

# Detection of electrolyte leakage by gas detection techniques

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# Motivation

## Current approach for verification of electrolyte leakage/venting in the EVS GTR

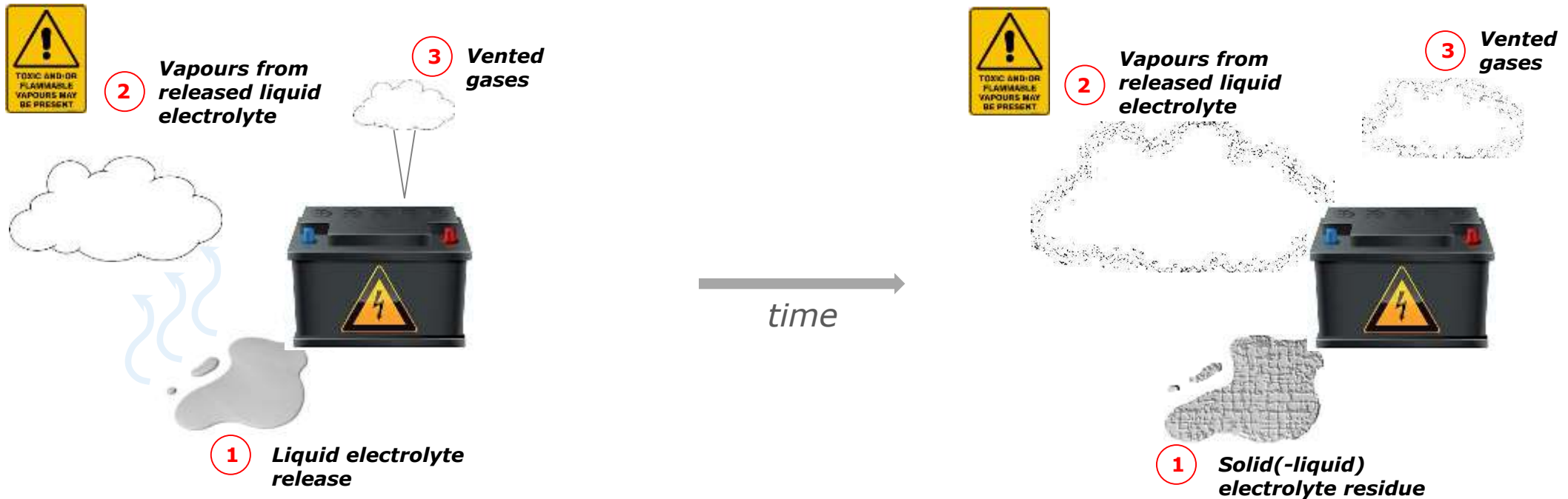
"...visual inspection without disassembling any part of the Tested-Device" is adopted in Phase 1 as a method for verification of the occurrence of electrolyte leakage and venting.

### JRC concerns:

- Due to high volatility of some electrolyte components and limited release volume, electrolyte leakage and venting may not always be easily detectable, while potentially creating hazardous environment.
- Special measures may be required to ensure safety of inspecting personnel.
- Release of other substances, e.g. coolant, is currently treated equally to release of electrolyte.

**JRC work** will focus on the development of more robust method(s) to first verify the occurrence of the electrolyte release and/or venting and, if possible, to quantify such release.

