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The Use of Gas Chromatography – Mass Spectrometry in Process Safety

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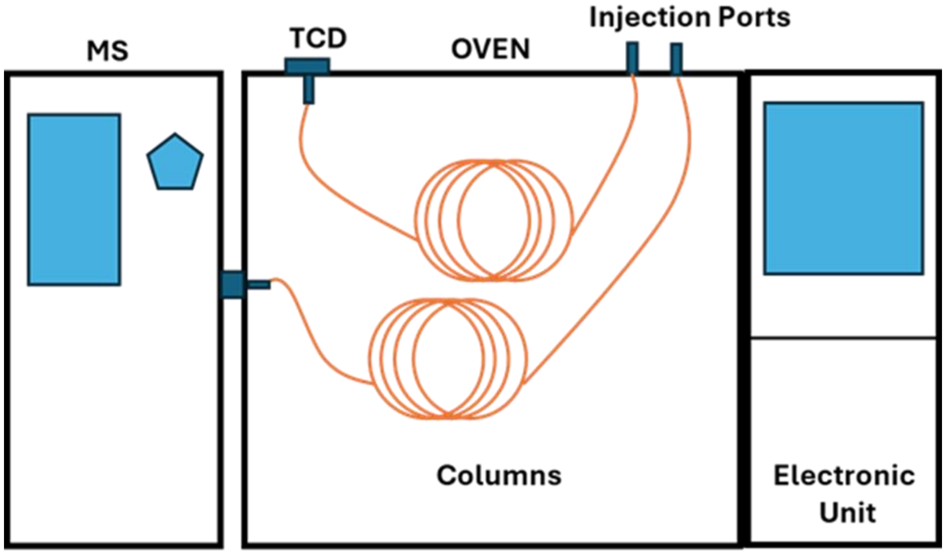
Contents

Principles of GC-MS

Separate, identify, and quantify chemical compositions in volatile or semi-volatile mixtures.

- Liquid and gas compounds can be analyzed by direct injection into GC.
- Solid samples can be evaluated via thermal desorption/solvent extraction techniques.



General Use of GC-MS in Process Safety – Overview

1. Leak Detection and Monitoring

- to detect gases, e.g., CH_4, NH_3, H_2S, VOCs, etc.

2. Process Monitoring and Control

- to continuously or periodically analyze gas stream or reaction mixture.

3. Contaminant Analysis and Monitoring

- to ensure raw materials, intermediate products, and final goods within safety thresholds.

4. Emissions Monitoring and Environmental Compliance

- to track VOCs, greenhouse gases, and other pollutants within regulatory standards.

Case 1: Gas Quantification for Lithium-Ion Battery Thermal Runaway

UL 9540A Test Method for evaluating thermal runaway fire propagation in battery energy storage systems.

- ⇨ Battery thermal runaway
- ⇨ Gas generation/composition
- ⇨ Flammability characteristics:
  - lower flammable limit (LFL)
  - maximum explosion pressure (P_{max})
  - burning velocity (BV)

Jiliang He, *et al.* Assessing the Risks of Thermal Runaway and Fire Propagation in Battery Energy Storage Systems Using UL 9540A Methodology, *21st Global Congress on Process Safety*, Dallas, TX, April 6-10, 2025.

