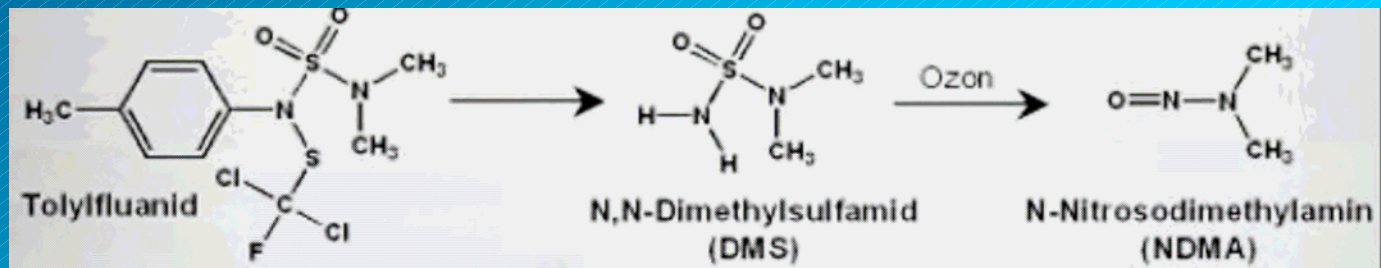


# Solid Phase Extraction Tubes for Extracting Nitrosamines From Drinking Water





Tolyfluanid used as fungicide (100-250 tons in 2006)  
main metabolite DMS

converted into NDMA by  
chlorination (not used in Germany)  
ozonation

detailed information:  
Carsten K.Schmidt TZW Karlsruhe/Rheinenergie AG

# Method Overview

## EPA Method 521

- Sample extraction & concentration
  - 7 nitrosamines in drinking water
  - 0.5L water + surrogates
  - SPE
    - 80/120 mesh activated charcoal – 2g/6mL cartridge (#26032)
    - Methylene chloride elution
  - Extract dried, concentrated, and spiked with IS
- Analysis
  - Fused silica capillary column
  - GC/MS/MS with Large volume injection (LVI)
  - Operated in Chemical Ionization (CI) Mode
  - ID and quantitation in MS/MS mode



# Target Compound List

Analyte	Chemical Abstract Services (CAS) Registry Number
N-Nitrosodimethylamine (NDMA)	62-75-9
N-Nitrosomethylethylamine (NMEA)	10595-95-6
N-Nitrosodiethylamine (NDEA)	55-18-5
N-Nitrosodi-n-propylamine (NDPA)	621-64-7
N-Nitrosodi-n-butylamine (NDBA)	924-16-3
N-Nitrosopyrrolidine (NPYR)	930-55-2
N-Nitrosopiperidine (NPIP)	100-75-4