# Approaches to release detection



## Possible approaches for detection of electrolyte release

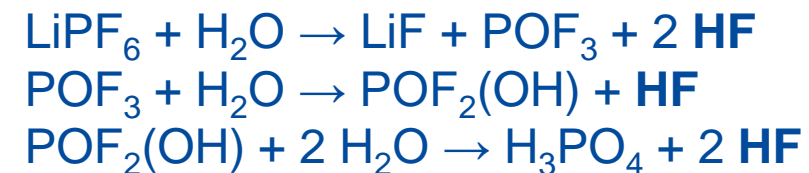
**1** Detection of Li-ion presence

**2** + **3** Gas detection

# Electrolyte components and their toxicity

Name	H phrase in case of leakage	PAC-levels (-1,-2,-3) / ppm
<b>Carbonates</b>		
Dimethyl carbonate (DMC)	H225: Highly flammable liquid and vapour	11, 120, 700
Ethyl methyl carbonate (EMC)	H225: Highly flammable liquid and vapour	n/a
Diethyl carbonate (DEC)	H226: Flammable liquid and vapour.	12, 140, 810
Propylene carbonate (PC)	H319: Causes serious eye irritation.	34, 370, 2200
Ethylene carbonate (EC)	H319: Causes serious eye irritation.	30, 330, 2000
γ-Butyrolactone (γ-BL)	H336: May cause drowsiness or dizziness.	n/a
...		
<b>Ethers</b>		
1,2-Dimethoxymethane (DMM)	H225: Highly flammable liquid and vapour	n/a