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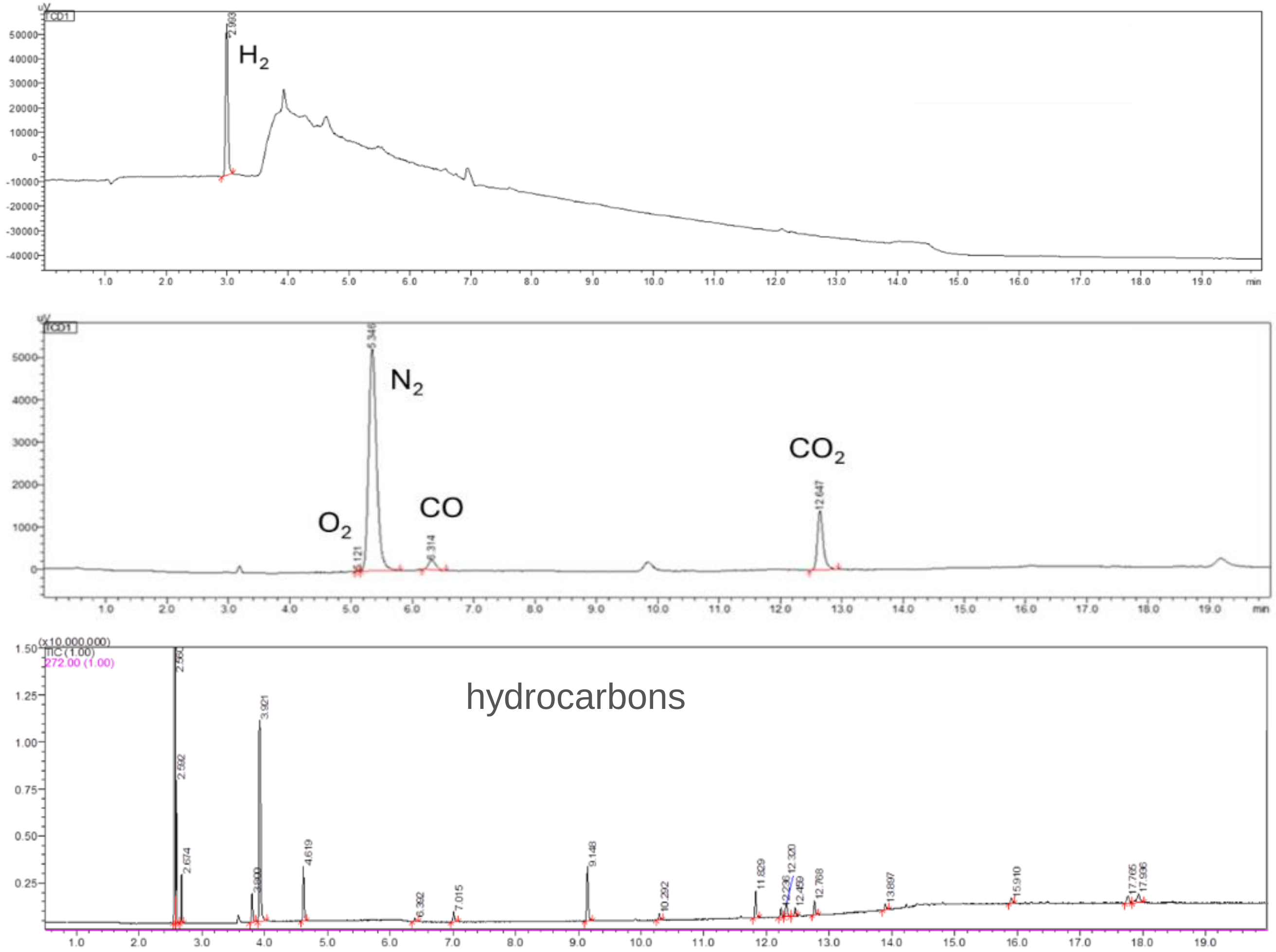

Example 1.

Assay of battery vent gas

by GC-TCD and GC-MS.

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Gas	Measured mole %
H_2	9.69
O_2	0.21
N_2	79.59
CO	0.98
CO_2	3.12
CH_4 (Methane)	1.438
C_2H_6 (Ethane)	0.215
C_2H_4 (Ethylene)	0.946
C_3H_8 (Propane)	0.079
C_3H_6 (Propylene)	0.825
C_3H_4 (Propadiene)	0.057
C4' *	0.342
C_5H_{12} (Isopentane)	0.001
n-C_5H_{12} (Pentane)	0.081
C_6H_{14} (Hexane)	0.005
***Individual C4 Compounds**	
Isobutane	0.009
n-Butane	0.032
trans-2-Butene	0.118
1-Butene	0.015
Isobutene	0.118
cis-Butene	0.015
1,3-Butadiene	0.036
SUM	**97.58**

Renormalized

Excluding O_2/N_2 & unidentified

Gas	Measured mole%
H_2	54.53
CO	5.512
CO_2	17.533
CH_4 (Methane)	8.091
C_2H_6 (Ethane)	1.208
C_2H_4 (Ethylene)	5.326
C_3H_8 (Propane)	0.445
C_3H_6 (Propylene)	4.642
C_3H_4 (Propadiene)	0.319
C4' *	1.927
C_5H_{12} (Isopentane)	0.006
n-C_5H_{12} (Pentane)	0.457
C_6H_{14} (Hexane)	0.028
***Individual C4 Compounds**	
Isobutane	0.051
n-Butane	0.180
trans-2-Butene	0.663
1-Butene	0.082
Isobutene	0.663
cis-Butene	0.082
1,3-Butadiene	0.205
SUM	**100.00**

The composition is used to replicate a gas mixture for flammability tests e.g. LFL, P_{max}, BV.

Flammable gas evolution from polymeric products leading to fire. (video)

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Case 2: UN Test U.1, Substances Liable to Evolve Flammable Vapours

"Expandable polymeric beads or Plastics moulding compounds, evolving flammable vapours" for declassification of UN2211 or UN3314.

Test procedure

The substance is placed in 3 x 50 ml serum bottles at 50°C for 14 days.

The headspace is analyzed by GC-MS and GC-TCD for flammable gases.

Test criteria and method of assessing results

Substances need not to be classified as Polymeric beads, expandable (UN2211) if the concentration of flammable vapors is less than or equal to 20% of the Lower Explosive Limit (LEL) of the flammable vapors in all of the three-repetition tests.

