In Situ Mass Analyzer – ISMA

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Eurokin workshop, Louvain-la-Neuve, February 15th, 2023

Technology for a better society

Background

- TEOM = Tapered element oscillating microbalance
- TEOM 1500 originally produced by Rupprecht & Patashnick Co. Inc
- Studies on catalysis, adsorption, diffusion, etc. since early 1990's
- Last decade limited supply of crucial parts
- "Necessity is the mother of invention" => ISMA
- SINTEF since 2017

Ind. Eng. Chem. Res. 1993, 32, 2969–2974 2969

Simultaneous Measurement of Adsorption, Reaction, and Coke Using a Pulsed Microbalance Reactor

Frank Hershkowitz* and Paul D. Madiara
Exxon Research & Engineering Company, Route 22 East, Annandale, New Jersey 08801

ELSEVIER Applied Catalysis A: General 137 (1996) L1–L8
APPLIED CATALYSIS A: GENERAL

Letter

Catalyst deactivation studied by conventional and oscillating microbalance reactors

De Chen [a], A. Grønvold [b], H.P. Rebo [a], K. Moljord [b], A. Holmen [a,*]
[a] *Department of Industrial Chemistry, Norwegian University of Science and Technology, N-7034 Trondheim, Norway*
[b] *SINTEF Applied Chemistry, N-7034 Trondheim, Norway*

Received 27 November 1995; accepted 10 December 1995

1934 Ind. Eng. Chem. Res. 1998, 37, 1934–1942

TEOM: A Unique Technique for Measuring Adsorption Properties. Light Alkanes in Silicalite-1

W. Zhu,* J. M. van de Graaf, L. J. P. van den Broeke, F. Kapteijn, and J. A. Moulijn
Industrial Catalysis, Department of Chemical Engineering, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

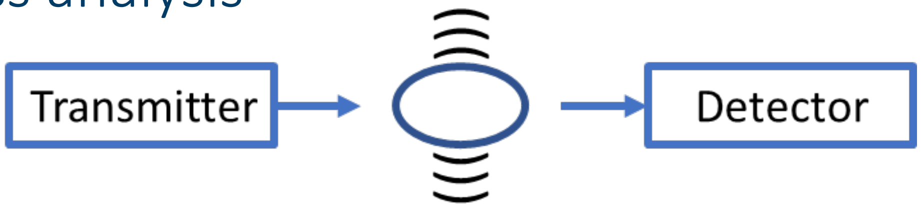
Concept

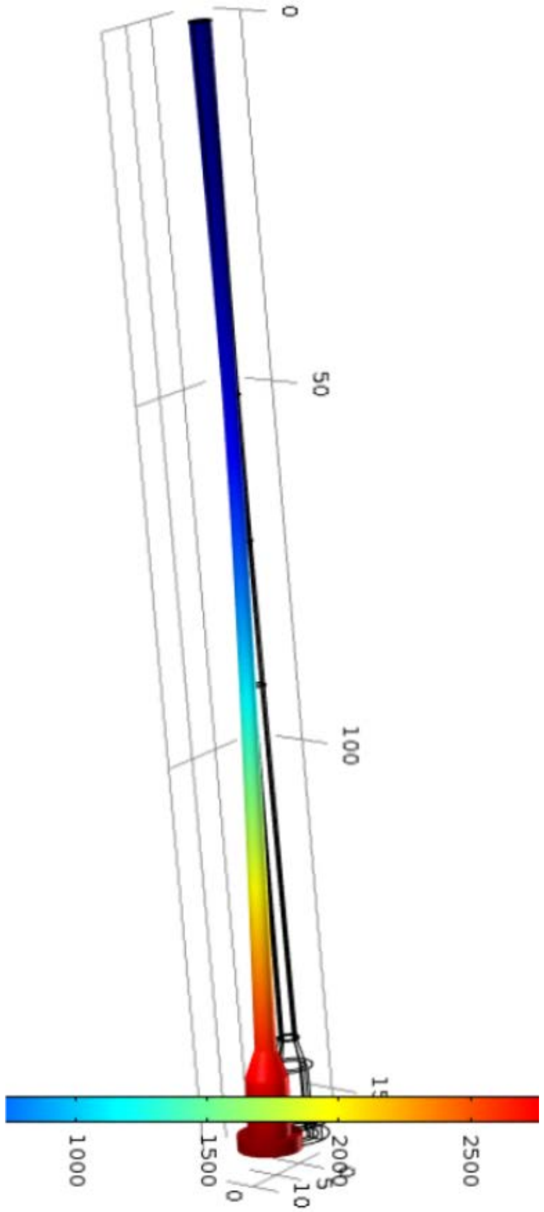
- Frequency and mass are related

$$f^2 = \frac{k}{m} \quad => \quad \Delta m = m_1 - m_0 = k\left(\frac{1}{f_1^2} - \frac{1}{f_0^2}\right)$$

  - f = frequency
  - m = mass
  - k = constant, and unique for each element

- *In situ* frequency measurements of an oscillating quartz element => *in situ* mass analysis

