

# Controlled Sampling on Packed Micro Extraction Needles (NeedleTrap)

Professional Analytical Systems

Dietmar Hein PAS Technology Deutschland GmbH Singapore, 28<sup>th</sup> of Juli

# Outline

- NeedleTrap (NT or NTD /NeedleEx) fundamentals :
  - geometry and packings, conditioning, transport, storage
- Sampling
  - Ambient air/room air
  - Process sampling
  - dynamic and P & T sampling with or without external purge gas
- Sampling case
- NT desorption of "wet" or "dry" samples
- Automated injection devices
- Summary



# **VOC** applications

BREATHGAS

Industrial hygiene

Imissions

Plant metabolism

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lechnology

Quality controll

ODORANTS

Emission controll

In-door air controll



#### Packings:

- porous organic polymere (Tenax, DVB, PDMS, ...)
- graphitized carbons (Carbopack, ...)
- carbon molecularesieve (Carbosieve, Carboxen, ...)



Working range of typical sorbents:

Carboxen 1000: C 2 to C 6 (strong sorbent)

Carbopack X: C 3 to C 8 (middle strong sorbent)

PDMS: C 4 to C16 (week sorbent, lowest polarity)

Tenax: C 7 to C 20 (week sorbent)

DVB: C 7 to C 20 (week sorbent, relative high polarity)

Any sorbent with 60 - 120 mesh in any possible combination of up to three different sorbents can be packed.





Shinwa Chemical Industries Ltd., Kyoto, Japan has developed a range of selective co-polymere packings:

- Organic solvent: most organic solvents which include polar and non-polar solvents
- Trimethyl amine: lower amines can be selectively absorbed
- Fatty acid: propionic acid, isobtyric acid, n-butyric acid and isovaleric acid can be absorbed
- Petroleum: high selectivity for volatile petroleum compounds



#### **NT-Design:**

- Luer-Lock connection
- Lengths: between 50 mm and 70 mm (pending on temperature profile of injector!)
- dimensions: gauge 22 (0,72 mm/0,4 mm) or Gauge 23 (0,64 mm/0,35 mm)
- tip form: cone (side hole, blunt, ... on request)



#### **Conditioning:**

- (manual injected NT) in the GC-injector after desorption.
  - Switch injector mode from splitless to split after desorption.
  - Draw a small volume of some 100 µl carrier gas with a syringe
  - Eject after a few seconds. Repeat this step three times./
- use a commercially available 48 position NeedleTrapconditioner (up to 48 needles, 25 °C - 300 °C).



#### **Transport:**

Cap tip and luer-connection with PTFE-caps



• Use container for shipping.



 Special sized NTD are supplied with a glas container, screw cap and Si/PTFE septa.



#### Storage:

- PTFE capped NT can usually be stored a few days without any problem.
- Specifically labile or reactive compounds have a fewer chance for reaction or decomposition due to small surfaces and strong adsorption.
- Compared to other VOC sampling techniques (tedlar-bags, canister, thermal desorption tubes or even SPME) there is significantly less loss of compounds during transport and storage of NTD in most application.





Recoveries (%) of spiked breath gas samples after storage for 10 h (light gray), 3 days (medium gray), and 7 days (black).



General sampling conditions (pending on sorbent, matrix and analytes):

- Sampling flow: 5 15 ml/min
- Maximum mass of sampled compounds: typically in the range of some 100 ng absolute.
- Breakthrough volume: Typically in the range of some 100 ml, if concentration range is µg/l.