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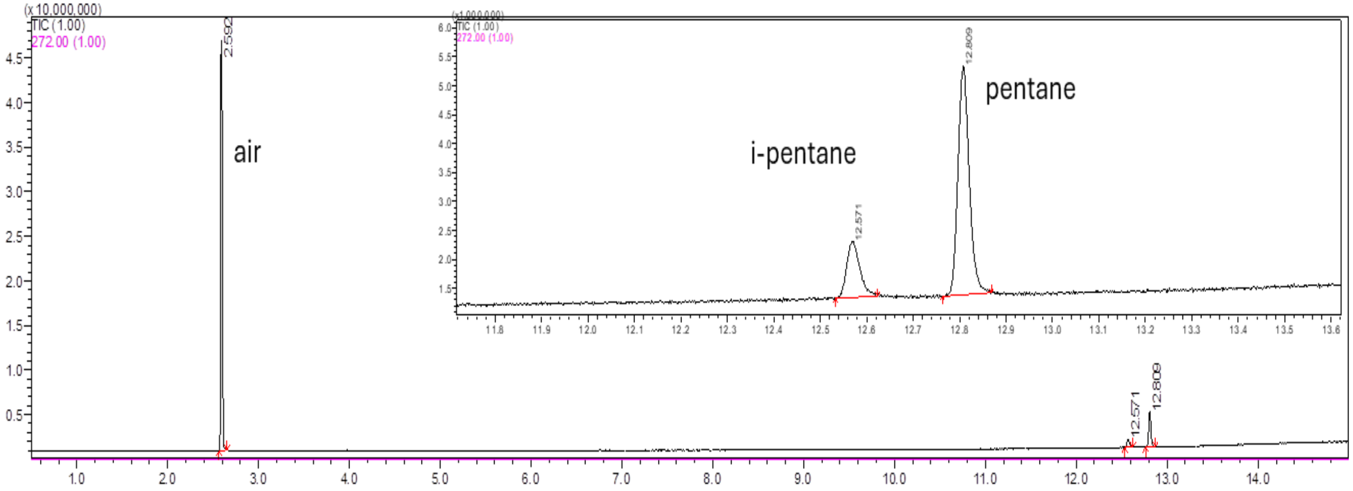
Headspace Gas from a Expandable Polymeric Bead after 14 days at 50°C

(Test Example)



Example 2: Test U.1 gas assay by GC-MS

An incident (2019) involving expandable polymeric bead caused significant damage to a container ship. https://wwz.cedre.fr/en/Resources/Spills/Spills/MSC-Zoe

(Test Example)

Composition	Measured Mole%				Lower Explosive Limit (%)*
	Bottle 1	Bottle 2	Bottle 3	Average	
Air	99.77	99.61	99.74	99.71	n/a
Isopentane	0.05	0.09	0.05	0.06	1.4
Pentane	0.18	0.30	0.21	0.23	1.5
Composite					1.48**

* OSHA Chemical Database: https://www.osha.gov/chemicaldata
**Composite LEL = $\sum(x_i/L_i)^{-1}$ where x_i is the fraction of flammable component i and L_i is the lower explosive limit of flammable component.

The concentration of the flammable component is 19.6% of the composite LEL.

Sample is not classified as UN2211 substance.

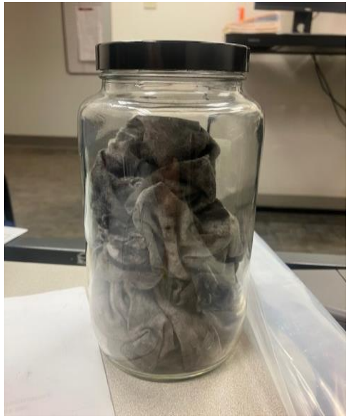
Case 3: ASTM E1618, Ignitable Liquid Residues in Extracts from Fire Debris

