

Detection of electrolyte leakage by gas detection techniques

Stephan Hildebrand
Natalia Lebedeva

April 2021

Motivation

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

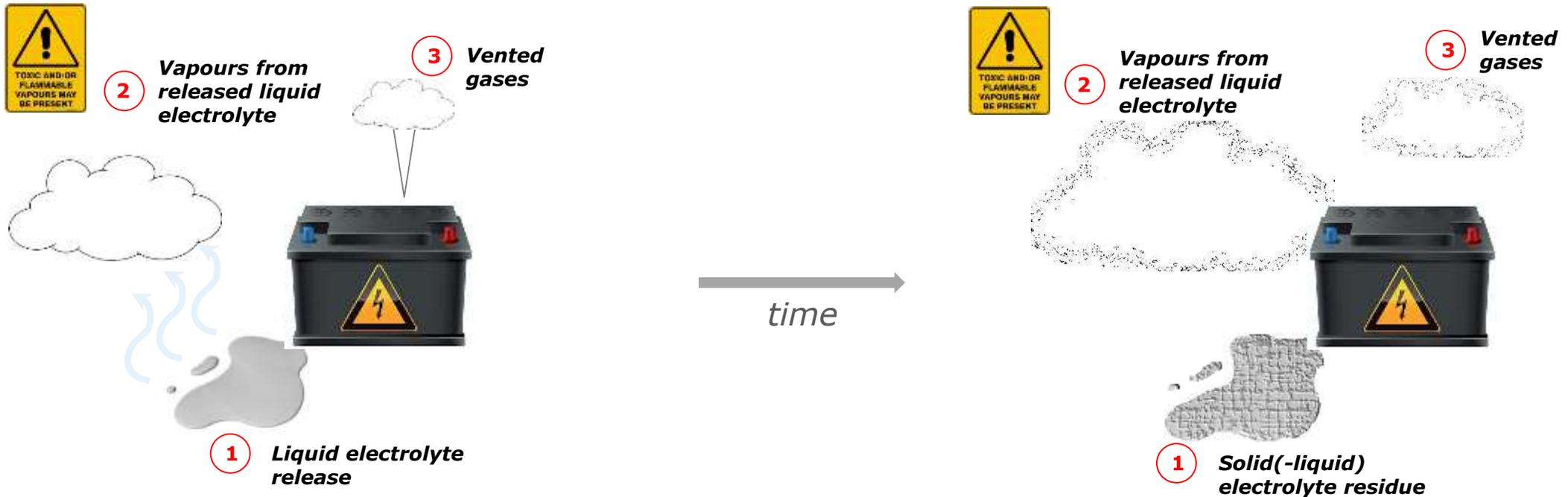
"...visual inspection without disassembling any part of the Tested-Device" is adopted in Phase 1 as a method for verification of the occurrence of electrolyte leakage and venting.

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

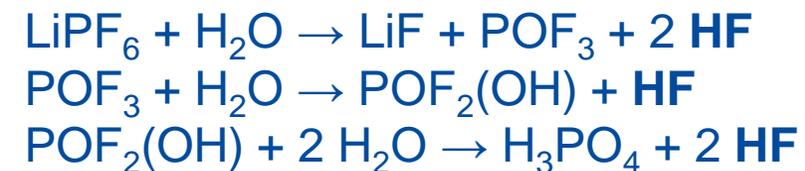
1 Detection of Li-ion presence

2 + **3** Gas detection

Electrolyte components and their toxicity

Name	H phrase in case of leakage	PAC-levels (-1,-2,-3) / ppm
Carbonates		
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
...		
Ethers		
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
Others		
Acetonitrile (AN)	H331: Harmful if inhaled.	13, 50, 150 (AEGL)
Tetramethylene sulfone (TMSO)	H302: Harmful if swallowed.	4.1, 45, 400