1,2-Dimethoxyethane (DME)	H360FD: May damage fertility. May damage the unborn child.	13, 140, 840
1,2-Diethoxyethane (DEE)	H360FD: May damage fertility. May damage the unborn child.	n/a
Tetrahydrofuran (THF)	H351: Suspected of causing cancer.	100, 500, 5000 (ERPG)
2-Methyl-Tetrahydrofuran (2-Me-THF)	H318: Causes serious eye damage.	4, 44, 260
1,3-Dioxolane (1,3-DL)	H360: May damage fertility or the unborn child.	60, 190, 1000
4-Methyl 1,3-Dioxolane (4-Me-1,3-DL)	H225: Highly flammable liquid and vapour.	n/a
2-Methyl 1,3-Dioxolane (2-Me-1,3-DL)	H225: Highly flammable liquid and vapour.	n/a
<b>Others</b>		
Acetonitrile (AN)	H331: Harmful if inhaled.	13, 50, 150 (AEGL)
Tetramethylene sulfone (TMSO)	H302: Harmful if swallowed.	4.1, 45, 400

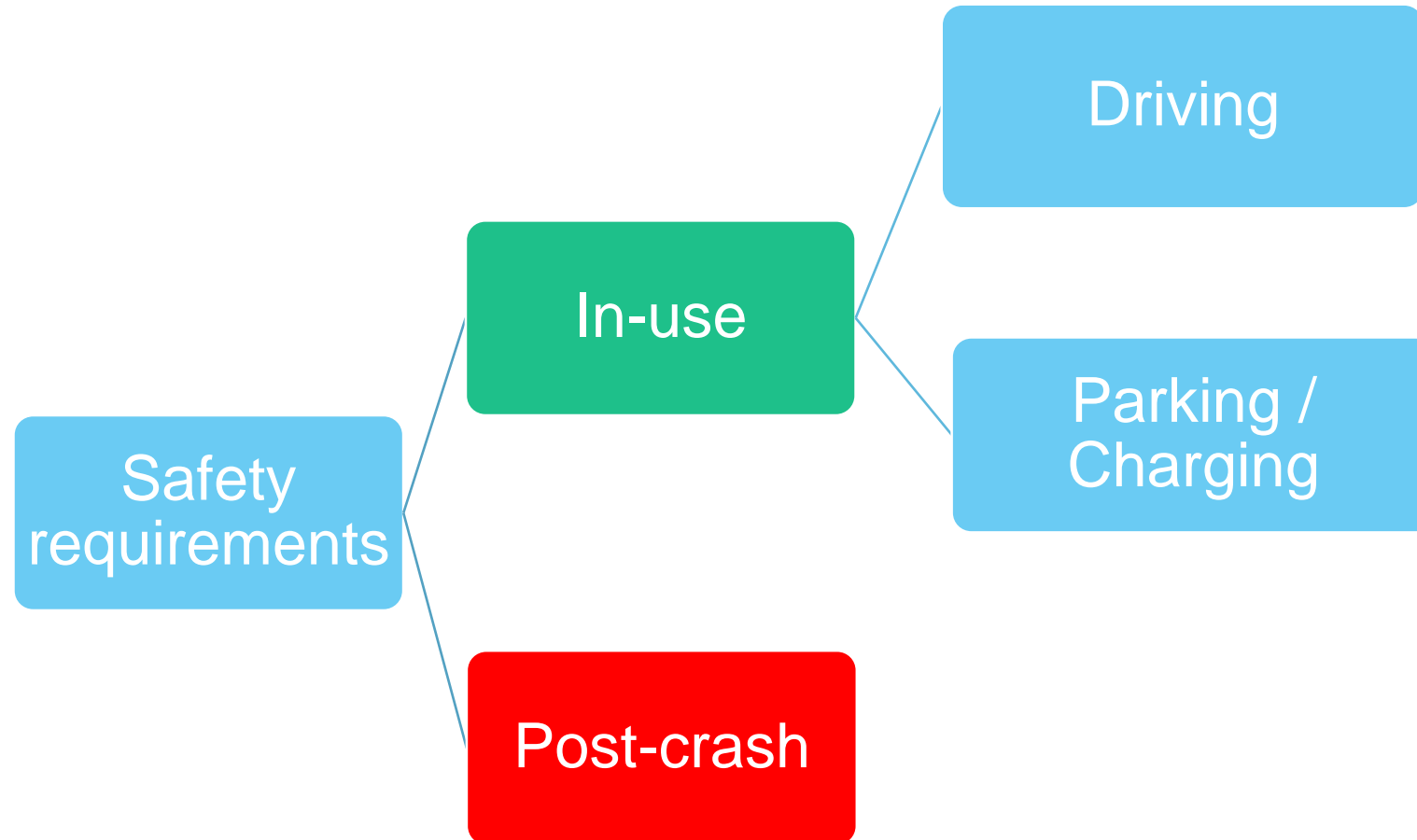
Conducting salt hydrolysis produces hydrogen fluoride