# Recovery Study

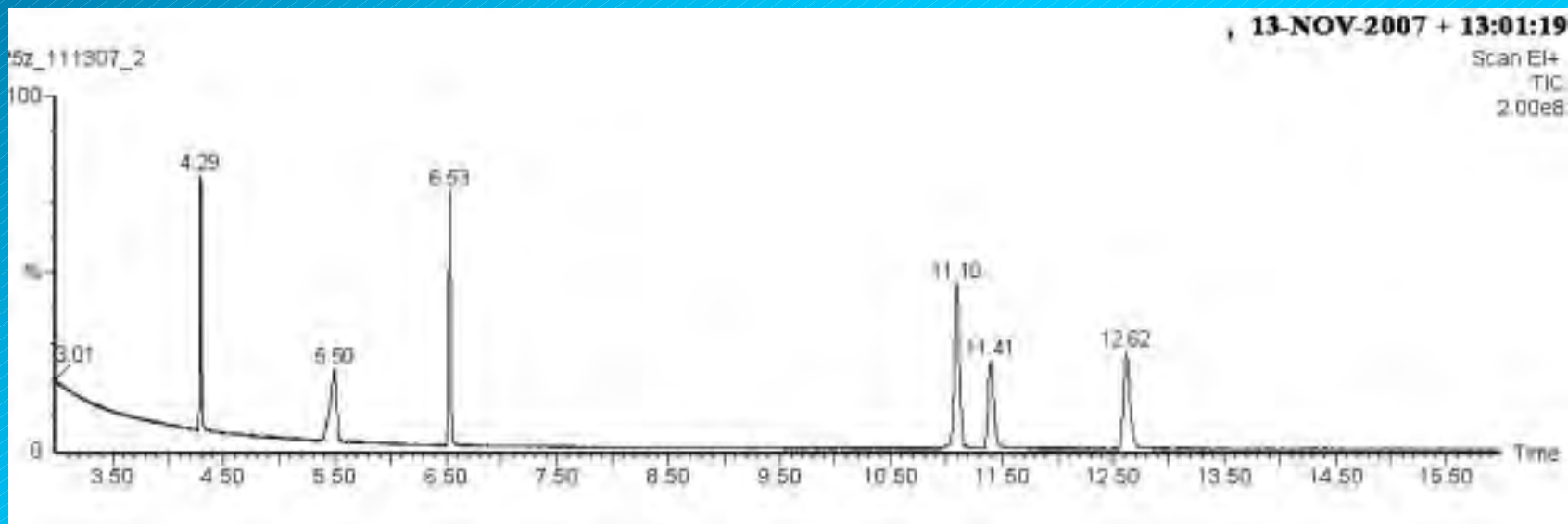
## SPE Extraction Method

Tubes	EPA Method 521, 6mL/2g cat#26032, lot# LN3-049, V20461
Conditioning	2 x 3mL CH <sub>2</sub> Cl <sub>2</sub> , 2 x 3mL methanol, 2 x 3mL deionized water
Spike stand.	100uL stock standard (1000mg/mL cat# 31427)
Sample	100mL deionized water
Dry	1mL methanol 35-40min lab air
Extraction	2 x 5mL CH <sub>2</sub> Cl <sub>2</sub> collected to ~ 5mL mark

Lot#	% Recovery	Stdev	n=
LN3-049	99.2	7.85	10
V20461	97.0	0.13	2

# Nitrosamine Standard

10ug/mL in CH<sub>2</sub>Cl<sub>2</sub> (~ 10ng on-column)



Retention time, min	Identification
4.29	NDMA
5.50	NMEA
6.53	NDEA

Retention time, min	Identification
11.10	NDPA
11.41	NPYR
12.62	NPIP
12.62	NDBA

# GC-MS Conditions

Column: Rtx<sup>®</sup>-CLPesticides 30m, 0.25mm ID, 0.25 $\mu$ m  
(cat.# 11123)

Sample: 10 $\mu$ g/mL NDMA standard (cat.# 31427) in CH<sub>2</sub>Cl<sub>2</sub>