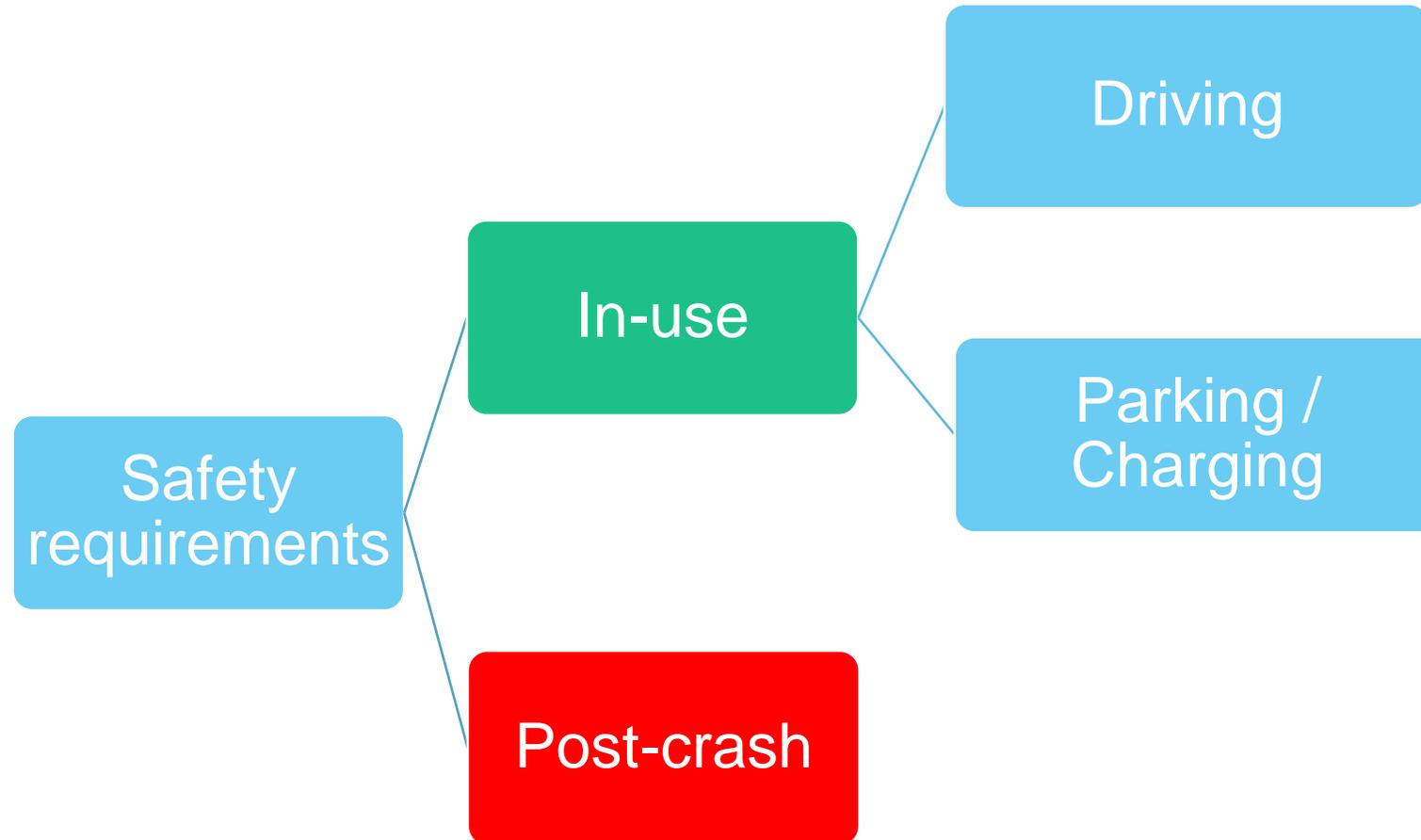
Conducting salt hydrolysis produces hydrogen fluoride