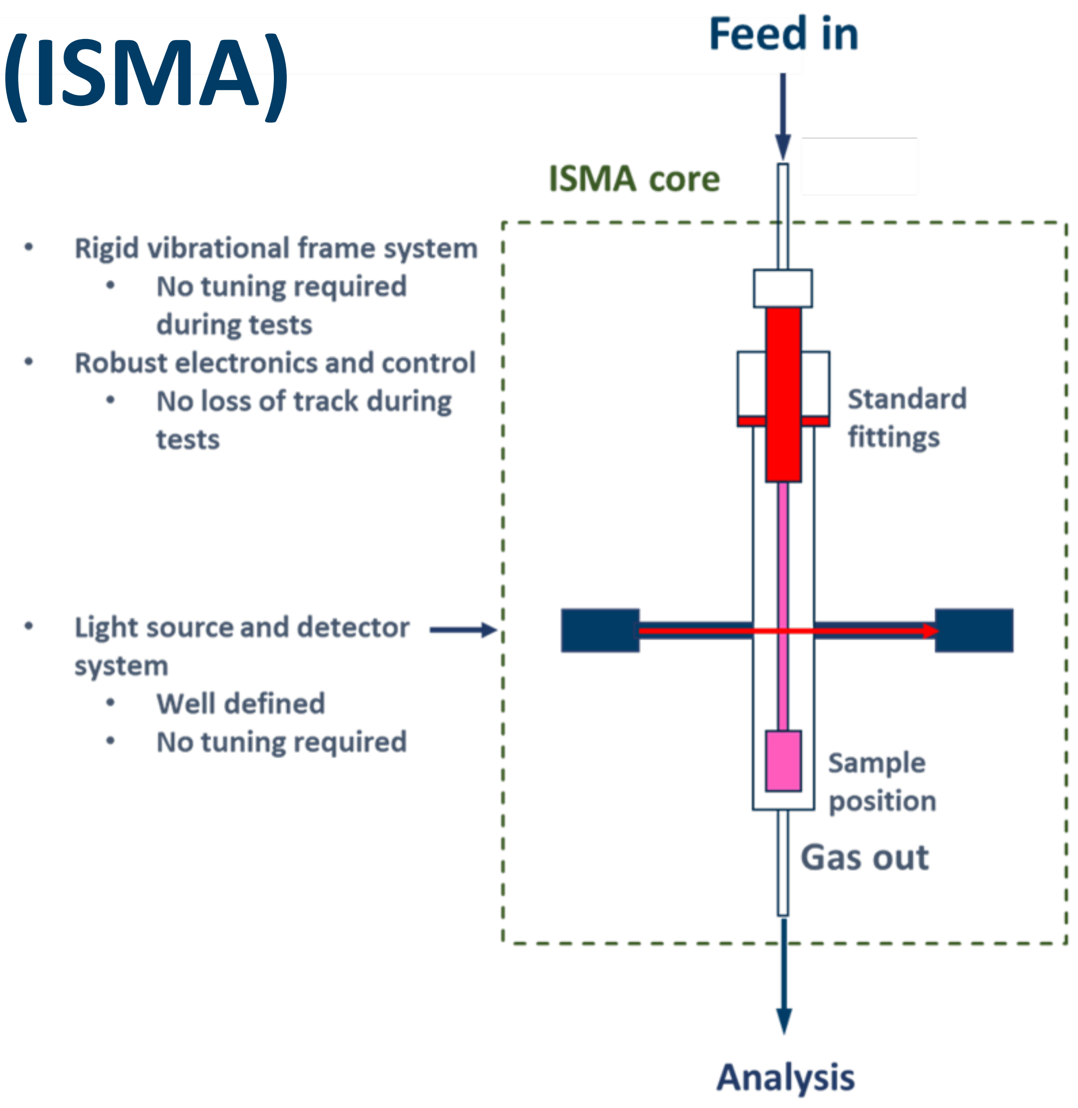




In situ mass analyser (ISMA)

Some specifications of our system

- T_{max} = 700 °C
- P_{max} = 65 bar
- Loading = 100 – 500 mg
- Fixed-bed
- *t*-resolution: seconds
- Mass sensitivity: μg
- Full automated (LabVIEW)
  - Control, data logging, analysis