Inj.: 1.0 $\mu$ L splitless (hold 0.5 min.), 3.5mm Siltek single  
gooseneck inlet liner (cat.# 20961-214.1)

Inj. temp.: 220 $^{\circ}$  C

Carrier gas: helium, constant flow

Flow rate: 1.5mL/min.

Oven temp.: 40 $^{\circ}$  C (hold 1min.) to 90 $^{\circ}$  C @10 $^{\circ}$  C/min. hold for 10min.

Det: HP 5973 MSD

Transfer line temp.: 280 $^{\circ}$  C

Scan range: 40-600 amu

Ionization: EI

Mode: TIC scan

# SPE Tube Advantages

- Batch tested to ensure low background & consistent recoveries
- High quality polypropylene tubes & frits to minimize interference
- Specially treated charcoal & frits are used to minimize fines that result in inconsistent recoveries

# Performance Criteria

- Physical Characteristics (fines)
- Background (cleanliness)
- % Recovery

# Physical Characteristics Lot Variability

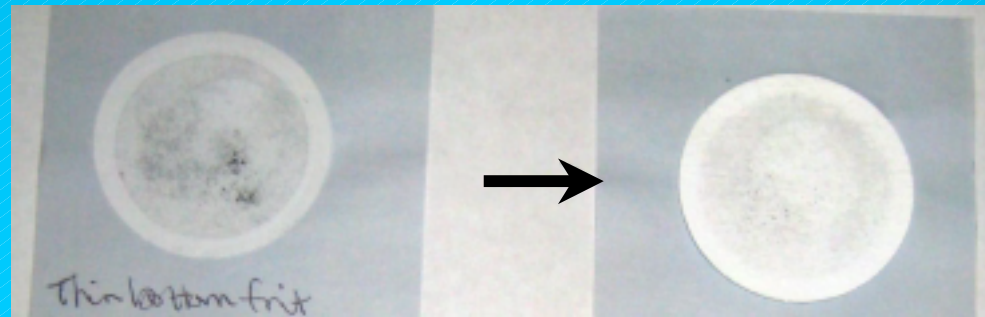
- Bed height is indirect measurement of density of charcoal and packing process
- Low number of fines improves recovery

