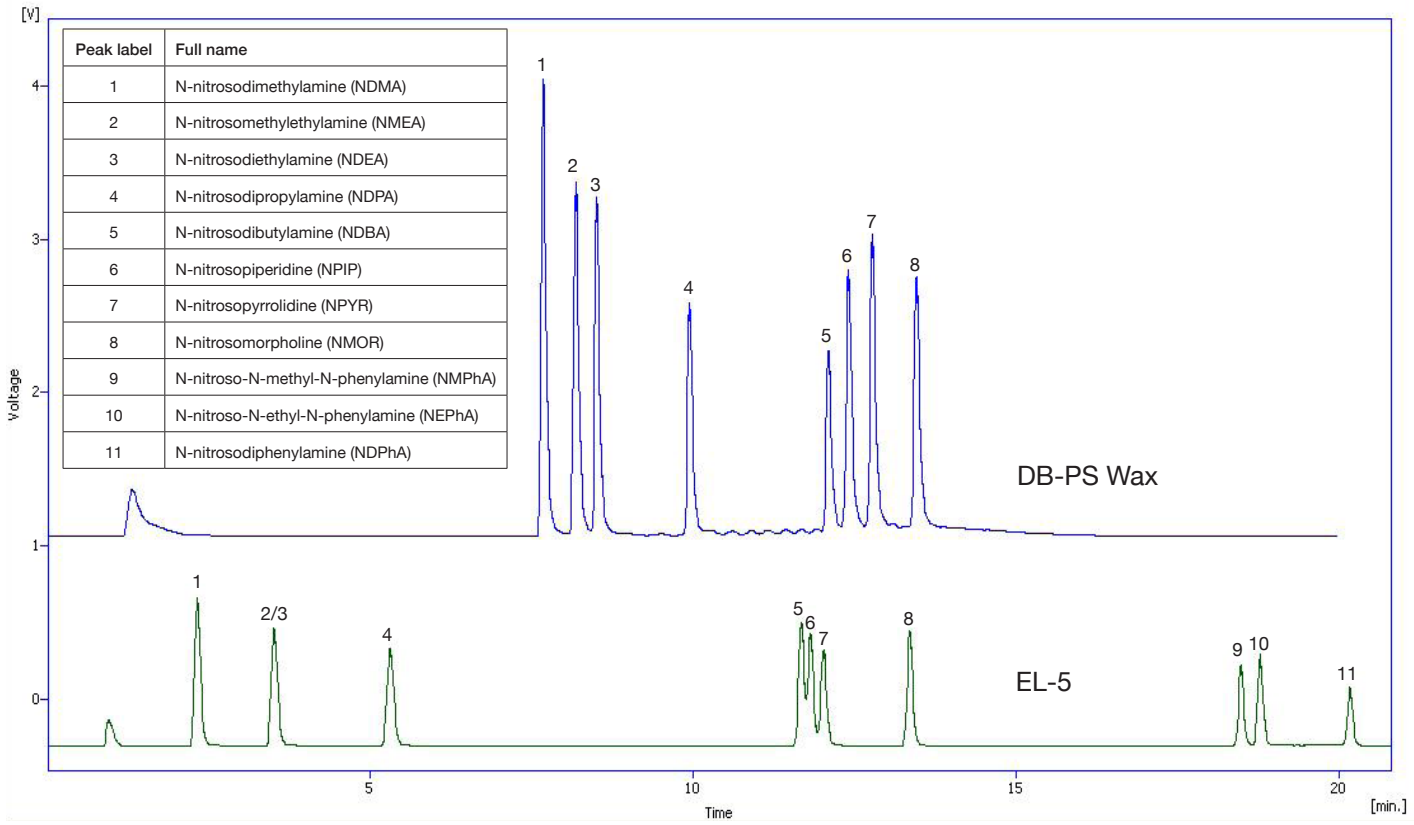
ISO EN 71-12 covers 13 different nitrosamines including some classified as low or non-volatile nitrosamines, this lack of volatility can be overcome by derivatisation. The high molecular weight nitrosamines (NMPhA, NEPhA and NDPhA) had a low response from the wax phase and the EL-5 column was needed for their separation. However the EL-5 column was unable to fully separate the lighter molecular weight nitrosamines.

Method

This ISO method covers 13 different nitrosamines including some low or non-volatile nitrosamines (nitrosodiethylamine NDELA), this can be overcome by derivatising the analyte first. A commercially available derivatisaton kit e.g. BSTFA + TMCS was used and can be injected directly from the reaction vessel. This derivatised NDELA peak will be elute before the other nitrosamine peaks within the multi mix when run on the wax column with the conditions listed below. The presence of high molecular weight nitrosamines – NMPhA, NEPhA etc, is indicated by a range of multiple peaks towards the end of the run.

