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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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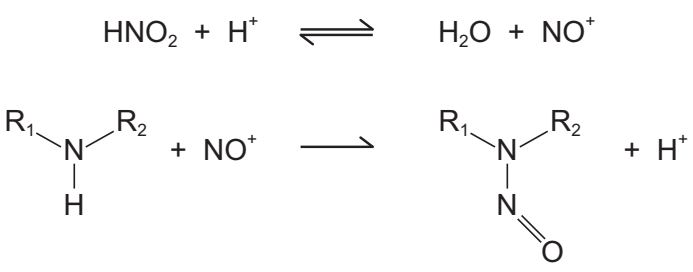
Short summary:

- 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.

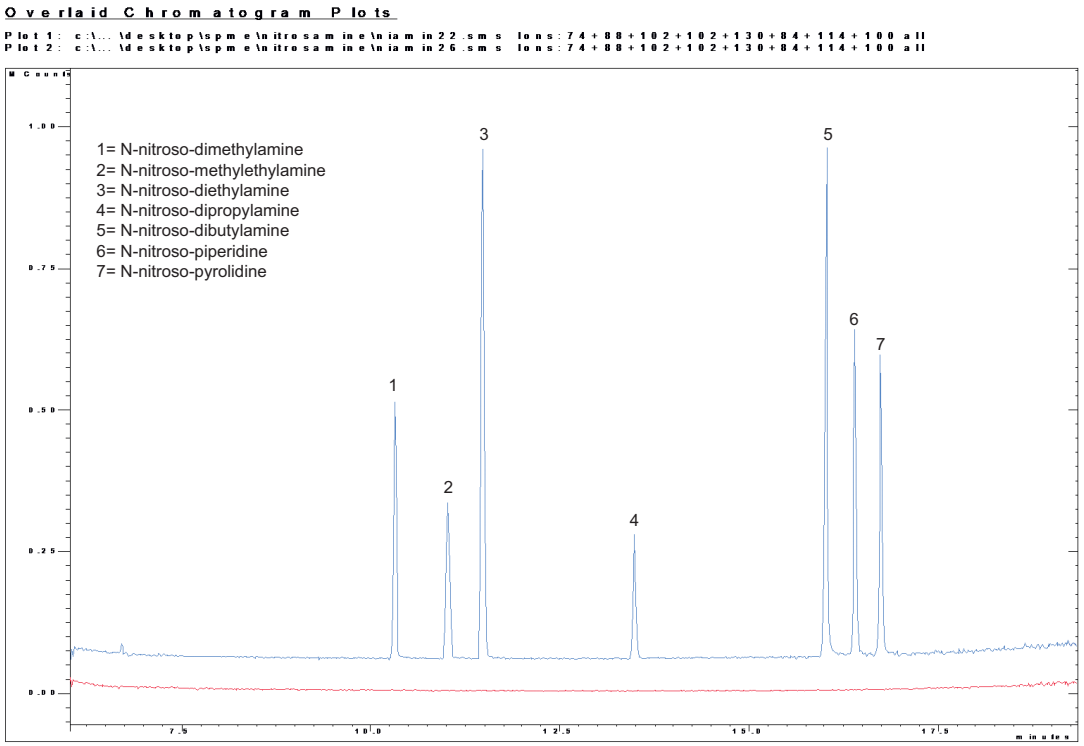


Fig. 1: Chromatograms of 1 µL of a 1 µg/L standard solution and blank direct injection