*N. P. Lebedeva, L. Boon-Brett, J. Electrochem. Soc. 2016, 163, A821-A830.*

Information on PAC levels is provided by the US-Department of Energy, PAC Rev. 29A Database, <https://edms.energy.gov/pac/Search>

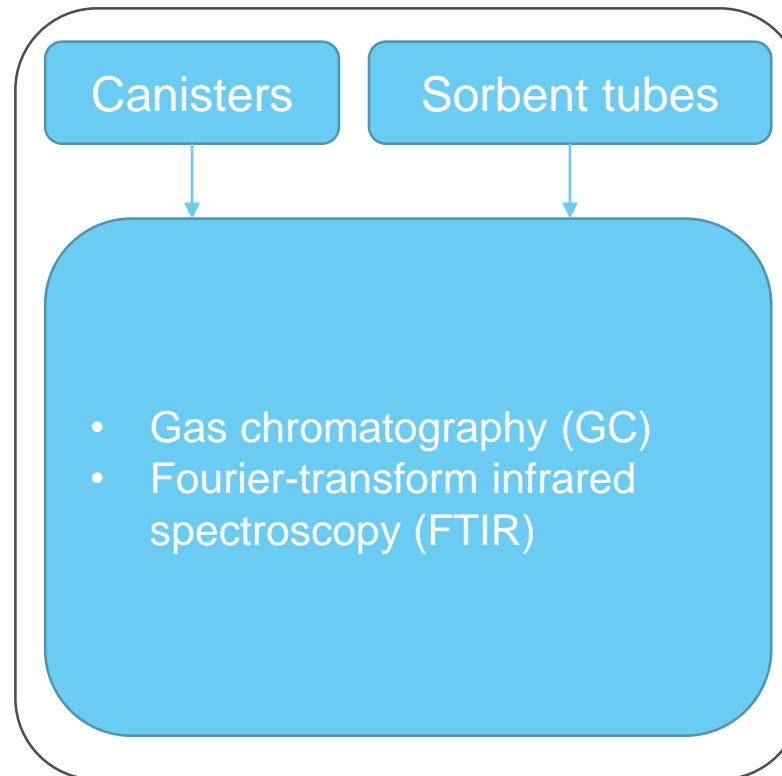
# Overview of potential scenarios



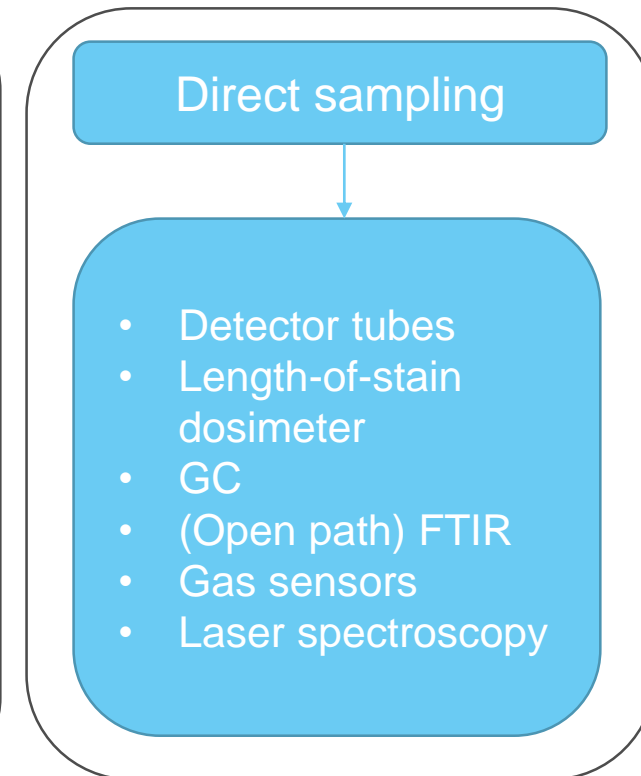
- Vehicle is outdoors
  - Gas detection serves as early warning system for occupants
- Vehicle is parked (indoors or outdoors) or being charged
  - Gas detection serves as early warning system for people in the vicinity
  - Gas detection serves as warning system for occupants and first responders after a crash

# Sampling and analysis methods

- Sampling and analysis independent in time



- Real-time analysis



# Sampling

- Canisters
  - Inert stainless steel containers at sub-atmospheric pressure
- Sorbent tubes
  - Collection of analyte by physisorption
- Direct sampling
  - Analyte is sampled by diffusion or suction and measured instantly



<https://www.entechinst.com/featured-products/air-gas-sampling-handling/silonite-minicans-for-to-vacuum-sampling/>



<https://www.skcltd.com/sorbent-tubes/>

# Detector tubes

- Air is pulled through the tube, reaction of the analyte with the chemical in the tube induces colour change



- HF detection tubes also available
- Tubes for organic carbonates are not on the market
- Cheap and easy to handle
- Standard deviation >10%
- Cross-sensitivity
- Measurement at one point at a time

## Hydrogen Fluoride 0.5/a

Order No. 81 03 251

<b>Application Range</b>	
Standard Measuring Range:	0.5 to 15 / 10 to 90 ppm
Number of Strokes n:	10 / 2
Time for Measurement:	approx. 2 min / approx. 20 s
Standard Deviation:	± 20 to 30 %
Color Change:	blue violet → yellow

<b>Ambient Operating Conditions</b>	
Temperature:	10 to 40 °C
Absolute Humidity:	30 to 80 %

<b>Reaction Principle</b>	
HF + pH indicator → yellow reaction product	

<b>Cross Sensitivity</b>	
Other mineral acids, e.g. hydrochloric acid or nitric acid, are indicated. Alkaline gases, e.g. ammonia, causes minus results or prevents an indication.	



  
www.BuyDraegerTubes.com  
Phone: (866) 905-9791  
Email: Sales@BuyDraegerTubes.com