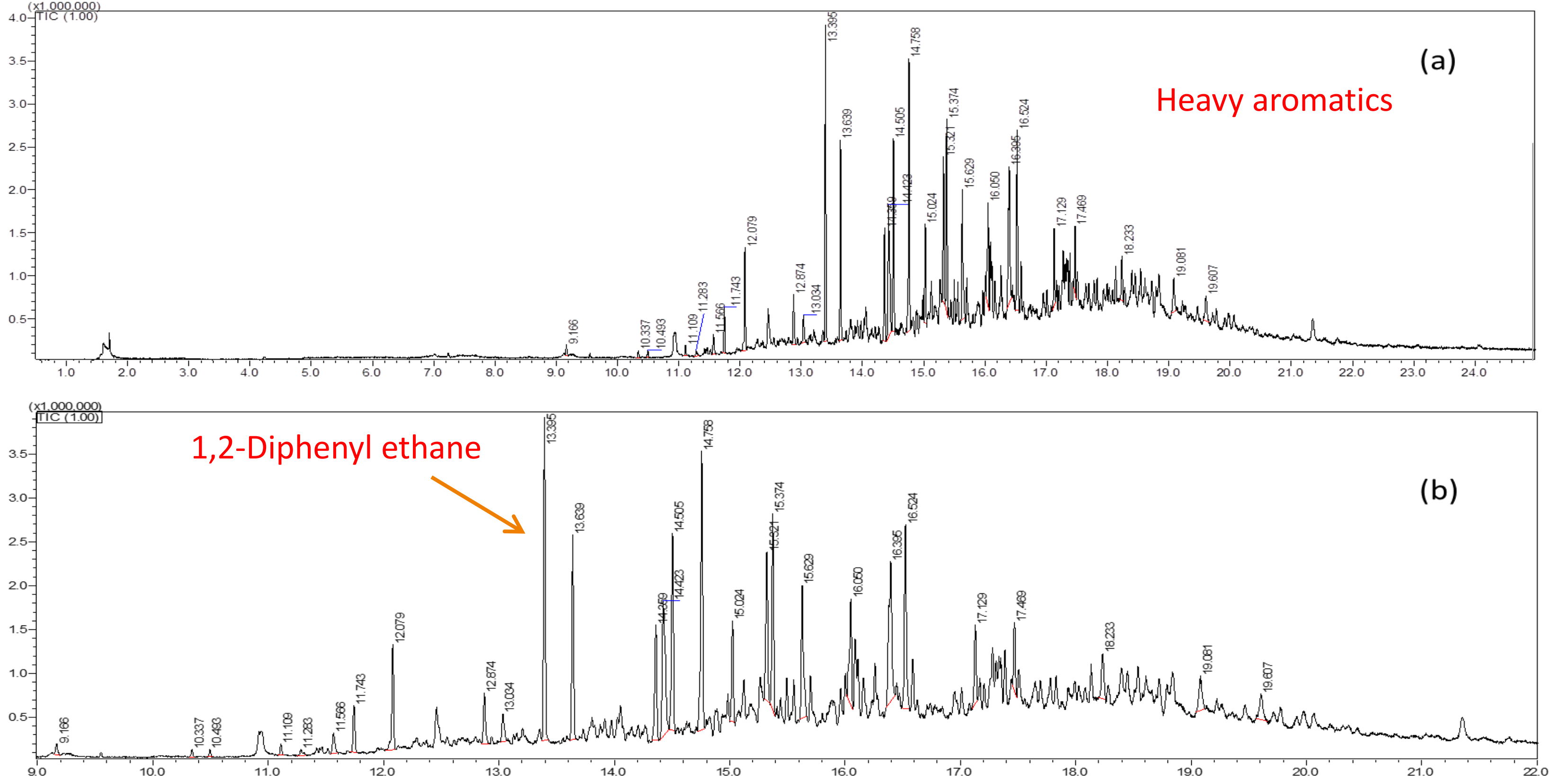
Classification of Ignitable Liquid Residues

1) aromatic products (e.g., xylenes and some lamp oils)
2) gasoline
3) petroleum distillates (e.g., kerosene and diesel fuel)
4) isoparaffinic products (e.g., some paint thinners and mineral spirits)
5) naphthenic-paraffinic products (e.g., cyclohexane-based solvents/products)
6) normal alkane products (e.g., pentane and some toners)
7) oxygenated solvents (e.g., alcohols and some fuel additives)
8) miscellaneous, if a sample does not meet the criteria for any of the seven categories.

A Deflagration Incident Investigation

A maintenance team was removing a rusty valve from a fuel gas line. During the process of cutting off bolts, a fire ignited around the cutting area, followed by a minor detonation that expelled black soot from the line. To determine whether ignitable liquid residues contributed to the fire, we analyzed the soot sample (collected in a rag shown in the bottle) — using the ASTM E1618 method.





Example 3: GC-MS Total Ion Chromatogram for the Extract of Residue from Fuel Gas Piping. (a) General View (top), (b) Zoom View (bottom)

1,2-Diphenyl ethane was identified as one of major ignitable liquid residue components.