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>

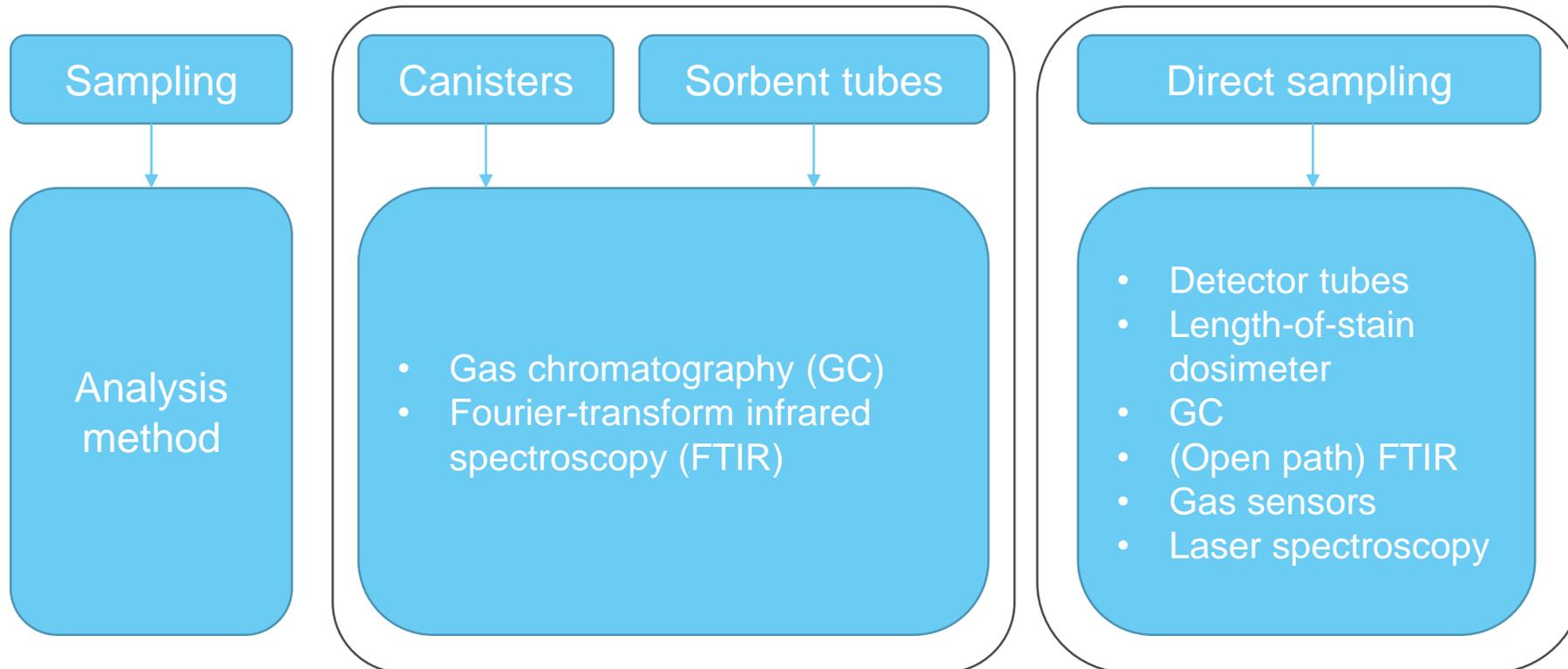
Overview of potential scenarios



- 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

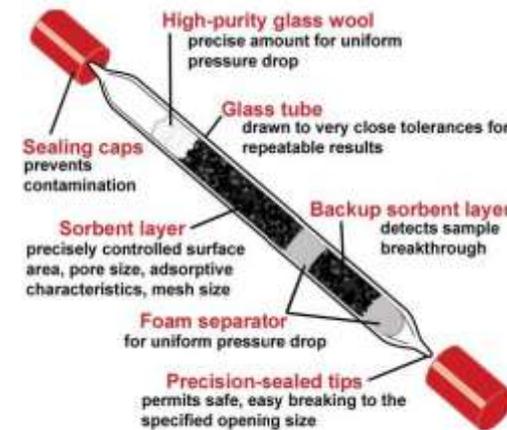


Sampling

- 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

Application Range	
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

Ambient Operating Conditions	
Temperature:	10 to 40 °C
Absolute Humidity:	30 to 80 %