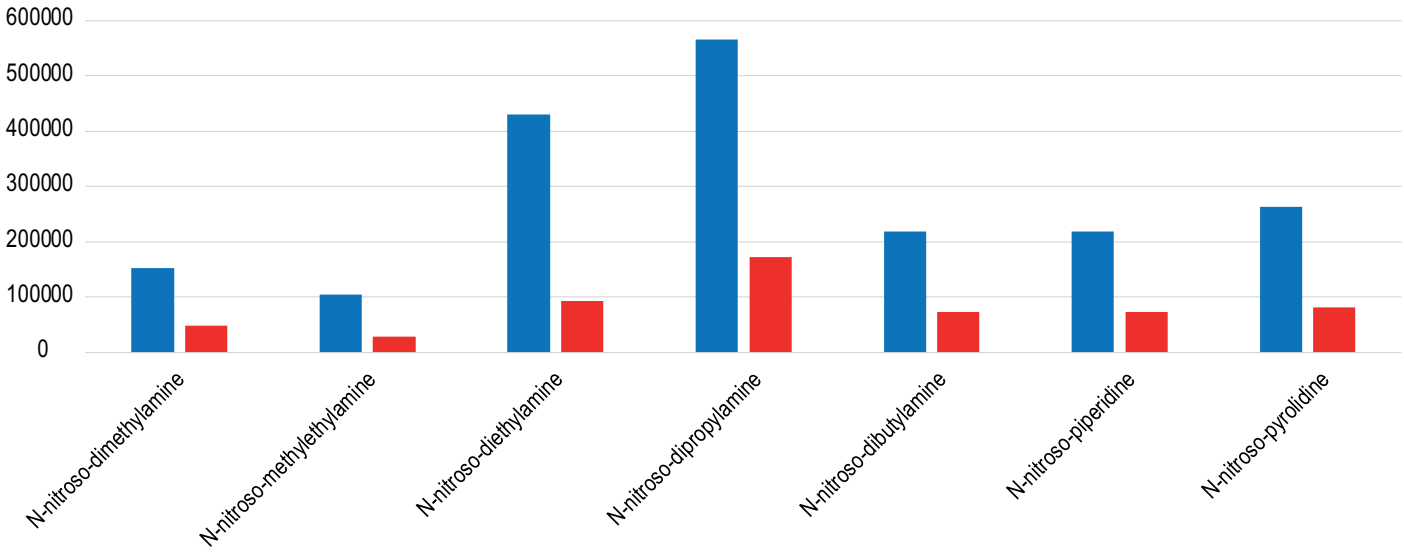
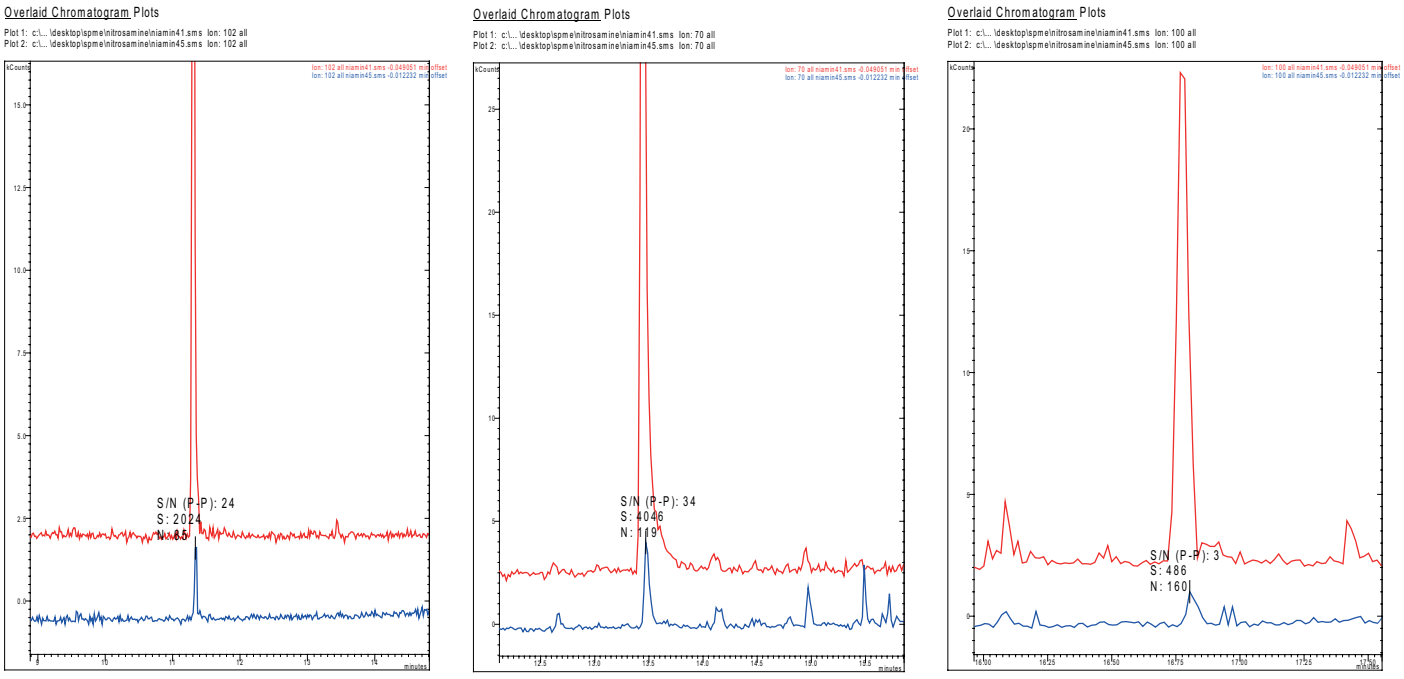