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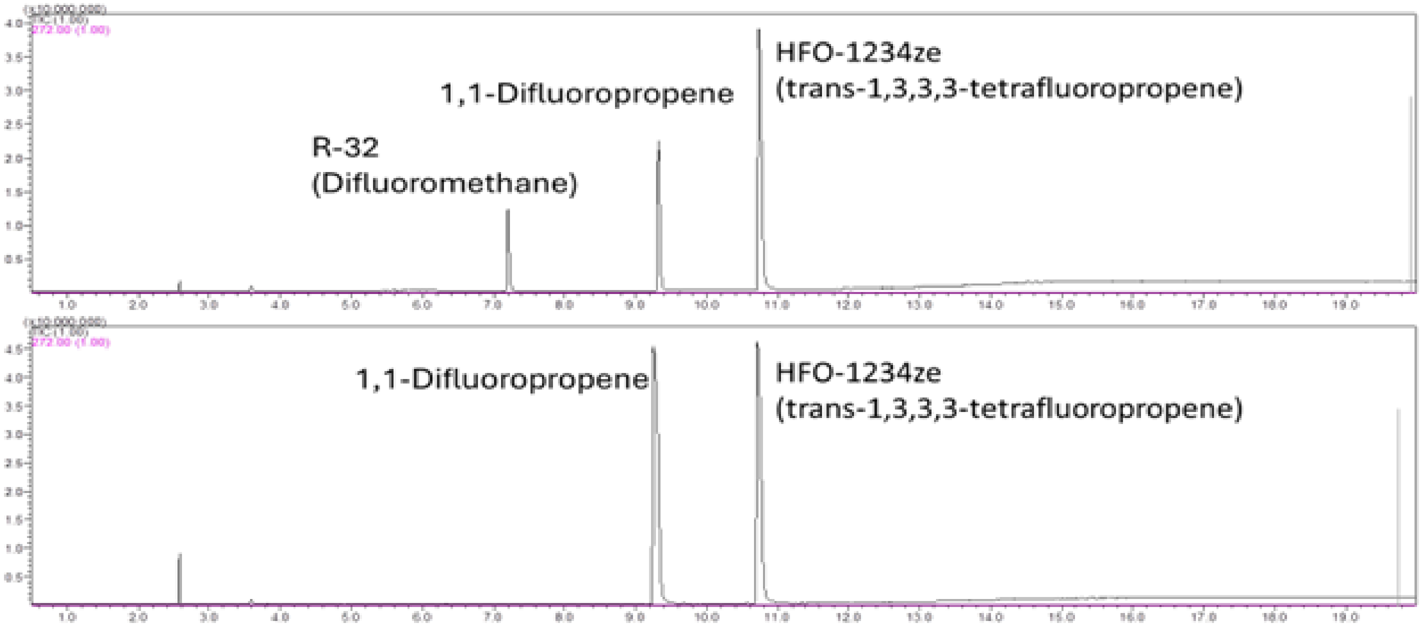
Case 4: ASHRAE 34, Refrigerant Blends and Safety Classification

Composition Verification

Composition Confirmation after Fractionation Test



Example 4: GC-MS TIC of refrigerant blends (a) three components, (b) two components.

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Coupling GC-MS with Calorimeters

Calorimeter (ARC, VSP) provides physical and kinetic data:

temperature, pressure, rates of temperature rise and pressurization

GC-MS reveals chemical information:

flammability, toxicity, corrosivity. (e.g, requirements of PSM and RPM)

The integration of GC-MS with Calorimeters aid in

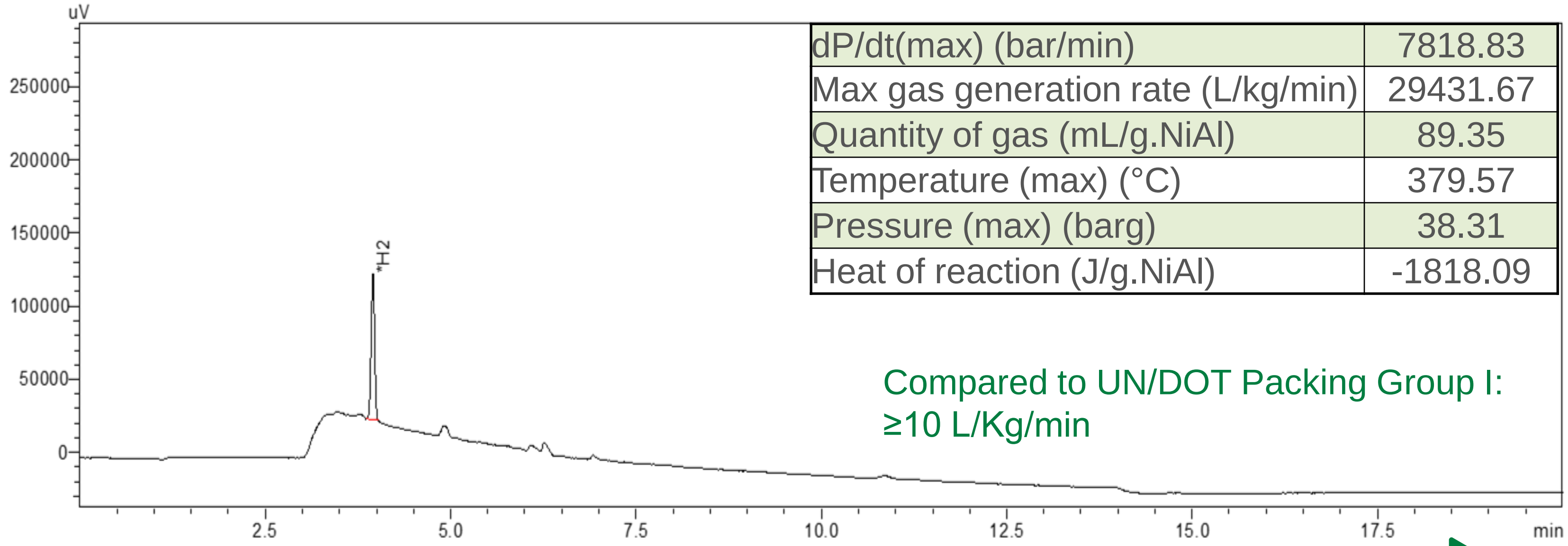
understanding reaction mechanisms, mitigating risks,

and preventing accidents during scale-up processes

Case 5: Dangerous When Wet Test (UN Test N.5)