Reaction Principle	
HF + pH indicator → yellow reaction product	

Cross Sensitivity	
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

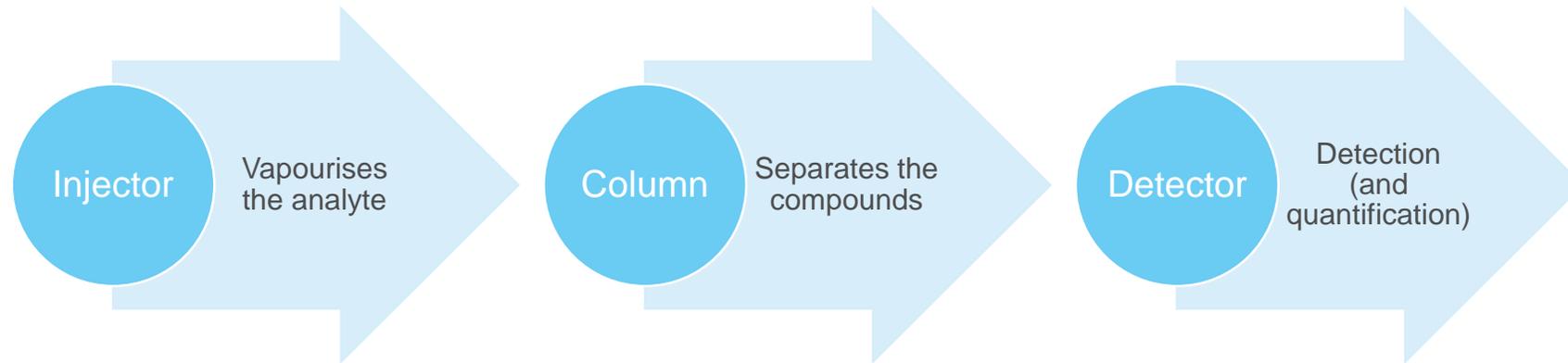
Length-of-stain dosimeter

- 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

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

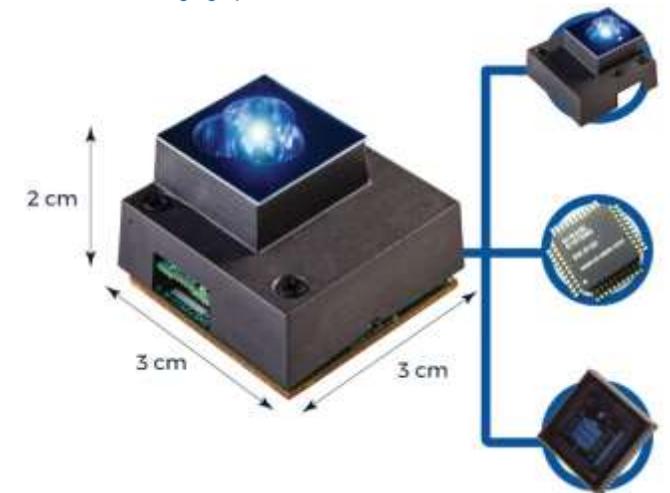
Fourier-transform infrared spectroscopy (FTIR)

- Polychromatic light is emitted onto a sample (mid-infrared, 2.5 to 14 μm , 4000 to 400 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 cm^{-1})
- Portable alternative: NeoSpectra® MEMS spectrometer (resolution 66.6 cm^{-1})



