联和层析
应用文章精选
2017 | 04

联和层析致力于**提供无限可能的色谱解决方案**。十多年来，我们与全球多家专业色谱厂商保持良好合作伙伴关係，并将他们优势产品引进到国内。本着**诚恳、实在、专业、负责**的理念，联合层析在样品前处理及自动化的领域已占据领先地位。

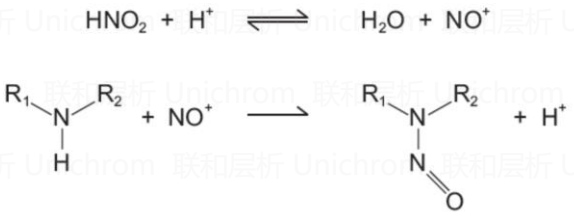
为服务广大客户对于了解国际间最新色谱应用方向的需求，联和层析定期精选并翻译应用文章，为国内的科技服务提升，略尽绵薄之力！

《透过 PAL SPME Arrow 和气相色谱/质谱仪自动化测定水中的亚硝胺》

Quantification of nitrosamines in water by automated PAL SPME Arrow and GC/MS；原文刊载于 CTC 于 2016 年 2 月发行的 GC Application Note；由联和层析贸易（上海）有限公司编译

【应用背景介绍】

对于许多动物（包含人类）而言，大多数亚硝基化合物是可疑致癌物。人类可能透过摄入或吸入环境中的化合物而接触致癌的亚硝胺。这些亚硝胺是由与胺类化合物反应形成，尤其是二级胺和三级胺或含亚硝酸盐的胺基化合物（例如：食物中的防腐剂）。NDMA 和 NDEA 是食品材料中最常见的亚硝胺。



【结论】

- 制定出一个为多种亚硝胺于水溶液样品中的定量分析方法
- 根据先前的研究，选定 Carboxen / PDMS SPME 纤维为吸附物
- Carbon WR SPME Arrow 提取率/检测器信号比 Carboxen / PDMS SPME 纤维提升 3-5 倍
- 检测限（=S/N>3）范围从 5ng/L（N-nitroso-dipropylamin）到 50N/L（n-nitroso-pyrolindinamine）
- 在 1µg/L 的重复性为 4-12%
- 运行一个样品的时间为 30 分钟提取+30 分钟 GC 运行时间。重叠提取 7 个样本的总运行时间约为 240 分钟
- PAL RTC/RSI 手臂配置 SPME Arrow 模块，可全自动进行 SPME 分析，并确保过程的安全及结果的高重复性

SPME Arrow → 萃取 → 解析/注射 → 调节

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GC Application Note

Quantification of nitrosamines in water by automated PAL SPME-Arrow and GC/MS

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Quantification of nitrosamines in water by automated PAL SPME-Arrow and GC/MS

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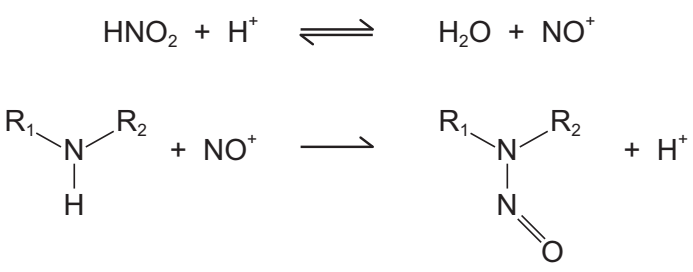
Short summary:

- A method for the quantitative analysis of a number of different N-nitrosamines from aqueous samples has been worked out.
- Carboxen/PDMS SPME fibers and Carbon WR SPME Arrow were compared. Carbon WR SPME Arrow gave a 3-5 x higher extraction yield/detector signal.
- The limits of detection (= S/N > 3) range from 5 ng/L for N-nitroso-dipropylamin to 50 n/L for N-nitroso-pyrolindin-amine.
- Repeatability @ 1 µg/L ranges from 4-12%.