Combination of Calorimeter and GC for heat release, pressurization rate, gas analysis

$$2NiAl + 8H_2O \rightarrow 2Al(OH)_3 + Ni(OH)_2 + 4H_2$$



dP/dt(max) (bar/min)	7818.83
Max gas generation rate (L/kg/min)	29431.67
Quantity of gas (mL/g.NiAl)	89.35
Temperature (max) (°C)	379.57
Pressure (max) (barg)	38.31
Heat of reaction (J/g.NiAl)	-1818.09

Compared to UN/DOT Packing Group I:
≥10 L/Kg/min

Example 5: DWW gas assay by GC-TCD

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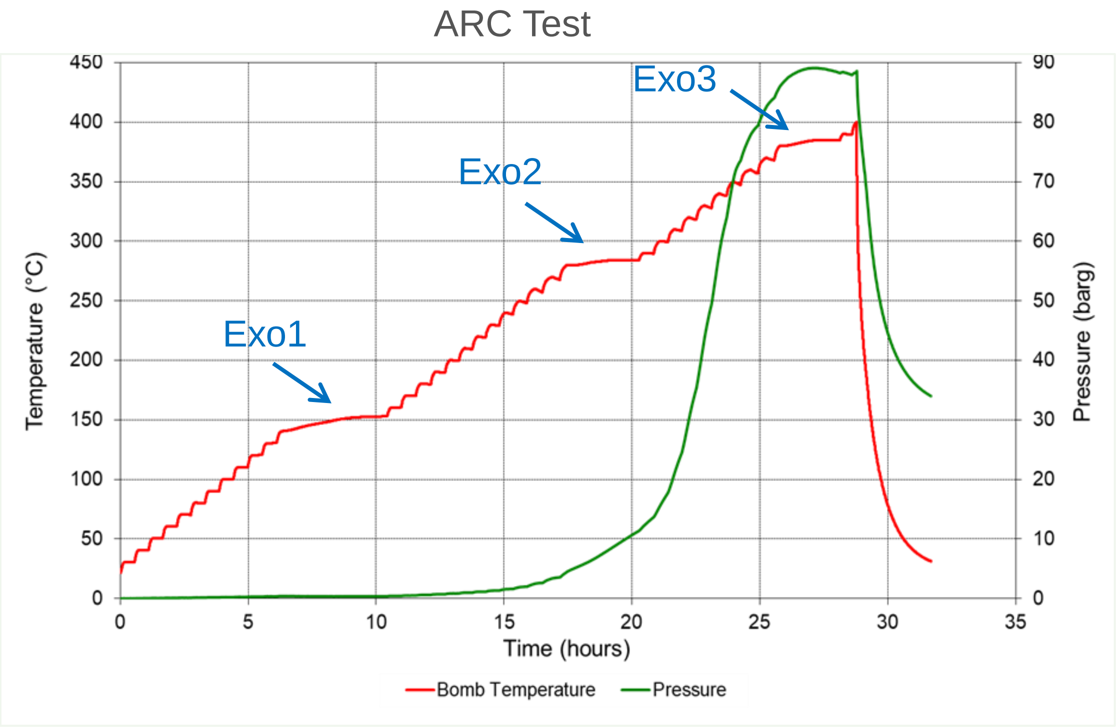
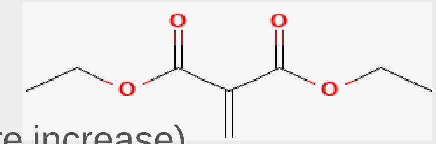
Case 6: Combined Use with Accelerating Rate Calorimeter

Diethyl 2-methylenemalonate thermal stability



Post-Test ARC Gas Analysis

Exo2:
(pressure increase)