	<b>Bed Height, cm</b> n = 25	<b>Bed Weight, g</b> n = 2	<b>Particle Size</b>
<b>Lot #V20461</b>	3.8 SD $\pm$ 0.06 % RSD 1.5	2.1	80 mesh 7% +80 120 mesh 7% -120
<b>Lot #V24281</b>	3.9 SD $\pm$ 0.07 % RSD 1.9	2.0	80 mesh 0.1% +80 120 mesh 1.2% -120

# Particle Breakthrough Competitor Comparison

Cartridges conditioned & extract filtered

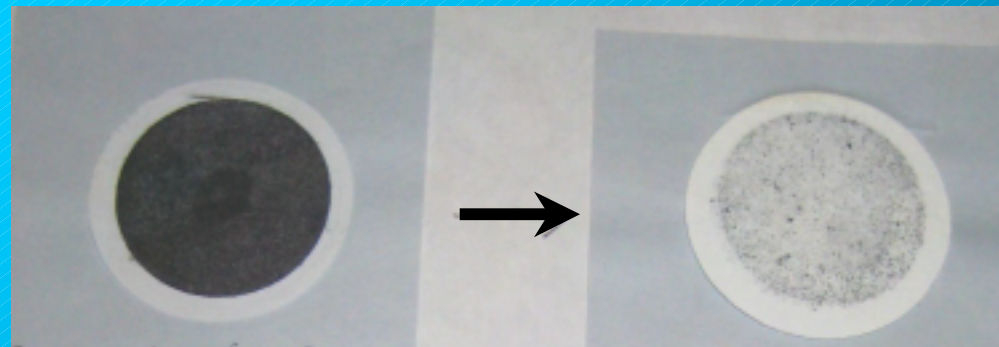
Resprep →



Teflon front filter

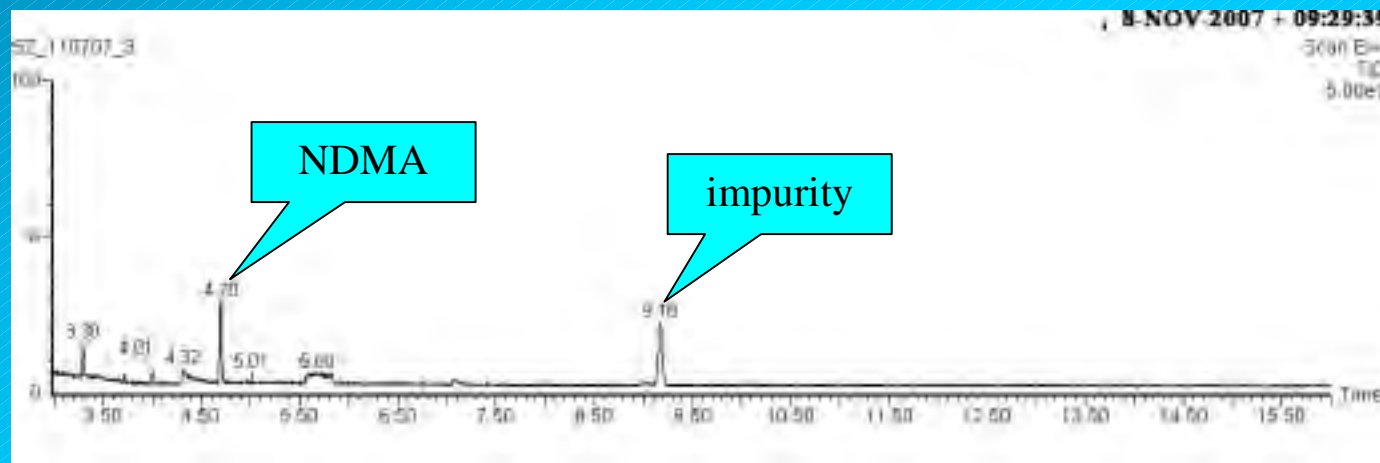
glass fiber filter back-up

Competitor →  
Contains significantly greater fines

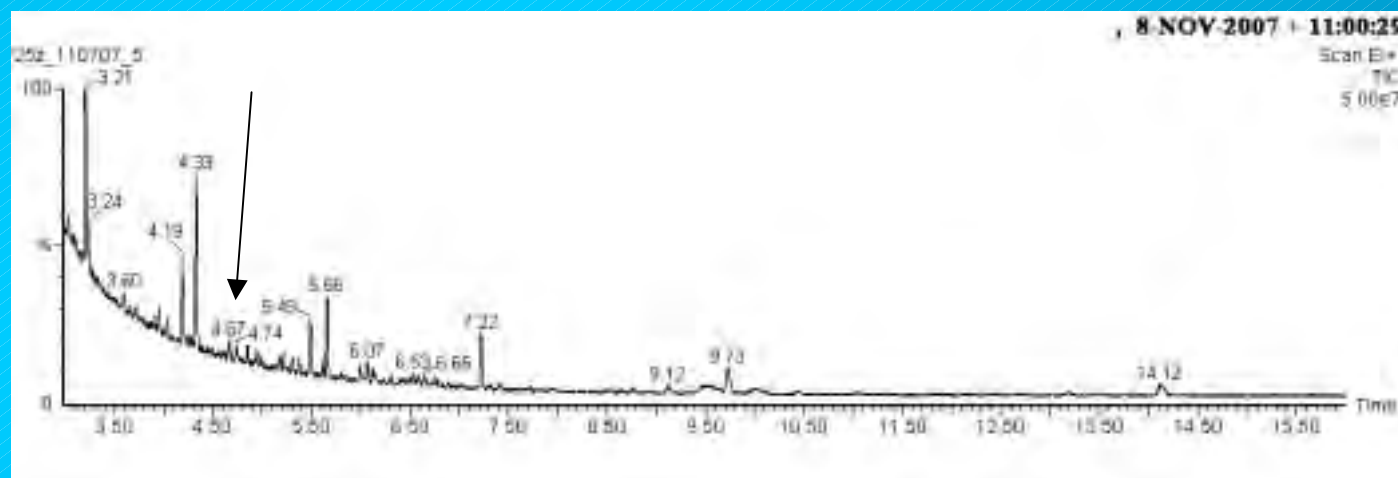


# Low Background Levels

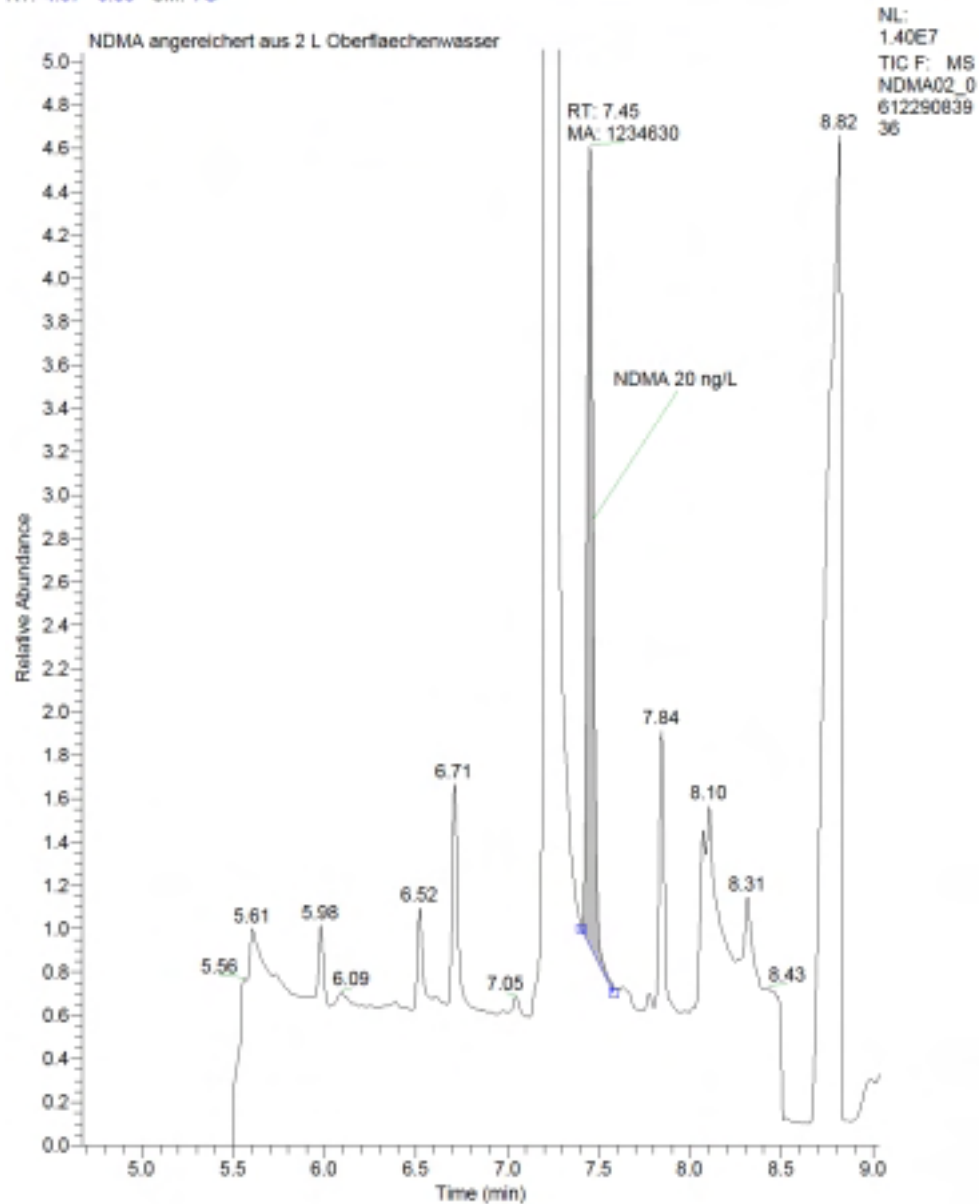
NDMA 20ng/mL  
standard,  
20pg on-column