Introduction:

Most nitroso compounds are suspected carcinogens in various animals including human beings. Human exposure to carcinogenic N-nitrosamines may result directly from ingestion or inhalation of preformed compounds from the environment. They are formed by the reaction of amines, especially secondary and tertiary amines or amino group containing compounds with nitrite (present e.g.as food preservative). N-nitroso-dimethylamine (NDMA) and N-nitroso-diethylamine (NDEA) are the most common nitrosamines found in food materials.



Experimental:

1. Immersion Extraction

Sample	10ml water in 20ml HS vial with 4g KCl
Fiber	Carbon WR SPME Arrow (PAL Sytem No: ARR11-C-WR-120-20-P1) Carboxen/PDMS SPME Fiber (part of Supelco kit, No: 57284-U)
Pre conditioning	0:30 min
Pre incubation time	1:00 min
Incubation temp	50°C
Agitation speed	500 rpm
Needle penetration	22 mm
Fiber penetration	30 mm
Extraction time	30 min
Desorption time/temp	2:00 min/ 260°C

2. Chemicals

Nitrosamines calibration standard (Restek No: 31898)
N-nitroso-dimethylamine
N-nitroso-methylethylamine
N-nitroso-diethylamine
N-nitroso-dipropylamine
N-nitroso-dibutylamine
N-nitroso-pyrolidone
N-nitroso-piperidine
Diluted in Methyl tert-butyl ether (Fluka No: 20249)

3. GC/MS

GC	Varian 3400
MS	Varian Saturn ion trap
Column	60 m; 0.25 mm ; 25 µm BGB Wax 20M
Carriergas	Hydrogen 10.0 psi
Temp. program	50°C for 1min, then 10°C/min to 240°C
Injector	260°C
Mass Range	42 bis 250 m/z

With the PAL RTC and RSI the entire SPME process is fully automated. This guarantees process safety and high reproducibility.

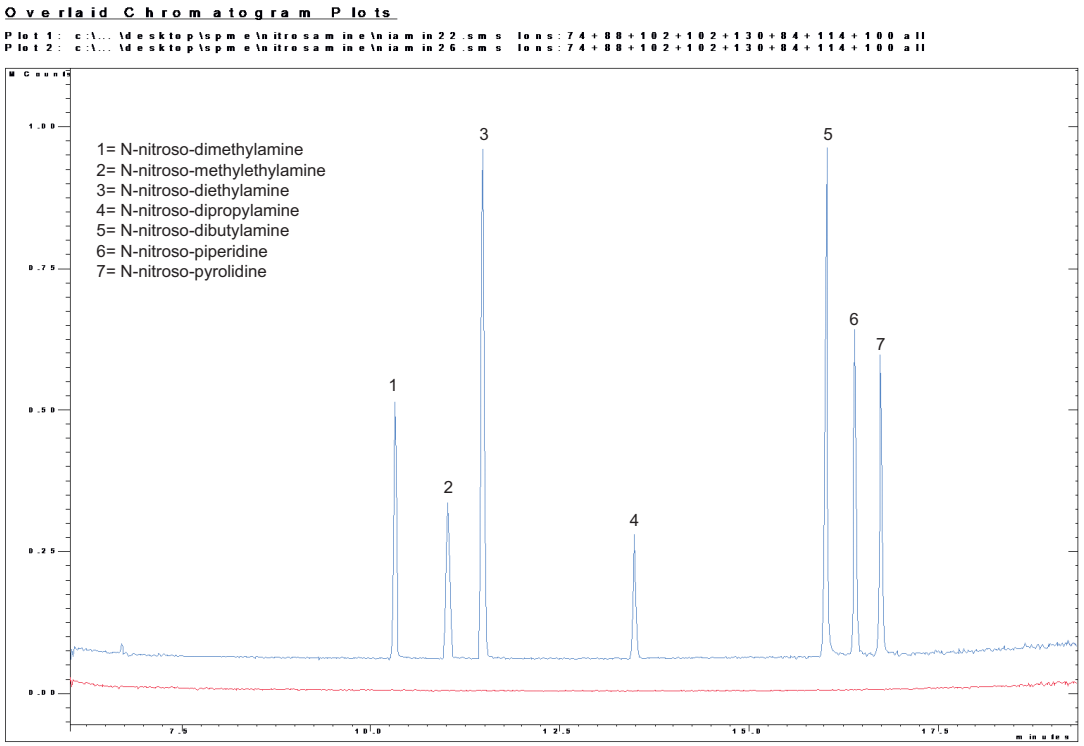


Fig. 1: Chromatograms of 1 µL of a 1 µg/L standard solution and blank direct injection