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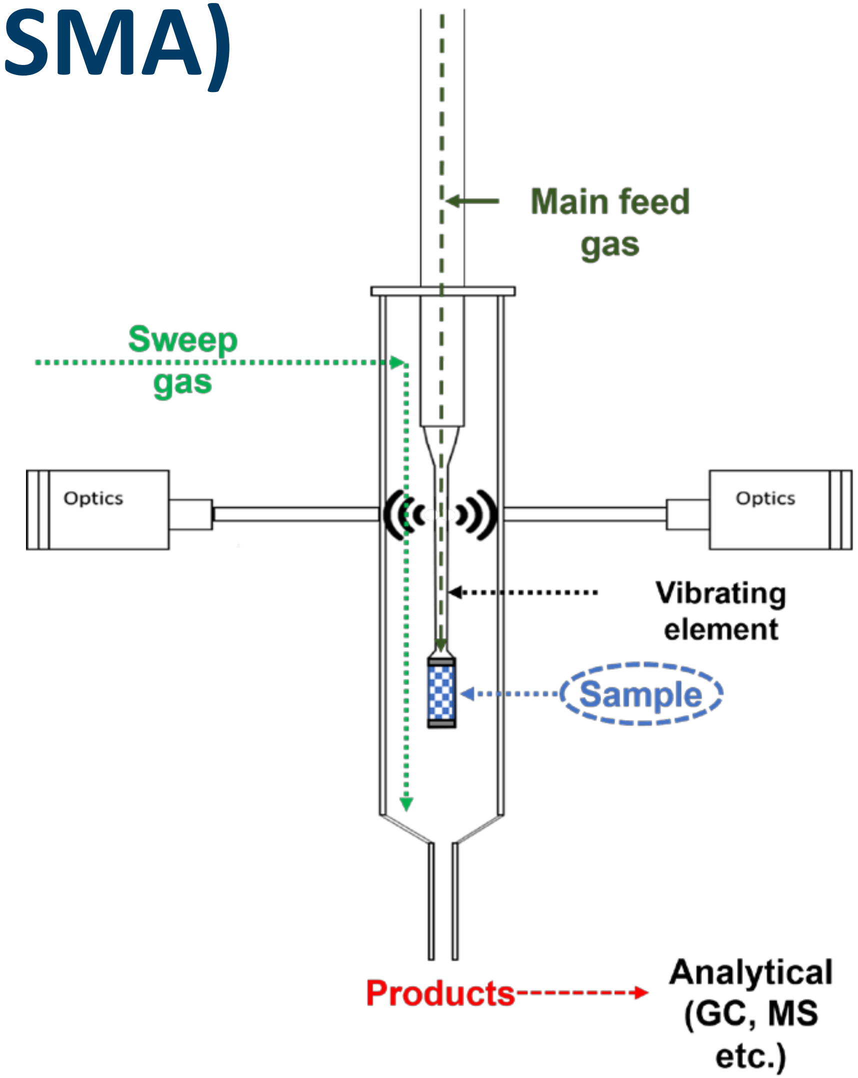
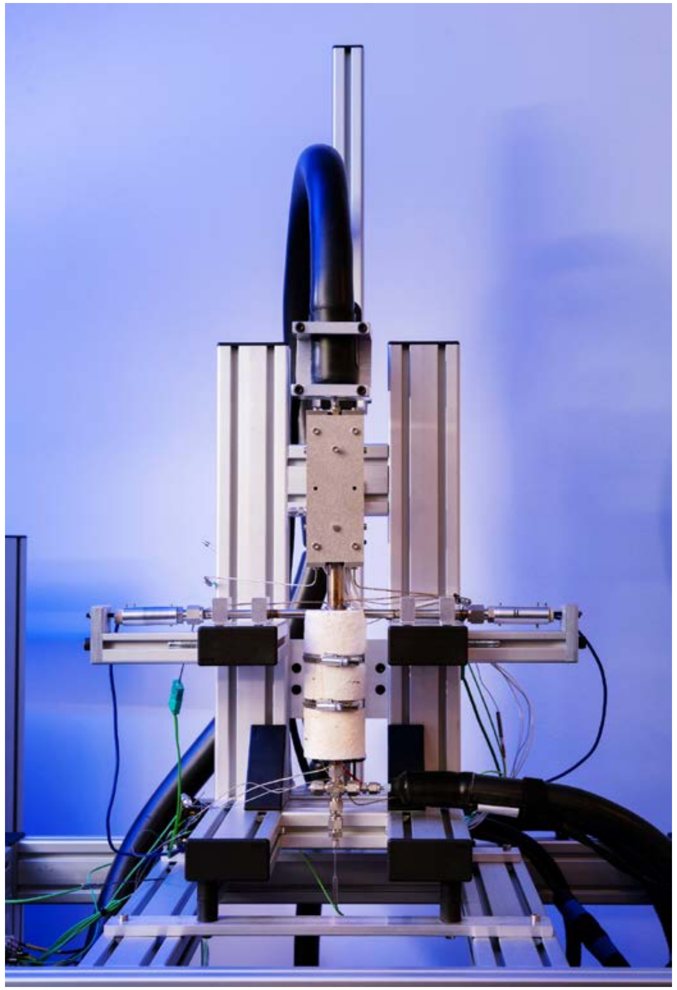
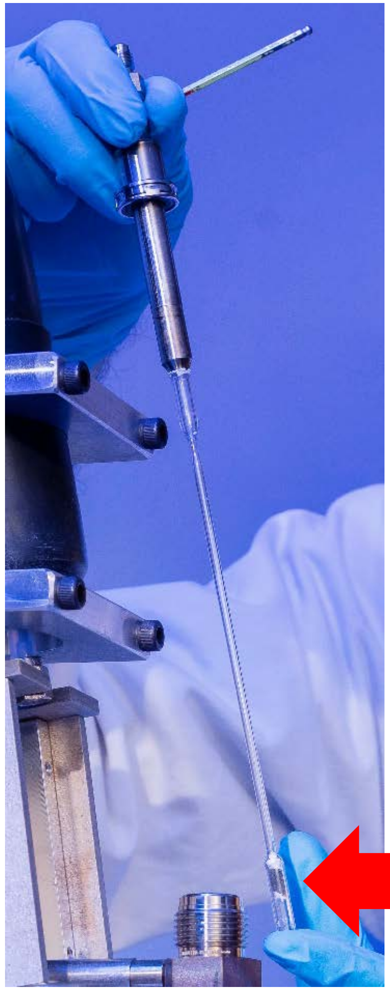


