

ANALYSIS OF N-NITROSAMINES AND NITROSATABLE SUBSTANCES FROM ELASTOMER OR RUBBER TEATS, SOOTHERS AND TOYS

AS PER BS EN 71-12:2016 AND BS EN 12868:2017

Testing for Nitrosamines

Nitrosamines are a group of carcinogenic and mutagenic compounds. Daily and prolonged contact with manufactured items such as toys and soothers, 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 BS EN 71-12:2016 (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 BS EN 12868:2017 approved method for analysing compounds containing nitroso groups.

In accordance to 93/11/ECC, total concentration for N-nitrosamines or N-nitrosatable substances must not exceed 10 µg/kg individually or 100 µg/kg cumulatively, furthermore, current BS EN 71-12:2016 emphasises that baby products should contain less than 10 µg/kg of any individual N-nitrosamine and less than 20 µg/kg of total N-nitrosamines per item sold.

Method

The BS EN 71-12:2016 method covers 13 different nitrosamines including some low or non-volatile nitrosamines such as N-nitrosodiethylamine (NDELA). This can be overcome by volatilisation using a commercially available derivatisation kit containing BSTFA + 1% TMCS.



GC Conditions

Injector Temperature (°C)	220
Linear Type	Focus Liner with Wool
Carrier Gas Type	Helium
Carrier Gas Control Method	Constant Flow
Gas Flow (PSI)	2
Injection Type	Split-less
Split-less Time (min)	0.5
Column Type	EL-FFAP 15m x 0.32 mm x 0.5 µm

Detector Conditions

Detector	810 TEA
Detector Temperature (°C)	250
Pyrolyser Temperature (°C)	500
Detector Sensitivity	230
Vacuum (torr)	0.39
Oxygen Flow (psi)	2
Column Type	EL-FFAP 15m x 0.32 mm x 0.5 µm

Column Temperature Program

Initial Temperature (°C)	60 (hold 0 mins)
Temperature Ramp 1	10°C min ⁻¹ to 160 °C (hold 0 mins)
Temperature Ramp 2	20 °C min ⁻¹ to 160°C (hold 3 mins)

Results

A variety of children and baby items that would fall within the scope of BS EN 71-12 were sampled and extracted using the Ellutia 810 TEA (Thermal Energy Analyser) and quantitation limits were calculated to prove the instrumentation achieves the necessary Limits of Quantitation (LOQ) in accordance with BS EN 12868:2017. The results shown in Table 1 and Figure 1 show how nitrosamines can be successfully separated by the 200 Series GC and detected with the 810 Series TEA with easily matching or exceeding Limits of Quantitation stated in the EN 12868:2017 method.

Peak No	Name	Abbreviation	CAS Number	BS EN 12868:2017 LOQ ($\mu\text{g}/\text{kg}$)
1	N-nitrosodimethylamine	NDMA	62-75-9	1.0
2	N-methylethylamine	NMEA	624-78-2	1.0
3	N-nitrosodiethanamine	NDEA	55-18-5	1.0
4	N-nitrosodipropylamine	NDPA	621-64-7	1.0
5	N-nitrosodibutylamine	NDBA	924-16-3	1.0
6	N-nitrosopiperidine	NPIP	100-75-4	1.0
7	N-nitrosopyrrolidine	NPYR	930-55-2	1.0
8	N-nitrosomorpholine	NMOR	59-89-2 / 67587-56-8	1.0
9	N-nitroso N-ethyl N-phenylamine	NEPhA	612-64-6	5.0
10	N-nitroso N-methyl N-phenylamine	NMPhA	614-00-6	5.0
11	N-nitrosodibenzylamine	NDBzA	5336-53-8	5.0

Table 1: List of N-nitrosamines used with subsequent BS EN 12868:2017 Quantitation Limit requirements.