Product note for the Draeger detector tube for HF detection



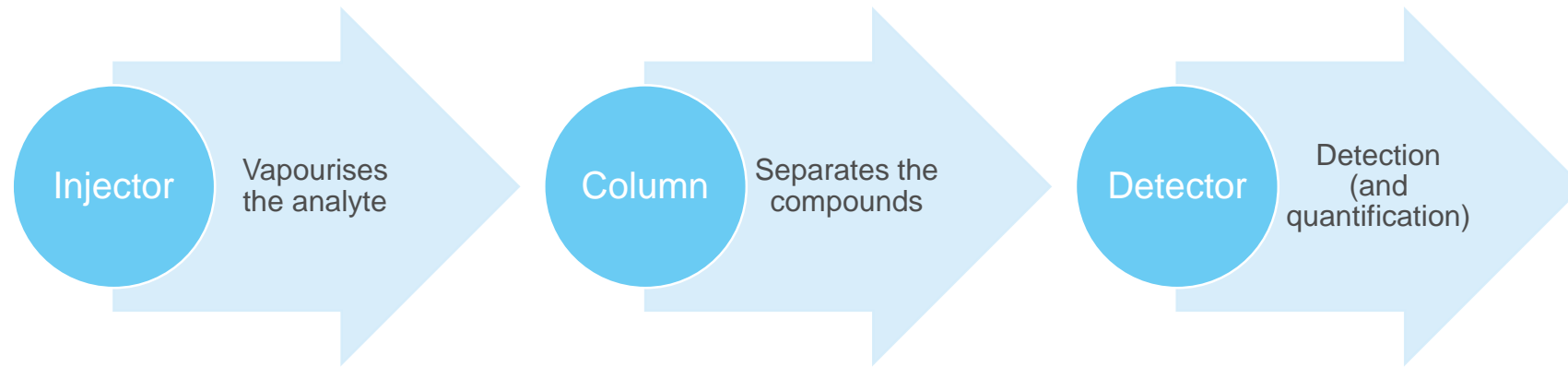
# Length-of-stain dosimeter

- Analyte diffuses through the tube, indication follows the same principle as detector tubes (Colour change)
- Cheap and easy to handle
- Suitable for (long term) air monitoring
- High cross-sensitivity and low accuracy



Dosimeter tubes for different gases  
(<https://afcintl.com/p/nextteq-gastec-dosimeter-tubes/>)

# Gas chromatography



- Separation of different compounds in the carrier gas by its interaction with a stationary phase of a column

## Columns

- Stationary phase is important for a proper separation and has to be carefully chosen
- In literature, polysiloxane or polystyrene based columns are used to detect gases in battery abuse tests

# Gas chromatography

## Detectors

- Flame ionisation detector (**FID**): Analyte is ionised by a hydrogen flame inducing a current. Cheap, and rugged, mass sensitive
- Photoionisation detector (**PID**): High energy UV photons ionise the analyte, no fuel gas needed, concentration sensitive
- Thermal conductivity detector (**TCD**): Identification of the analyte by difference in thermal conductivity. Concentration sensitive, fuel gas free, low power consumption
- Mass spectrometry detector (**MS**): multiplex signal allows high accuracy

# Gas chromatography – portable devices



<https://products.inficon.com/en-us/nav-products/product/detail/hapsite-er-identification-system/>

## INFICON Hapsite ER (GC-MS)

- Detection limit down to PPT
- Nitrogen carrier gas needed



[https://www.draeger.com/en\\_seeur/Products/X-pid-9000-9500](https://www.draeger.com/en_seeur/Products/X-pid-9000-9500)