ISMA core and quartz element

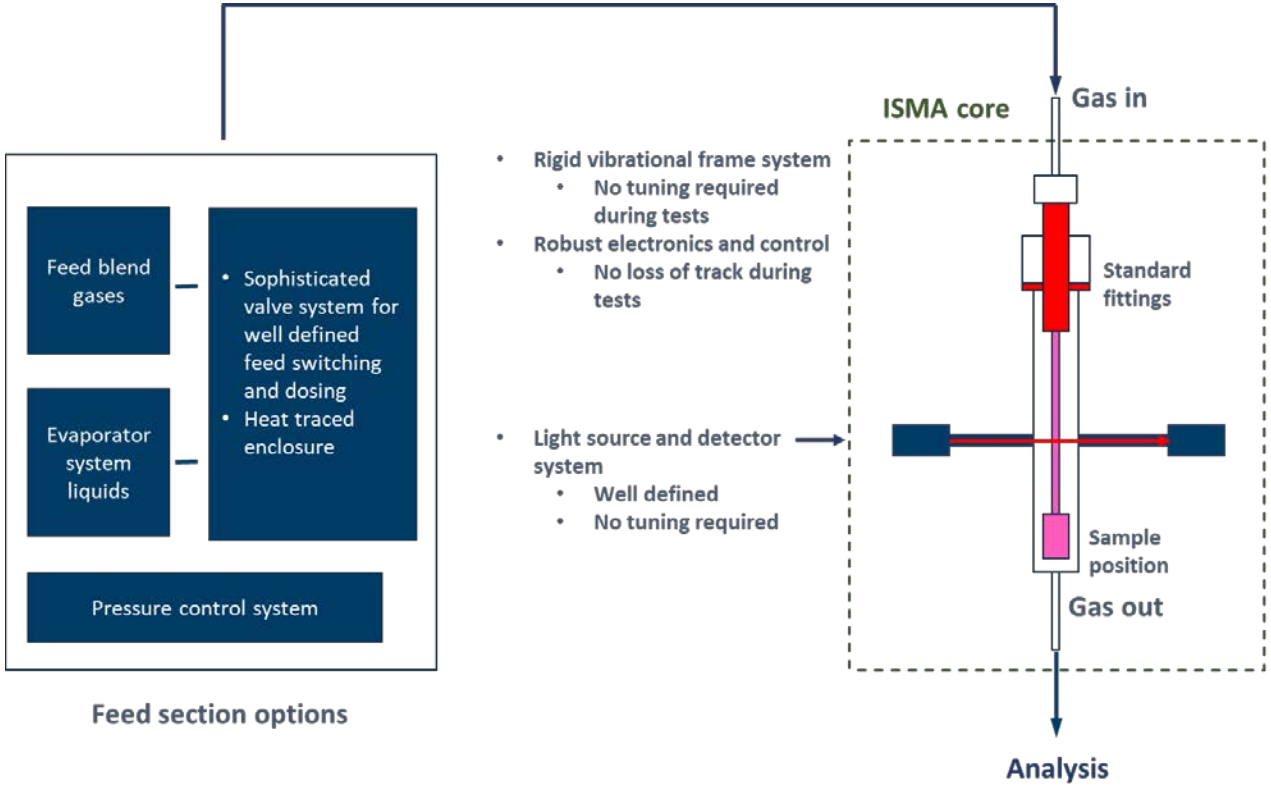




ISMA with infrastructure and flow sheet

ISMA with some infrastructure

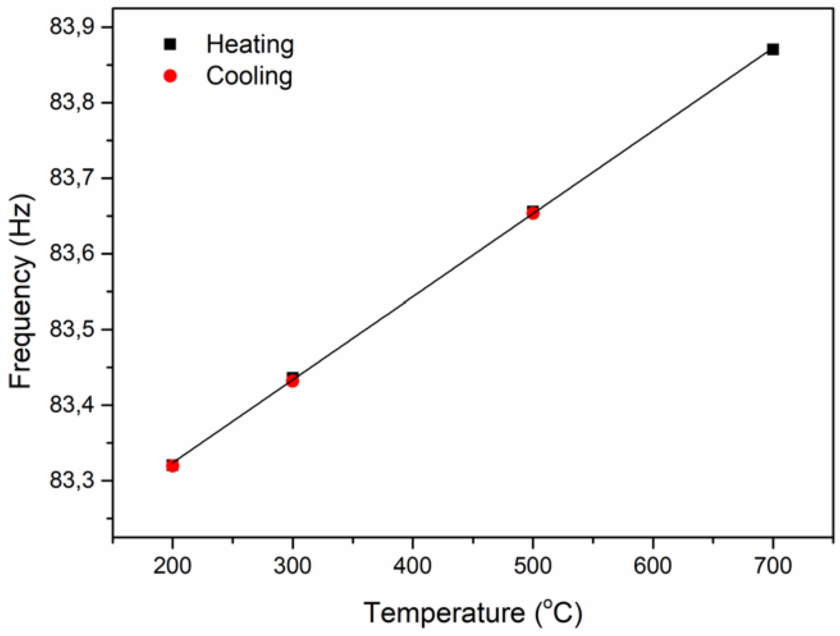
Flow sheet



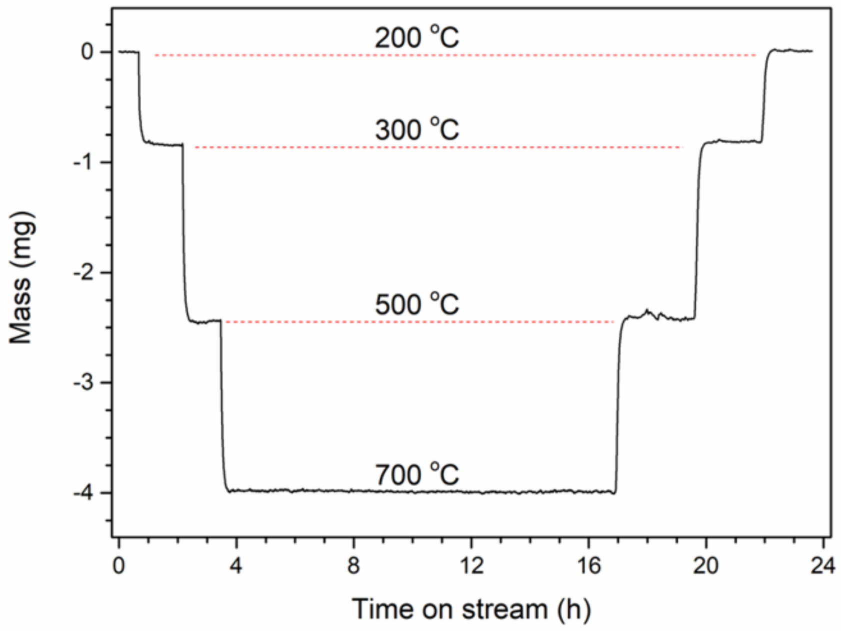
Stability: Temperature

$$f^2 = \frac{k}{m} => \Delta m = m_1 - m_0 = k(\frac{1}{f_1^2} - \frac{1}{f_0^2})$$