#### Sampling Devices:

- Gas-tight syringe with Luer-connector. A wide range of volumes is available (0.5 ml up to 100 ml)
- Hand sampling pump AP-20 (20, 50 and 100 ml)
- Sampling cases:

4 V DC, 10 Ah battery, 100 – 230 VAC charging station, Electronic MFC : 1 ml/min – 50 ml/min or 5 ml/min – 250 ml/min, Vacuumpump, Sampling volume: 10 ml – 10 l μ-processor controller, LCD display





#### Sampling Mode:

Ambient Air Sampling



Sampling Case

#### Sampling Mode:

Process Sampling





#### Sampling Mode:

Purge & Trap sampling





#### Sampling Mode:

Dynamic HS sampling





#### Sampling Mode:

• P & T sampling with external purge gas



#### Sampling Mode:

• Dynamic HS sampling with external gas





#### Sampling Mode:

• passive sampling (TWA, Time-Weighted Average sampling)





#### Impact of water, sampling human breath:

@37 °C, 100 % rH = 44 mg/l H2O

@22 °C, 100 % rH = 20 mg/l H2O

Sampling 20 ml: approx. 25 mg/l x 20 ml = 0,5 mg or 0,5 µl H2O

During desorption, this leads to approx. 500 µl H2O vapour.

Total dead volume of NTD is approx. (pending on geometry of needle) up to 5  $\mu$ l.

A pressure of up to 100 bar is build up, when water evaporates!

The water vapor purges the desorbed compounds out of the needle, on to the column.



#### **General Desorption Conditions:**

- Injection-mode: Splitless
- Desorption- (injector-) temperature is pending on sorbents (typically between 200 and 300 °C.)
- Column and GC-temperature program need to be selected, pending on the application.
- SPME-liner has to be installed!



#### Manual Desorption of "wet" samples:

- Remove PTFE cap on tip of NTD. Keep cap at luer-connection closed.
- Inject NTD, when "GC-Ready" and start GC.
- Remove NTD after 15 30 s.
- Alternatively NTD may remain additional 30 60 seconds in the injector to condition NTD. Open split of GC injector after desorption time.



#### Manual Desorption of "dry" samples:

- **Remove PTFE-cap on luer-connection and connect NTD with** • gastight luer-glas syringe (100 µl – 1 ml).
- **Remove PTFE cap on NTD tip and inject NTD** ٠ for 1 cm into injector (keep sorbent outside of hot area!) and draw 100 µl – 1 ml of carrier gas into syringe.
- When GC "ready" inject whole NTD, wait for ٠ 15 s and eject 100  $\mu$ I – 1 ml of the drawn gas.
- Start GC and remove NTD.
- Alternatively NTD may remain additional 30 -٠ 60 seconds in the injector to condition NTD. Open split of GC injector after desorption time.

 $_{2/1/201}$  praw and eject 3 times 100 µl – 1 ml, while NTD is in the injector. 24



# Automated desorption of NTD, using CONCEPT NT Autosampler

- CONCEPT NT can be adapted to any commercially available GC
- NTD are capped with a magnetic cap on the luer-connector and cap on the tip and put into position tray.
- Autosampler- and GC-sequence
  needs to be written
- System is started with CONCEPT Software.





#### Automated desorption of NTD, using CONCEPT NT Autosampler

 After "GC-Ready", the system takes the NTD by magnetic rod and moves NTD to the decapper station, where cap of the tip of NTD is





#### Automated desorption of NTD, using CONCEPT NT Autosampler

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- CONCEPT NT transfers NTD to the injector, injects and starts GC
- After desorption time, NTD is removed automatically and transferred back to the tray.
- When GC becomes ready again, NTD is taken and handled in way, until all tray loaded analyzed.



# Automated desorption of NTD for "dry" application

- "wet" application do have 100 % of transfer and no carryover, due to the water effect.
- Since there is no active gas flow through NTD during desorption, "dry" application may show incomplete transfer of compounds and high carryover!
- It is recommended to load an appropriate amount of vapor phase on NTD after sampling took place.
- New NTD-design, optimized for "dry" application is currently under evaluation and will be introduced soon.



#### Automated desorption of NTD for "dry" application





#### Summary:

- NT can handle most VOC-application.
- NT is easy to use.
- NT can achieve low detection limits (vppt vppb).
- NT gives additional information to SPME, since bounded compounds are analyzed, too.
- NT does not need any cryo-focussing.
- NT need low sample volumes and can sample very punctual.



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# Thank you!!!