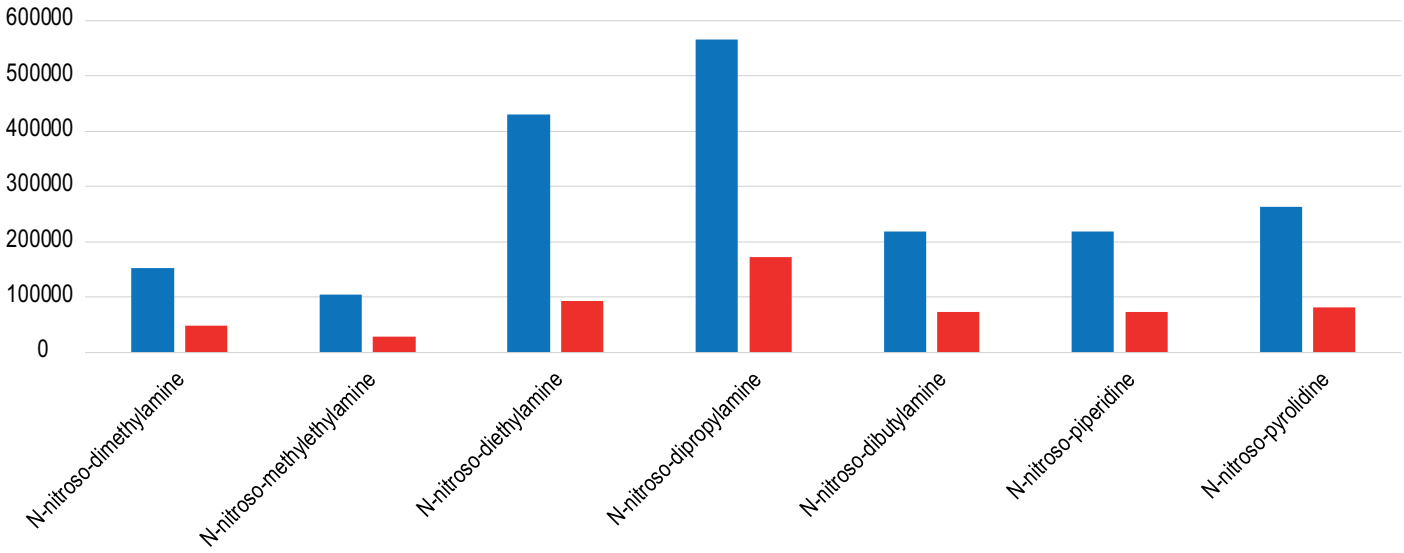
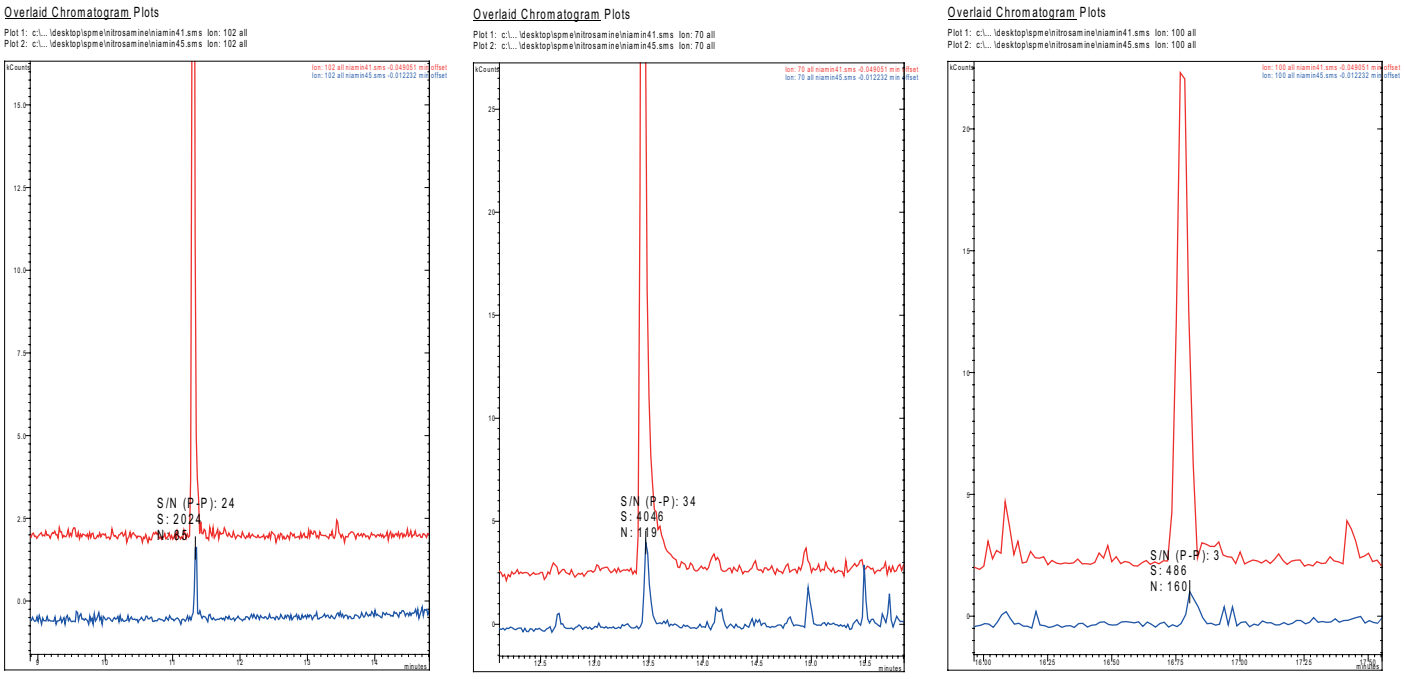