Cartridge Blank  
methylenechloride  
extract about 2g  
charcoal bulk



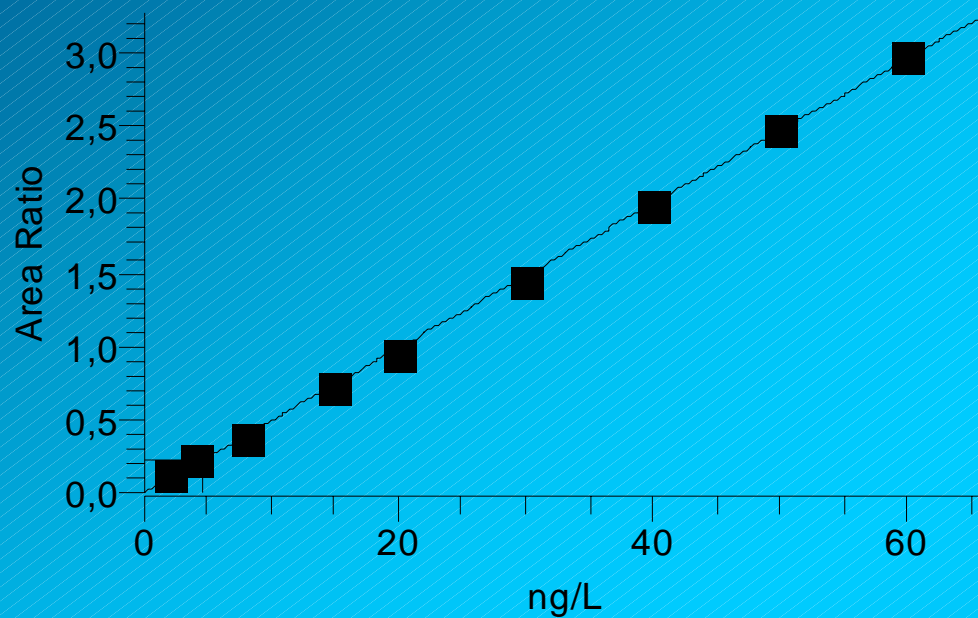
RT: 4.67 - 9.03 SM: 7G



Realprobe  
NDMA aus 2l  
Oberflächenwasser

auf Rtx-440  
30m x 0.25mm x  
0.25µm

Vielen Dank an Frau  
Preuß, Berg.Wasser-u.  
Umweltlabor



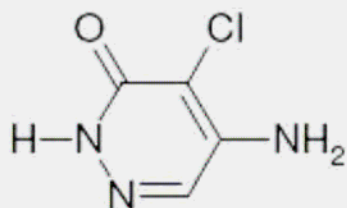
Kalibration NDMA  
5 bis 60 ng/L mit SPE  
Anreicherung von 2 L  
Wasser, Elution mit  
Dichlormethan,  
einengen auf 0.5 mL und  
Injektion von 1  $\mu$ L in den  
GC.  
Messung mit Cl.

Vielen Dank an Frau  
Preuß, Berg.Wasser-u.  
Umweltlabor

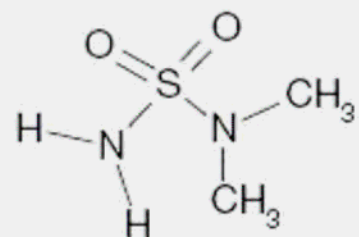
# Restek Advantage "Total Solutions"

- SPE tubes compliant with EPA method
  - Cited in Section 7.2.7.2
  - *7.2.7.2 Pre-packed coconut charcoal cartridges (#100 mesh) were also used, and are commercially available (Restek cat. # 26032).*
- GC column cited in method
  - Cited in Section 6.10.1
  - *6.10.1. Column - 30 m × 0.25 mm i.d. fused silica capillary column coated with a 1.0 micron bonded film of polyphenylmethylsilicone, (Restek Rtx 5SIL MS or equivalent).*
- Chemical standards & custom mixes also available
  - N-nitrosodimethylamine 62-75-9
    - 1,000µg/mL in methanol, 1mL/ampul ea. 31427
  - N-nitrosodimethylamine-d6 17829-05-9
    - 1,000µg/mL in methylene chloride, 1mL/ampul ea. 33910
  - N-nitroso-di-*n*-propylamine 621-64-7
    - 1,000µg/mL in methanol, 1mL/ampul ea. 31428
  - N-nitrosodi-*n*-propylamine-d14 93951-96-3
    - 1,000µg/mL in methylene chloride, 1mL/ampul ea. 33911

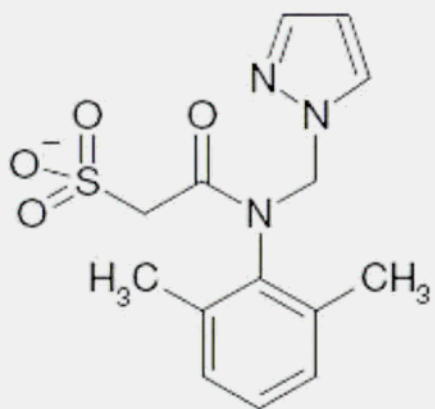




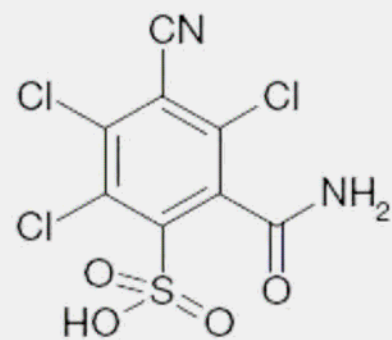
Chloridazon Metabolit B  
(Desphenyl-chloridazon)



Tolyfluanid Metabolit  
N,N'-Dimethylsulfamid  
(DMS)



Metazachlor Metabolit BH 479-8  
(Metazachlor-sulfonat)



Chlorthalonil Metabolit R 417888  
(Chlorthalonil-amido-sulfonat)