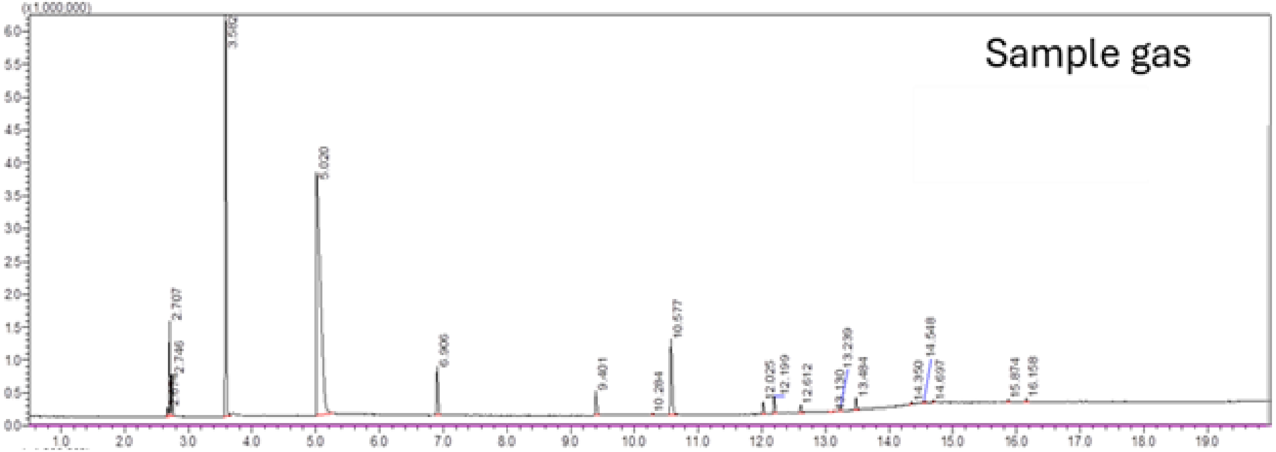


⟶ CO, CO_2, CH_4, C_2H_4, C_2H_6 (98 mol%)

Exo3:
(pressure decrease)

$2\ C_2H_4 \longrightarrow C_4H_8$; $CH_4 + C_2H_4 \longrightarrow C_3H_8$

$C_2H_4 + C_2H_6 \longrightarrow C_4H_{10}$



Gas	Measured mole %
CO	7.26
CO_2	62.90
CH_4 (Methane)	1.611
C_2H_6 (Ethane)	8.645
C_2H_4 (Ethylene)	17.122
C_3H_8 (Propane)	0.596
C_3H_6 (Propylene)	0.350
C_3H_4 (Propadiene)	0.000
C4 *	1.065
C_5H_{12} (Isopentane)	0.013
n-C_5H_{12} (Pentane)	0.040
C_6H_{14} (Hexane)	0.021
***Individual C4 Compounds**	
Isobutane	0.025
n-Butane	0.692
trans-2-Butene	0.092
1-Butene	0.129
Isobutene	0.011
cis-Butene	0.059
1,3-Butadiene	0.058
SUM	**99.62**

Example 6. Hydrocarbon assay by GC-MS

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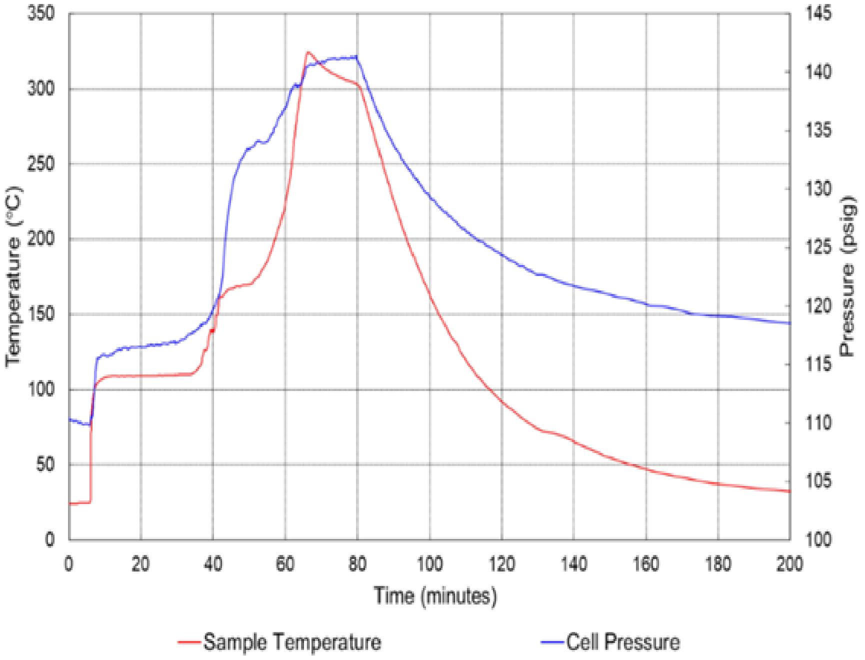
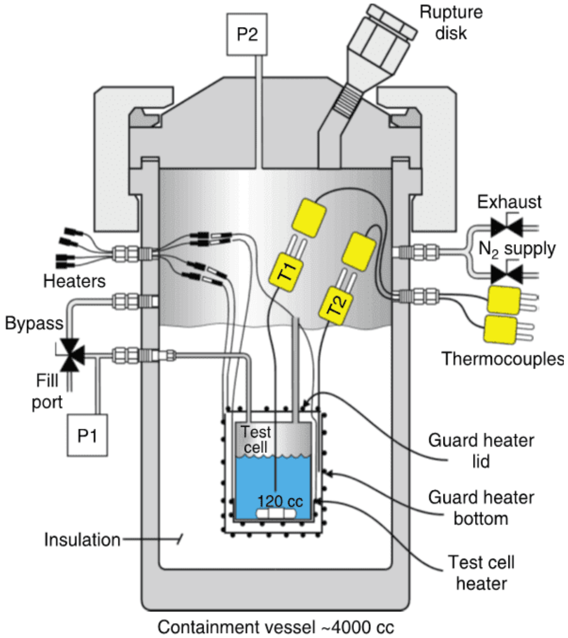
Case 7: Combined Use with Vent Sizing Package

$$Cl_2P(OCH_2CH_2CN) + 4\ Pr_2NH \xrightarrow[25^oC]{THF} (Pr_2N)_2P(OCH_2CH_2CN) + 2\ Pr_2NH.HCl$$