Fig. 2: Comparison of relative detector (MS) response for different nitrosamines @ 1 µg/L between Carbon WR SPME Arrow and Carboxen/PDMS SPME

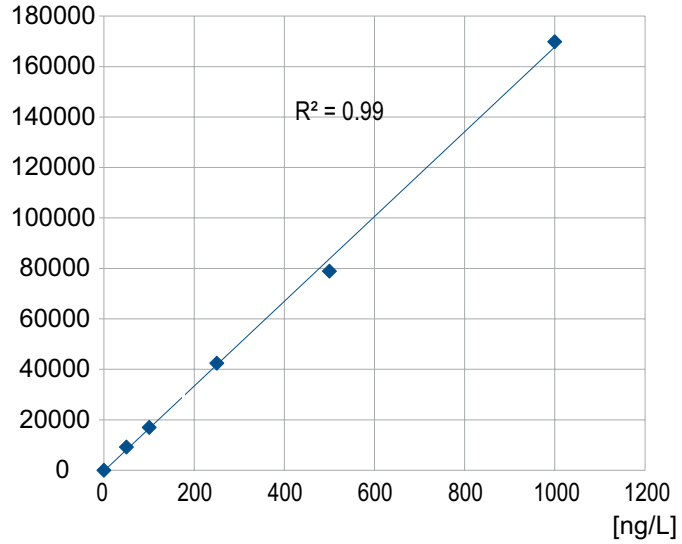
	N-nitroso-dimethylamine	N-nitroso-methylethyl-amine	N-nitroso-diethylamine	N-nitroso-dipropylamine	N-nitroso-dibutylamine	N-nitroso-piperidine	N-nitroso-pyrolidine
Average (n=5)	153621	1105607	430555	566316	218648	218468	264031
% RSD	11.9	8.8	5.9	4.2	6.8	14.1	10.4