SIGIS 2 by Bruker

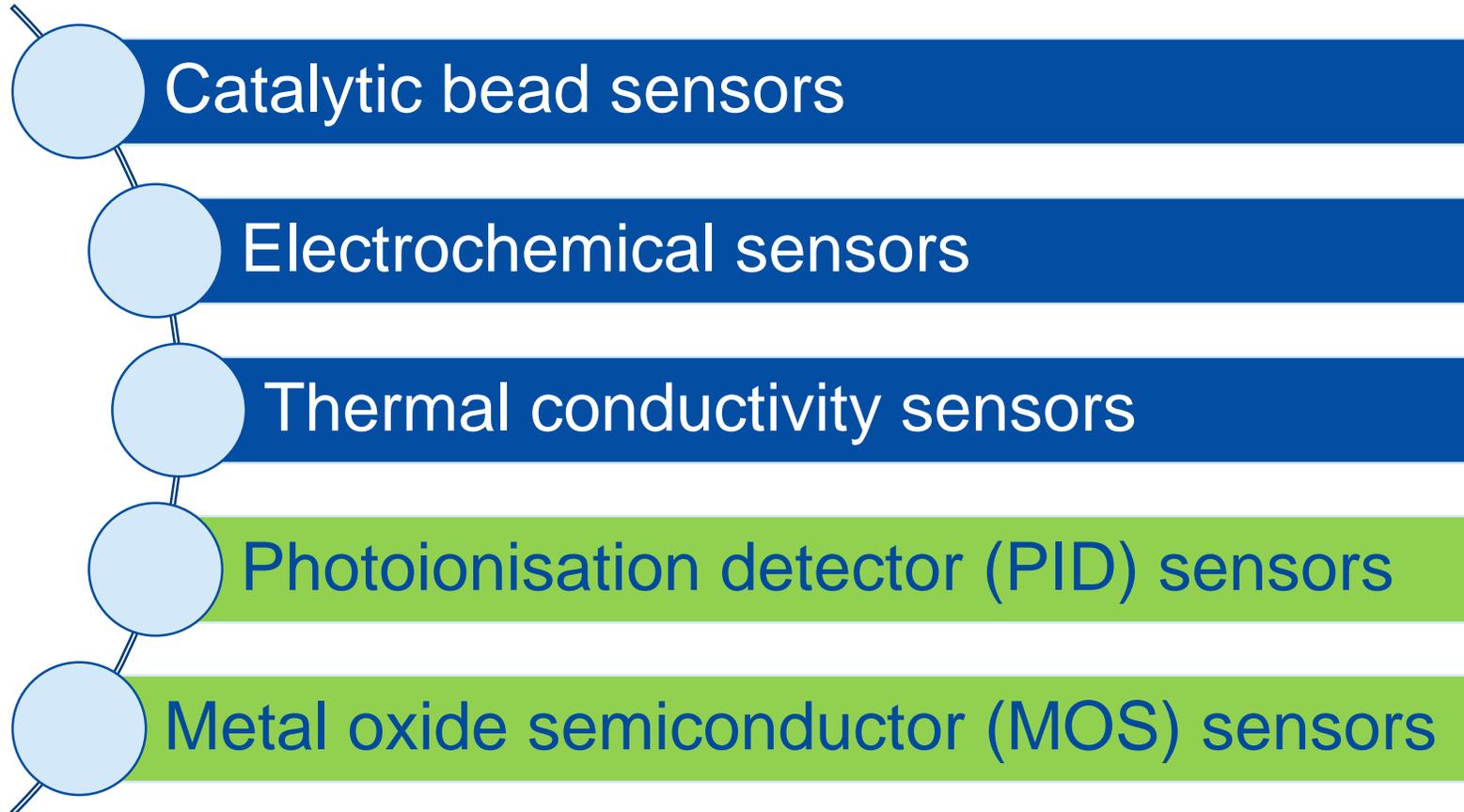
<https://www.bruker.com/content/bruker/int/en/products-and-solutions/infrared-and-raman/remote-sensing/sigis-2-gas-imaging-spectrometer.html>



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



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

TIGER handheld PID detector by ION Science Ltd

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



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

miniPID2 detector by ION Science Ltd

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

- 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

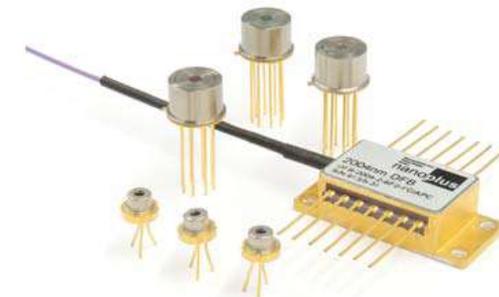
Tunable diode laser spectroscopy (TDLS)

- 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

Lasers spectroscopy

Quantum cascade lasers (QCL)

- Working principle based on electron transitions between energy bands
- 6 to 14 μm 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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