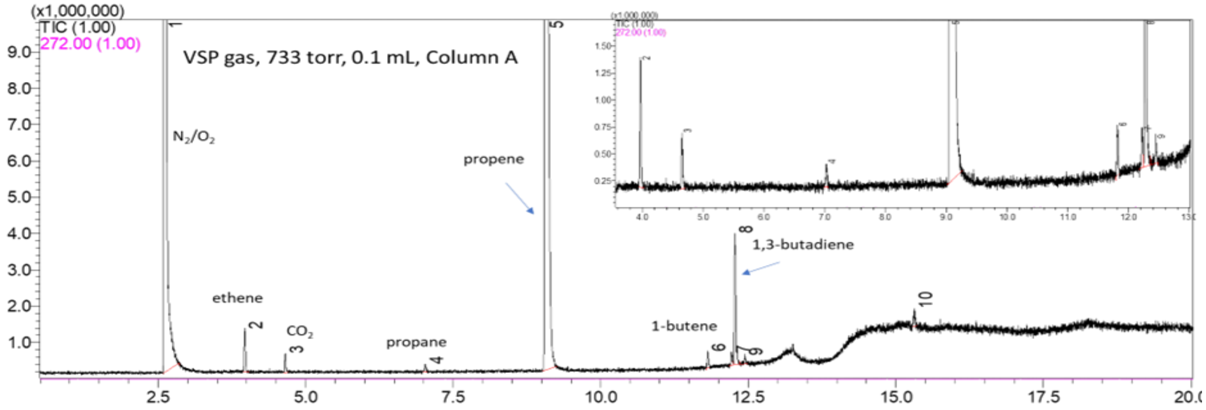


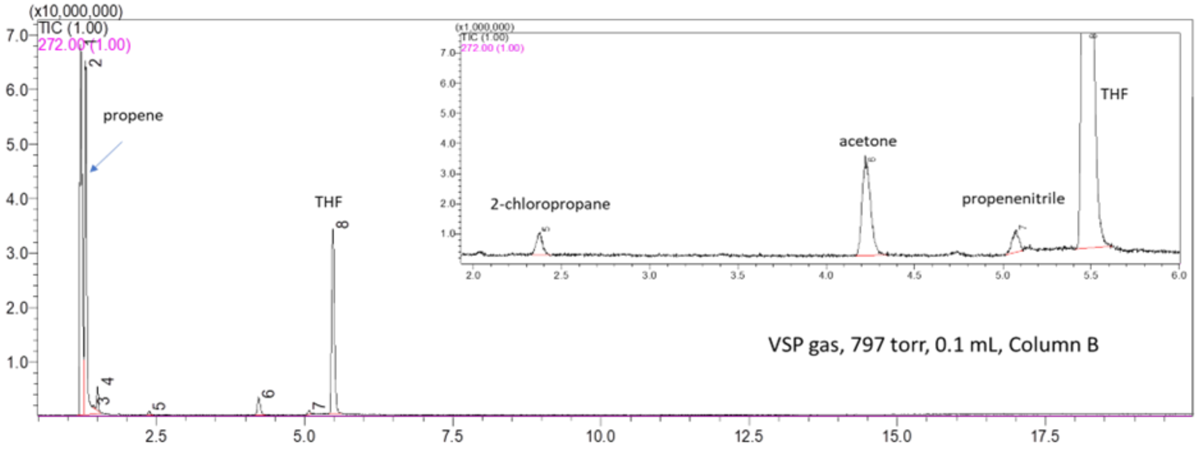


VSP2 Open Cell Test

To analyze vapor composition & properly handle the effluents during relief in an external fire scenario.

(Pad 110 psig)





$(Pr_2N)_2P(OCH_2CH_2CN) \xrightarrow{THF}$

Composition	mole%
CO_2	2.71
C_2H_4 (Ethylene)	1.11
C_3H_8 (Propane)	0.34
C_3H_6 (Propylene)	61.63
1-Butene	0.29
trans-2-Butene	0.29
1,3-Butadiene	4.64
Isobutene	0.17
2-Chloropropane	1.01
Acetone	2.45
Propenenitrile	0.25
THF	25.11
SUM (excluding O_2, N_2 & Unidentified)	**100.00**

Example 7. GCMS Chromatograms for gas from VSP open cell test, column A (top), and column B (bottom)

Concluding Remarks

- GC-MS is an indispensable tool in process safety, providing detailed chemical analysis.

- The integration of GC-MS with calorimeters will continue to enhance the ability to effectively manage process safety and mitigate risks associated with chemical hazards.

Acknowledgement

Thank Dr. Michael Carolan and Mike Snyder for valuable discussions.

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Questions and Comments

Thank you!