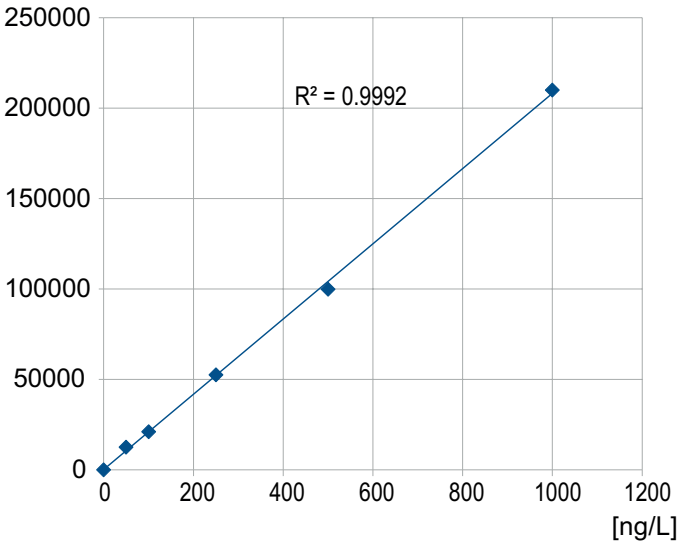
Tab. 1: Reproducibility for the quantification of different nitrosamines @ 1 µg/L with Carbon WR SPME Arrow.



N-nitroso-diethylamine @ 50 ng/L, S/N 24 | N-nitroso-dipropylamine @ 50 ng/L, S/N 34 | N-nitroso-pyrolidinamine @ 50 ng/L, S/N 3 (=LOD)

Fig. 3: Chromatograms for selected N-nitrosamines, @ 1000 ng/L and 50 ng/L with Carbon WR SPME Arrow.





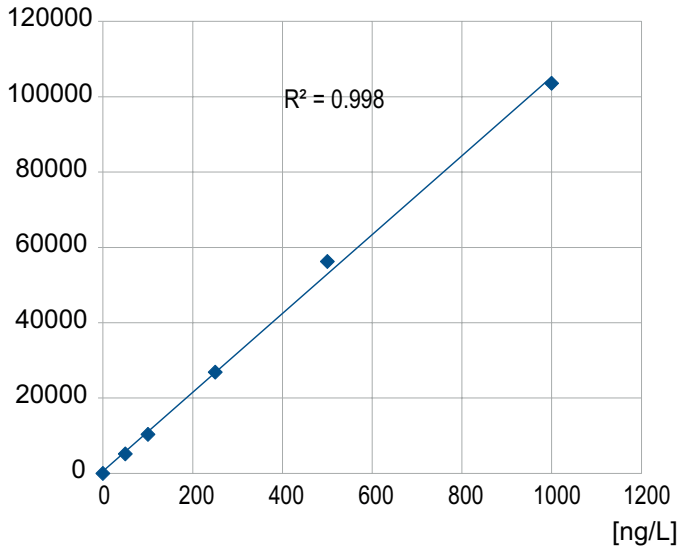


Fig. 4, 5, 6: Calibration curves for N-nitroso-diethylamine (top), N-nitroso-dipropylamine (middle) and N-nitroso-pyrolidineamine (bottom)

Conclusions:

- A method for the quantitative analysis of a number of different N-nitrosoamines from aqueous samples has been worked out.
- Based on previous publications (ref.1) Carboxen/PDMS SPME fibers have been selected as sorbent material
- Carboxen/PDMS SPME fibers and Carbon WR SPME Arrow were compared. Carbon WR SPME Arrow gave a 3-5 x higher extraction yield/detector signal.
- The limits of detection (= S/N > 3) range from 5 ng/L for N-nitroso-dipropylamin to 50 n/L for N-nitroso-pyrolindinamine.
- Repeatability @ 1 µg/L ranges from 4-12% @ 1 µg/L.
- Time for one sample was 30 min extraction + 30 min GC runtime. With overlapped extraction (e.g. with PAL Sample Control http://www.palsystem.com/index.php?id=243 , or many other chromatographic data systems) the total runtime for 7 samples was approximately 240 min.

References:

[1] Grebel JE, Young CC, Suffet IH, J. Chrom. A, 1117 (2006) 11–18

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Imprint

Date of print: 02.2016

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