***f*(*T*)**



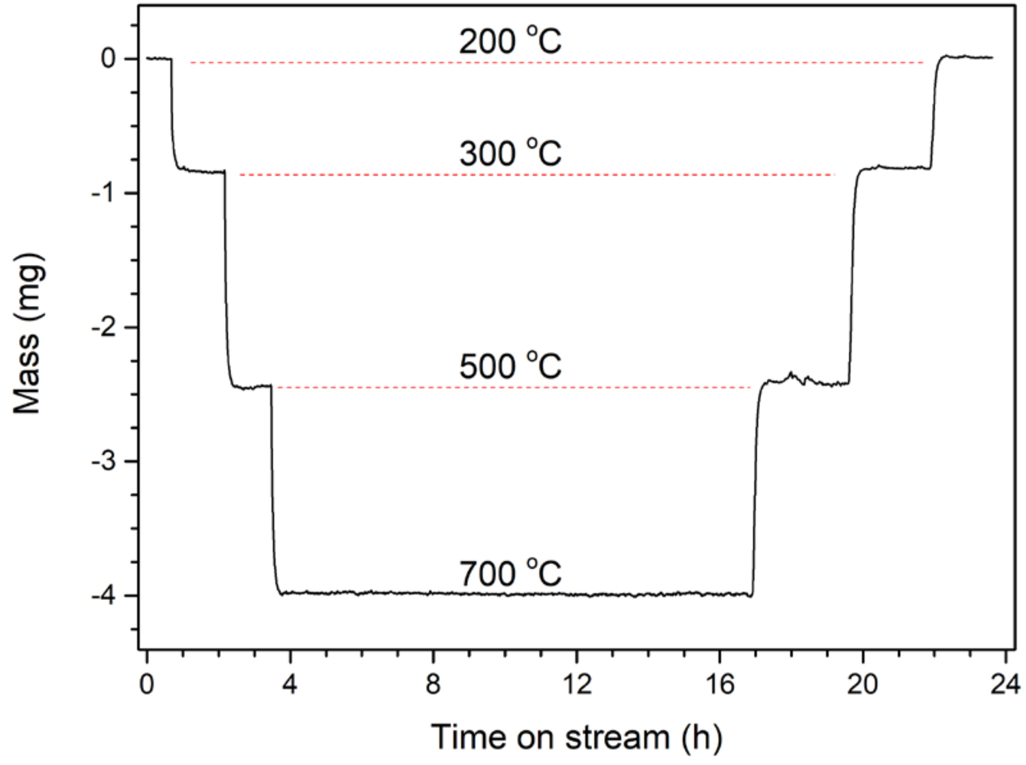
***m*(*T*)**



Stability: Temperature

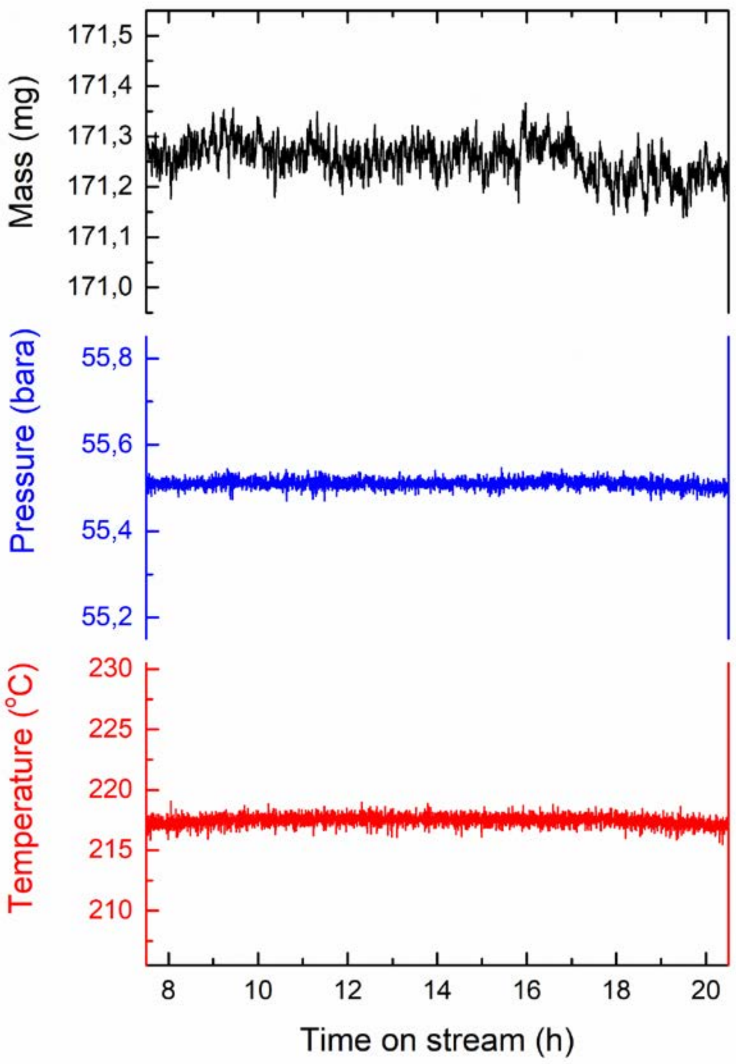
- *T*-steps 200 – 700°C at 1 atm
- Rapid stabilization at all temperatures
- Excellent reproducibility
- Low noise => microgram level