Fig. 2: Comparison of relative detector (MS) response for different nitrosamines @ 1 µg/L between Carbon WR SPME Arrow and Carboxen/PDMS SPME

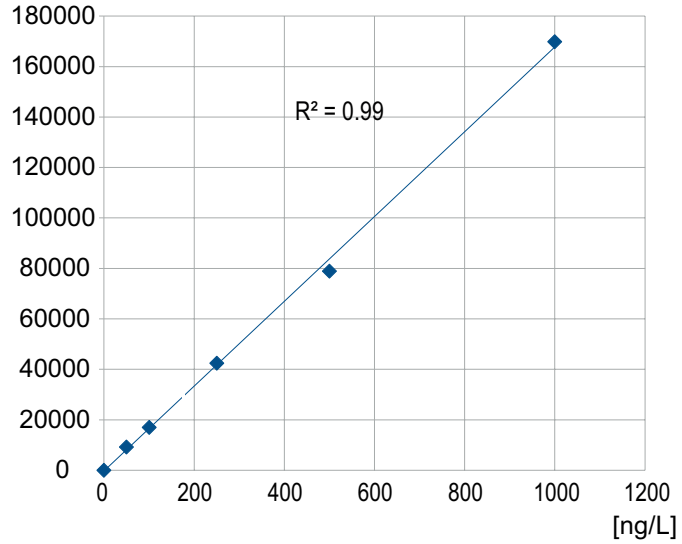
	N-nitroso-dimethylamine	N-nitroso-methylethyl-amine	N-nitroso-diethylamine	N-nitroso-dipropylamine	N-nitroso-dibutylamine	N-nitroso-piperidine	N-nitroso-pyrolidine
Average (n=5)	153621	1105607	430555	566316	218648	218468	264031
% RSD	11.9	8.8	5.9	4.2	6.8	14.1	10.4

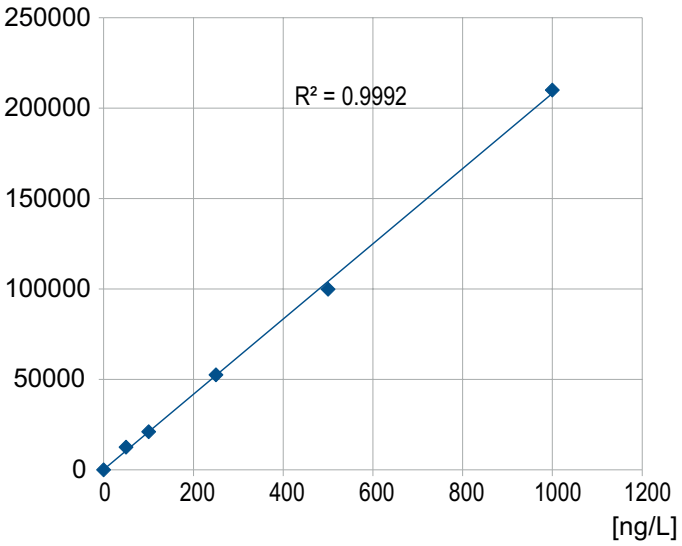
Tab. 1: Reproducibility for the quantification of different nitrosamines @ 1 µg/L with Carbon WR SPME Arrow.



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.





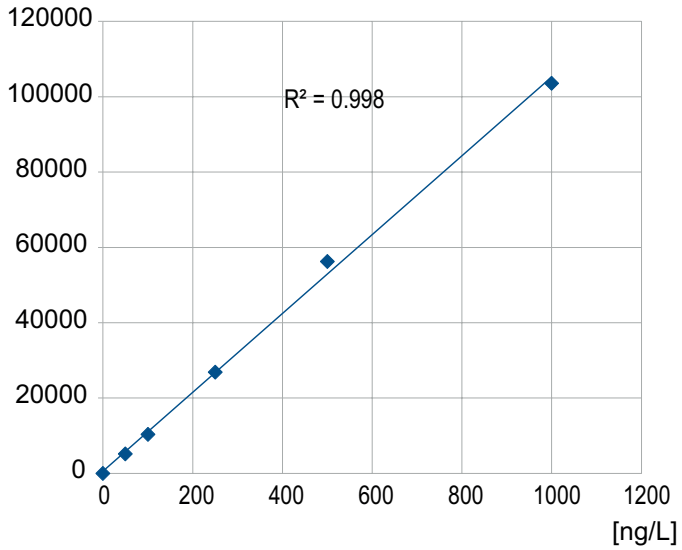


Fig. 4, 5, 6: Calibration curves for N-nitroso-diethylamine (top), N-nitroso-dipropylamine (middle) and N-nitroso-pyrolidineamine (bottom)

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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