## Dräger X-pid Series (GC-PID)

- Measurement fully automatised through a software interface



<https://www.defiant-tech.com/frog-portable-gas-chromatograph-gc/>

## Frog 5000 (GC-PID)

- Lightweight instrument: 2.2 kg
- Results in 10 mins

# Fourier-transform infrared spectroscopy (FTIR)

- Polychromatic light is emitted onto a sample (mid-infrared, 2.5 to 14  $\mu\text{m}$ , 4000 to 400  $\text{cm}^{-1}$ )
- Interaction between the emitted light and the molecules cause vibrations at characteristic wavelengths, affecting every molecule with a dipole
- SIGIS 2 open-path FTIR suitable to measure gas clouds over long distances for continuous surveillance (resolution 0.5  $\text{cm}^{-1}$ )
- Portable alternative: NeoSpectra® MEMS spectrometer (resolution 66.6  $\text{cm}^{-1}$ )



SIGIS 2 by Bruker

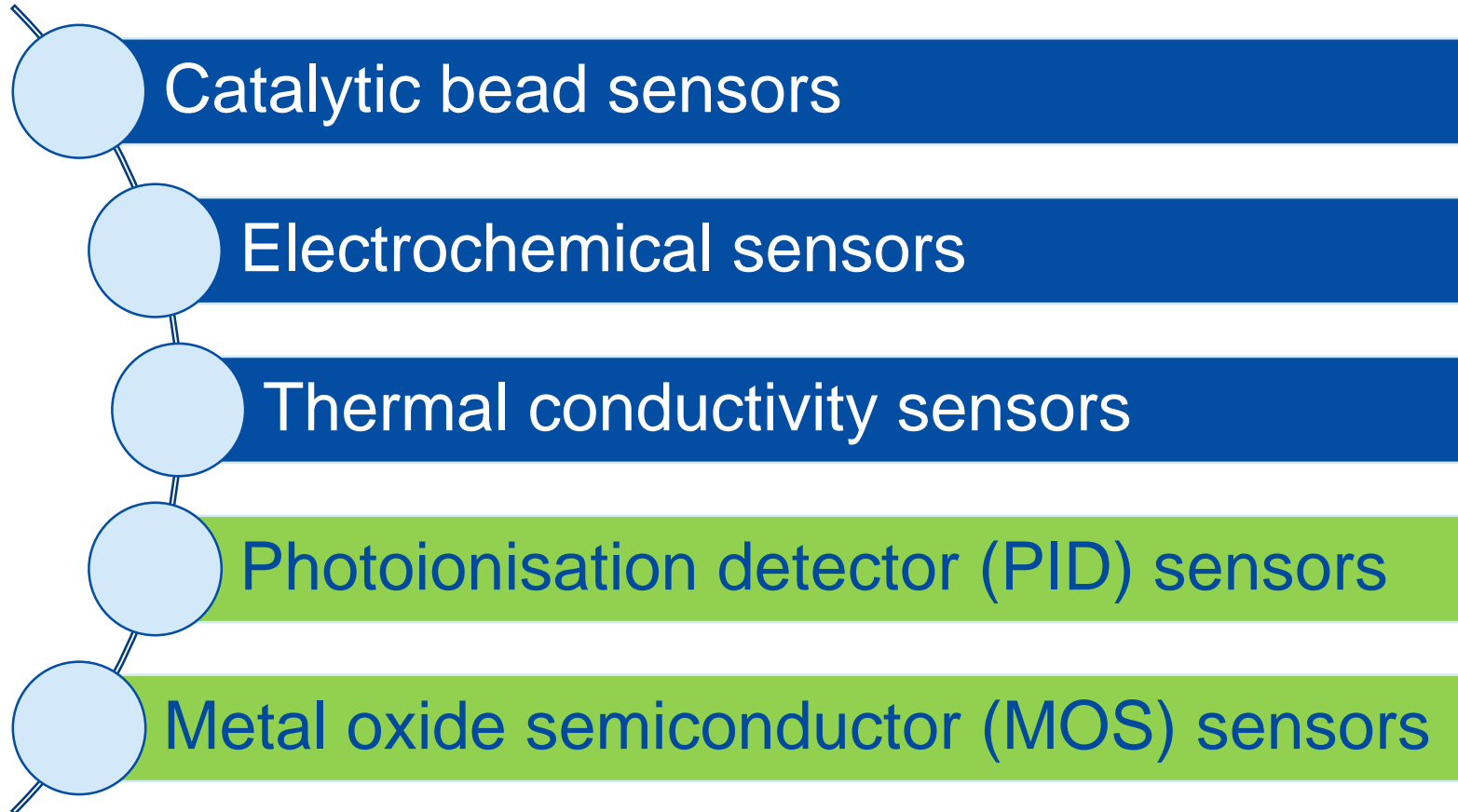
<https://www.bruker.com/content/bruker/int/en/products-and-solutions/infrared-and-raman/remote-sensing/sigis-2-gas-imaging-spectrometer.html>