Temperature [°C]	Std.dev. [µg]	
	Heating	Cooling
200	3	2
300	3	4
500	3	8
700	7	



Stability: Pressure

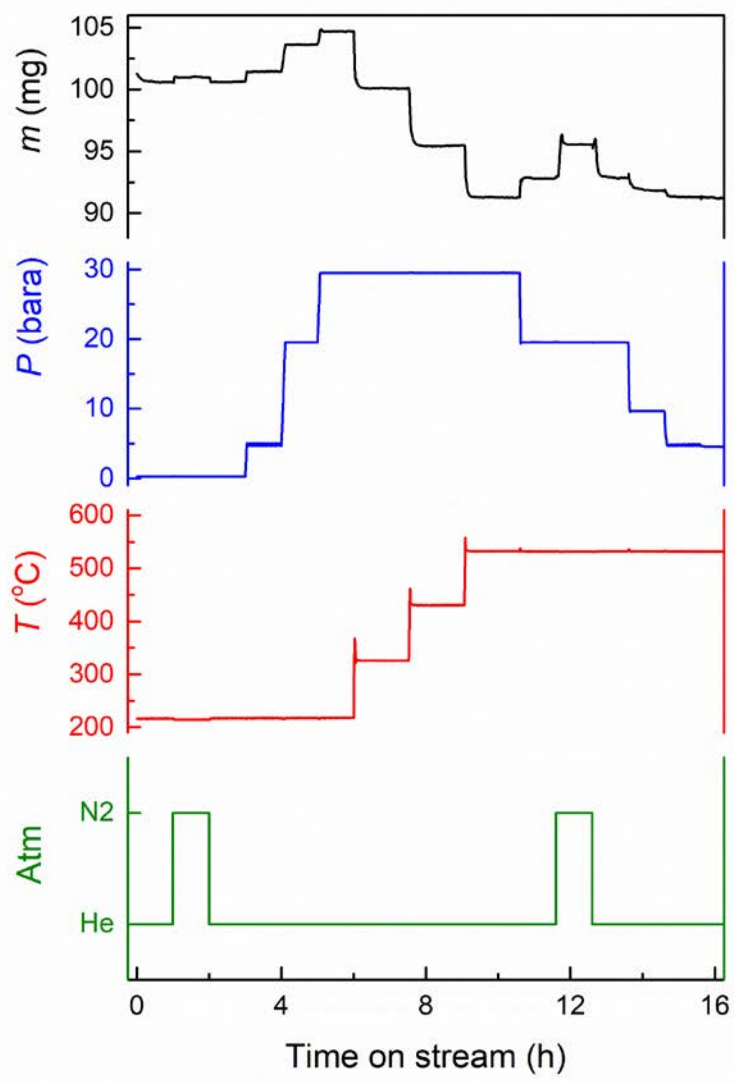
- Fixed *m*, *T* and *P*
- Measured
  - $m = 171.26 \pm 0.04$ mg
  - $P = 55.51 \pm 0.01$ bara
  - $T = 217{,}5 \pm 0.4$ °C



Multiple steps

- Switch between conditions
  - *T*, *P*, composition, flow rates etc. can be changed during run
- Fully automated
  - PC w/ LabVIEW
  - *T*, *P*, flows etc are controlled and logged
  - Analytics (e.g. GC) fully integrated

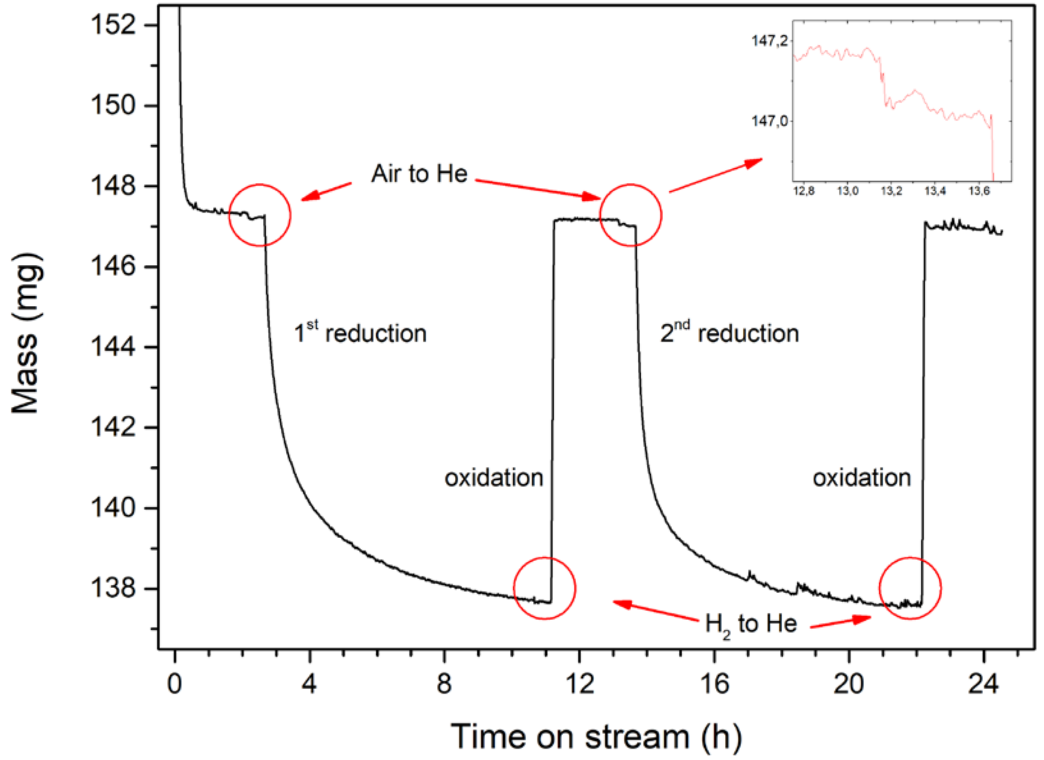
We have run >10.000 steps over 5 weeks in one experiment (not shown here)