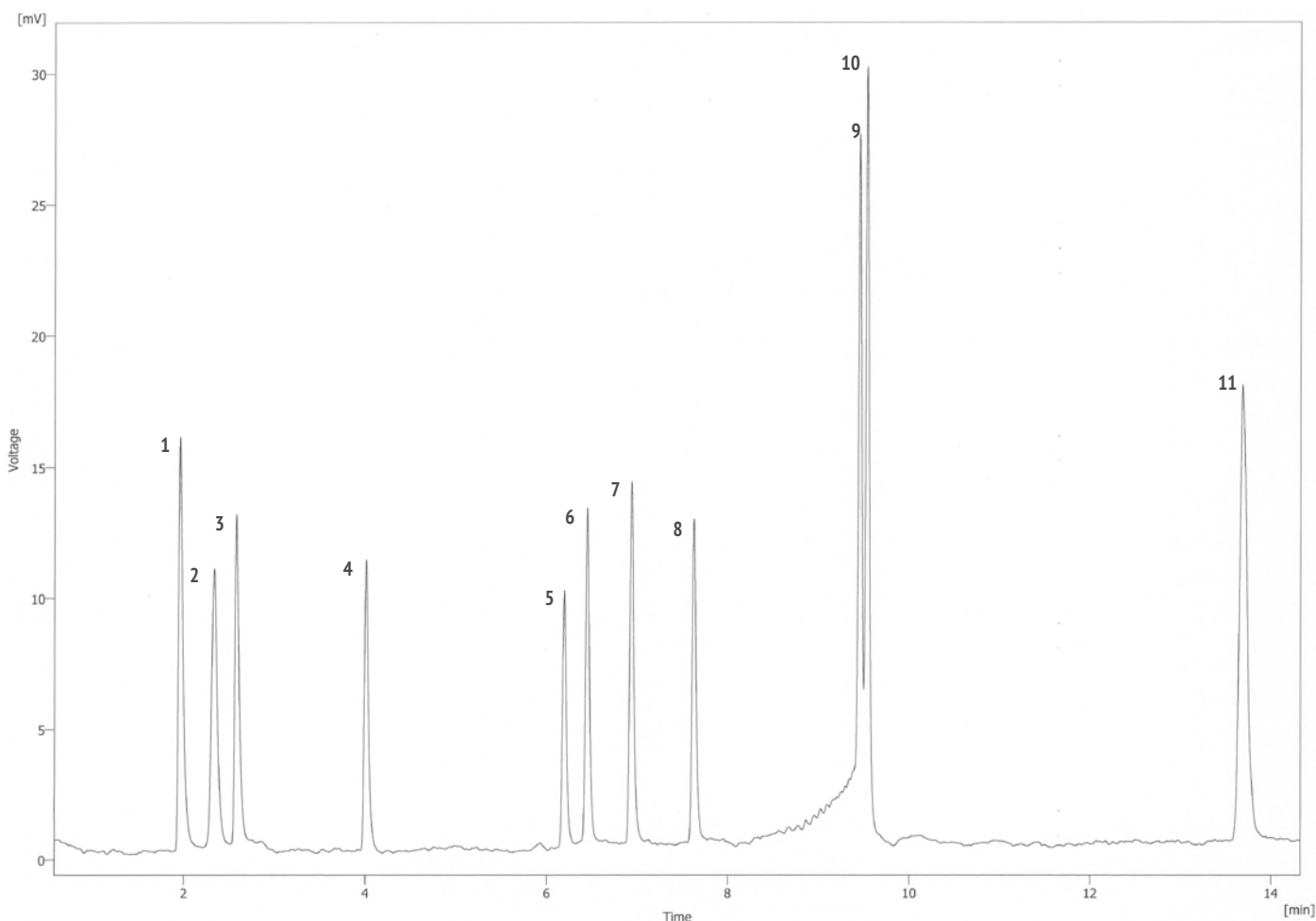


Figure 1: A chromatogram showing the separation of a multi-component nitrosamine standard.

	Concentration measured in $\mu\text{g}/\text{kg}$		
	NDELA	NDMA	NDEA
Blank IS	(2.1)	(3.4)	-
Finger-paints	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

Table 3: Concentration of Nitrosamines found in toys and soothers ($\mu\text{g}/\text{kg}$).

The legislation also 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 necessary. A blank reading was taken for the solutions with an internal standard. Spike and recovery calculation were used to determine the analyte detection, as seen in Table 3.

Current EU and U.S. legislations (FDA and CPSC) for nitrosamines recommend that baby products should contain less than $10 \mu\text{g}/\text{kg}$ of any individual and $20 \mu\text{g}/\text{kg}$ of total nitrosamines per item sold. The above data presents that, whilst most products tested showed the presence of nitrosamines, N-nitrosodimethylamine (NDMA) and NDELA were observed in every tested sample at low levels, whereas N-nitrosodiethylamine (NDEA) was only found in the balloons. Therefore, none of the samples tested were found to contain levels above the legislation for individual and total nitrosamines.



Conclusion

As the TEA is a Nitrogen specific detector, the sensitivity and selectivity for the compounds tested is superior to other detectors. The ease of set up and use sets the TEA aside from more costly and complicated systems.

Separation of N-nitrosamines within the BS EN 12868:2017 recommended LOQs can be performed on Ellutia 810 Thermal Energy Analyser. Baseline separation and reproducible chromatography was obtained for the compounds within the concentration range of $1 - 5 \mu\text{g}/\text{kg}$ with LODs and LOQ matching or exceeding those stated in EN 12868:2017.

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. The Ellutia 810 Thermal Energy Analyser system manifests compliance with appropriate European legislations and the method demonstrates enhanced sensitivity in ability to detect and quantify these harmful compounds.

Ordering Guide

Main Instruments

TEA 810 - 115V or 230V	Part no. 32000810
Cold Trap Replacement	Part no. 32090001
200 Series Gas Chromatograph - 11V	Part no. 20501130
200 Series Gas Chromatograph - 230 V	Part no. 20500130
Ellution Software, Single Instrument	Part no. 23001001
EL - FFAP 15m x 0.32mm x 0.5 µm Capillary Column	Part no. 51100343

Optional

Ellutia EL3100A Automatic Liquid Autosampler 15 position	Part no. 30500011
Ellutia EL3000A Automatic Liquid Autosampler 121 position	Part no. 30500010
Ellutia EL3200A Automatic liquid Autosampler 209 position	Part no. 30500012
Ellution Autosampler Control Software	Part no. 23001012

Accessories

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

Solutions Required

BSTFA
TMCS