NeoSpectra® micro

<https://www.si-ware.com/our-offerings/neospectra-micro/>

# Gas sensors



- Many different sensor types on the market
- PID and MOS selected due to their promising application as handheld device and miniature sensors.

# Gas sensors

## Photoionisation (PID) sensors



TIGER handheld PID detector by ION Science Ltd

<https://ionscience.com/products/tiger-handheld-voc-gas-detector/>

- Min. sensitivity of 1 ppm
- DMC in the list of measurable analytes



miniPID2 detector by ION Science Ltd

<https://ionscience.com/products/high-sensitivity-gas-sensor/>

- Min. sensitivity of 1 ppb
- DMC in the list of analytes

- Ionisation energy must be high enough to ionise analyte (10.47 eV for DMC)
- HF not detectable
- Total concentration of ionisable gases is measured

# Gas sensors



PEAKER © by UST Umweltsensortechnik

<https://www.umweltsensortechnik.de/en/devices/peakerR.html>

## Metal oxide semiconductor (MOS) sensors

- Metal oxide changes its electrical properties depending on the surrounding atmosphere
- Small, light and cheap but not selective
- High energy consumption due to high temperatures during measurement
- A range of handheld and miniature sensors commercially available mostly used for gas leak detection



# Lasers spectroscopy

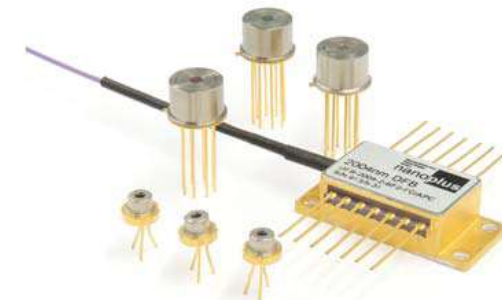
## Tunable diode laser spectroscopy (TDLS)

- HF detection by targeting the vibrational-rotational bands of the molecule
- Near-infrared region (800 to 2500 nm)
- Detection limit down to 50 ppb with commercial LaserGas™ III Portable HF Analyser
- Miniature sensors available



LaserGas™ III Portable HF Analyser

<https://www.ankersmid.eu/en/product/lasergas-iii-portable-2/>



Laser diodes by Nanosystems and Technology GmbH

[https://nanoplus.com/fileadmin/user\\_upload/Data\\_sheets/nanoplus\\_DFB\\_1100-1300nm.pdf](https://nanoplus.com/fileadmin/user_upload/Data_sheets/nanoplus_DFB_1100-1300nm.pdf)

# Lasers spectroscopy

## Quantum cascade lasers (QCL)

- Working principle based on electron transitions between energy bands
- 6 to 14  $\mu\text{m}$  wavelength (mid-infrared) to detect VOCs
- Open path system where gas interferes with the laser and which is able to detect Sarin in ppb range with a distance of several hundred metres.
- Eyesafe



"LaserWarn" system by Block Engineering  
<https://www.blockeng.com/products/laserwarn.html>

# Conclusions and outlook

Literature review showed many promising candidates suitable for electrolyte leakage detection

- On-board miniature measurement devices for integration into the vehicle
- Bulkier detection methods can be used for air monitoring during parking and charging in an enclosed environment

## Next steps

- Experiments to assess the suitability of selected methods for the detection of electrolyte vapours

# Thank you



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