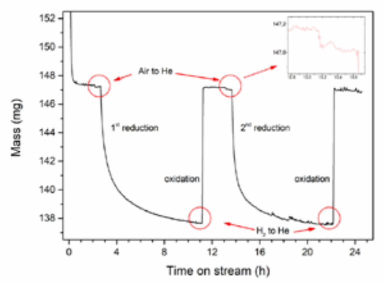
Example 1: NiO oxidation/reduction

- 45 wt% $Ni/Al_2O_3 + MgO + SiO_2$
- T = 600 °C
- Loading= 100,6 mg

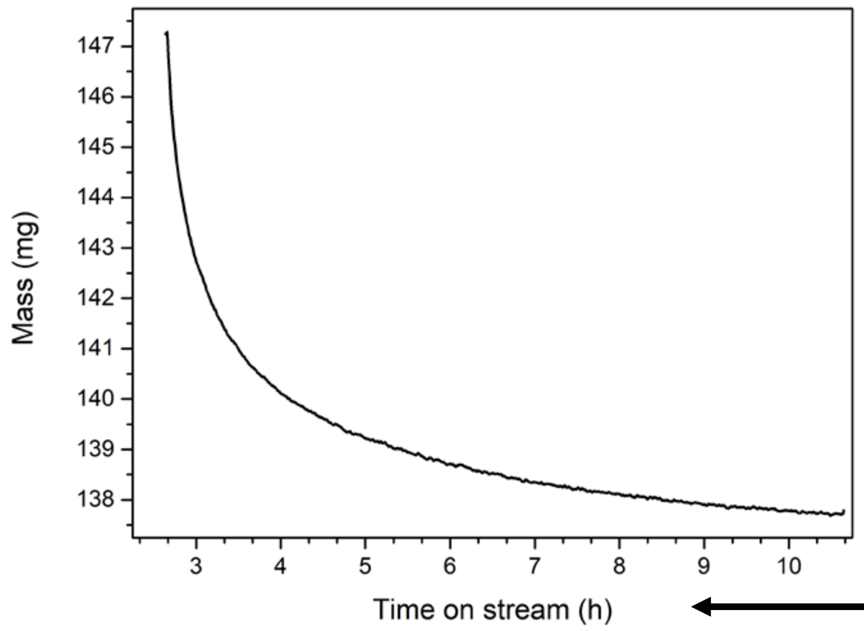
Δm (mg)		% of theoretical	
Reduction	Oxidation	Reduction	Oxidation
-9,57	-	100.7	-
-	+9,35	-	98,4
-9,41	-	99,0	-
-	+9,24	-	97,2