These nitrosamines had a low affinity for the standard column used however the normal nitrosamines have a low affinity for the column showing good affinity for the Phenyl nitrosamines. Practically, the best solution is to analyse the sample and if any sign of peaks after N-nitrosomorpholine, a confirmatory analysis should be done using the different column.

GC Conditions	8 Nitrosamine Mix	11 Nitrosamine Mix
Injector Temperature (˚C)	150	200
Carrier Gas Type	Helium	Helium
Carrier Gas Control Method	Constant Flow	Constant Flow
Column Flow (ml min^{-1})	18.6	10.0
Split Flow (ml min^{-1})	20	20
Column Pressure	4 psi	4 psi
Injection Volume (µl)	1.0	1.0
Column Type	DB-PSWAX 20 m x 0.53 mm x 1.0 µm	EL-5 30 m x 0.53 mm x 1.5 µm
Column Temperature Program		
Initial Temperature (˚C/Hold Time (min)	40˚C/hold 1 minute	80˚C/hold 1 minute
Temperature Ramp (˚C/ min^{-1})	15	5
First Temperature (˚C)	150	
Second Temperature Ramp (˚C min^{-1})	10	
Upper Temperature (˚C)/ Hold Time (min)	190/1	200/1
Detector	810 TEA	810 TEA



Peak label	Full name
1	N-nitrosodimethylamine (NDMA)
2	N-nitrosomethylethylamine (NMEA)
3	N-nitrosodiethylamine (NDEA)
4	N-nitrosodipropylamine (NDPA)
5	N-nitrosodibutylamine (NDBA)
6	N-nitrosopiperidine (NPIP)
7	N-nitrosopyrrolidine (NPYR)
8	N-nitrosomorpholine (NMOR)
9	N-nitroso-N-methyl-N-phenylamine (NMPhA)
10	N-nitroso-N-ethyl-N-phenylamine (NEPhA)
11	N-nitrosodiphenylamine (NDPhA)

40 ppm Nitrosamine Mix

Results

A variety of children and baby items that would fall into the scope of ISO EN 71-12 were tested to demonstrate this application. Items were sampled and extracted in accordance with ISO EN 71-12 and anlaysed on an Ellutia 200 GC fitted with an Ellutia 810 TEA (Thermal Energy Analyser). A 1 µl injection was analysed. ISO EN 71-12 requires the use of a deuterated internal standard, however as this analysis is GC-TEA and not GC-MS, the internal standards used in this study were not deuterated. A blank reading was taken for the solutions and internal standard used for each sample, and this value was subtracted from calculated concentrations to give the results shown in the table below.

	Concentration measured in mg/kg		
	NDELA	NDMA	NDEA
Blank	(21)	(3.4)	-
Fingerpaints	3.3	2.2	-
Toy 1	0.7	0.3	-
Toy 2	0.8	0.1	-
Looms	1.4	0.2	-
Soothers	0.8	0.5	-
Balloons	-	1.5	0.2

Conclusion

The results shown on the figure above shows how nitrosamines can be successfully detected on an Ellutia 200 GC-TEA. Whilst most products tested showed minimal nitrosamines, N-nitrosodimethylamine (NDMA) and NDELA were present in almost every sample at low levels. Balloons were the only sample to have a positive response for any other nitrosamine – N-nitrosodiethylamine (NDEA). Current U.S. legislation (FDA and CPSC) for nitrosamines recommends that baby products should contain less than 10 ug/kg of any individual nitrosamine per item sold.

Further monitoring of nitrosamines within toys and other rubber/latex products is essential. Whilst manufacturers continue to reduce the exposure risk, it is paramount to reduce baby's and children's exposure to these carcinogenic compounds through strict monitoring and control.

Ordering guide

Main Instruments

TEA 810 - 230V	*(Part no. 32000810)*
Cold Trap Replacement (CTR)	*(Part no. 32090001)*
200 Series FID Gas Chromatograph	*(Part no. 20500130)*
Ellution Software, Single Instrument	*(Part no. 23001001)*
EL-5 30 m x 0.53 mm x 1.5 µm Capillary Column	*(Part no. 51100218)*

Optional:

Ellutia EL3100A Automatic Liquid Autosampler - 15 position	*(Part no. 30500011)*
Ellutia EL3000A Automatic Liquid Sampler - 121 position	*(Part no. 30500010)*
Ellutia EL3200A Automatic Liquid Sampler - 209 position	*(Part no. 30500012)*
Autosampler Control Software	*(Part no. 23001012)*

Accessories

2 ml Vials	*(Part no. 20511101)*
2 ml Vials Screw Caps	*(Part no. 20511107)*
1 µl Liquid Syringe	*(Part no. 20511204)*
Septa (pk50)	*(Part no. 20512101)*
20 ml Headspace Vial and Cap	*(Part no. 30501003)*

Solutions Required

BSTFA
TMCS

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