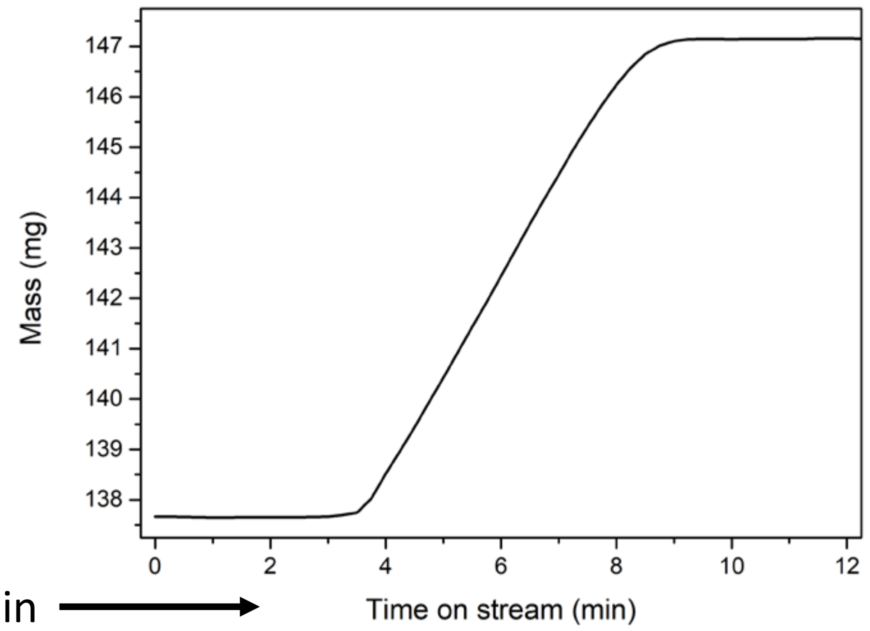
Example 1: NiO oxidation/reduction



Reduction

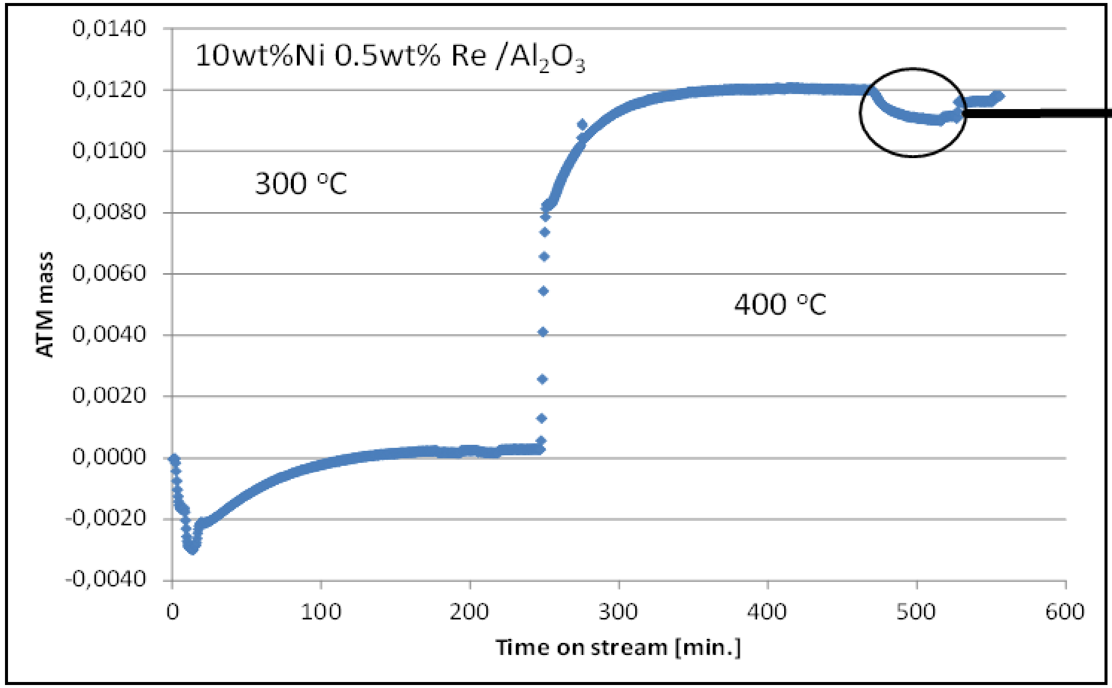


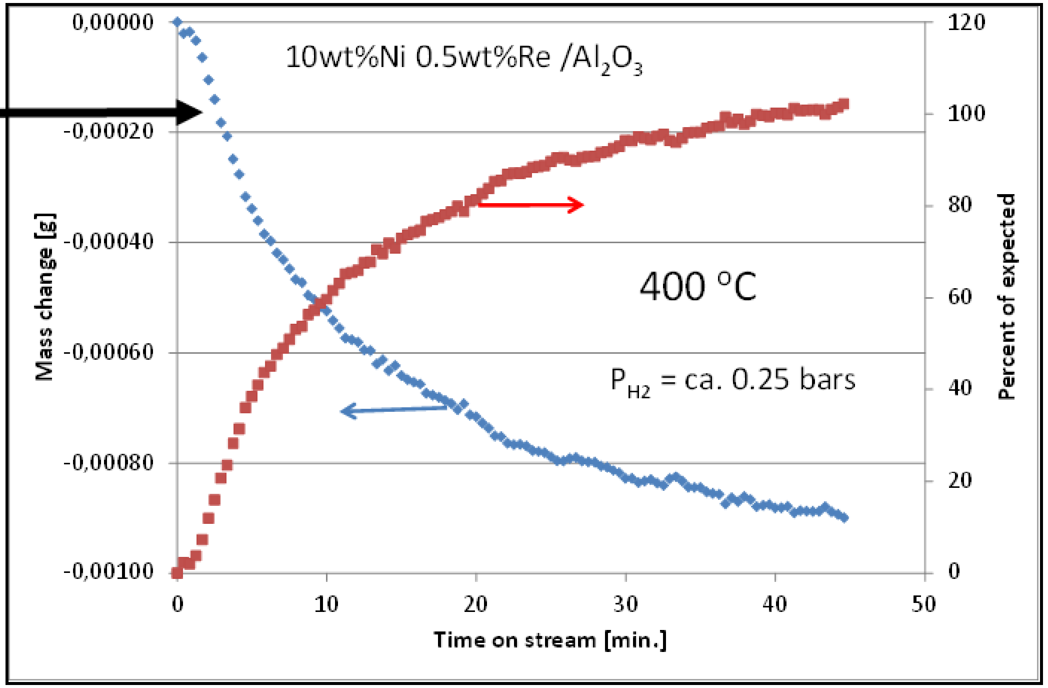
Oxidation



Note: h *vs.* min

Example 2: Catalyst pre-treatment





- Δm *vs.* time on stream
- $P(H_2)$ = 0,25 bar during catalyst pre-treatment

Final remarks

ISMA specifications

- T_{max} = 700 °C
- P_{max} = 65 Bar
- Space velocities: Typical catalytic processes
- Fixed bed configuration
  - Loadings up to 500 mg tested
- Automated control and data logging
  - Analytics integrated
- <u>User friendly and robust</u>

Demonstrated / exemplified

- Applicability to mass changes
- High stability / high reproducibility
- Microgram sensitivity; typical accuracy 0,01 mg
- Rapid (seconds)
- Long time stability (weeks)
- Multiple steps

Current activities

- Delivered three complete units to customers
- Contract research / project partners

SINTEF

Acknowledgements

Instrument development

- Arne Karlsson
- Rune Lødeng
- Karl Henrik Haugholt
- Duncan Akporiaye

Financial support

- SINTEF internal funding

Contacts

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- knut.thorshaug@sintef.no

- Visits are welcome
- The instrument is located in Oslo

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