

Presentation

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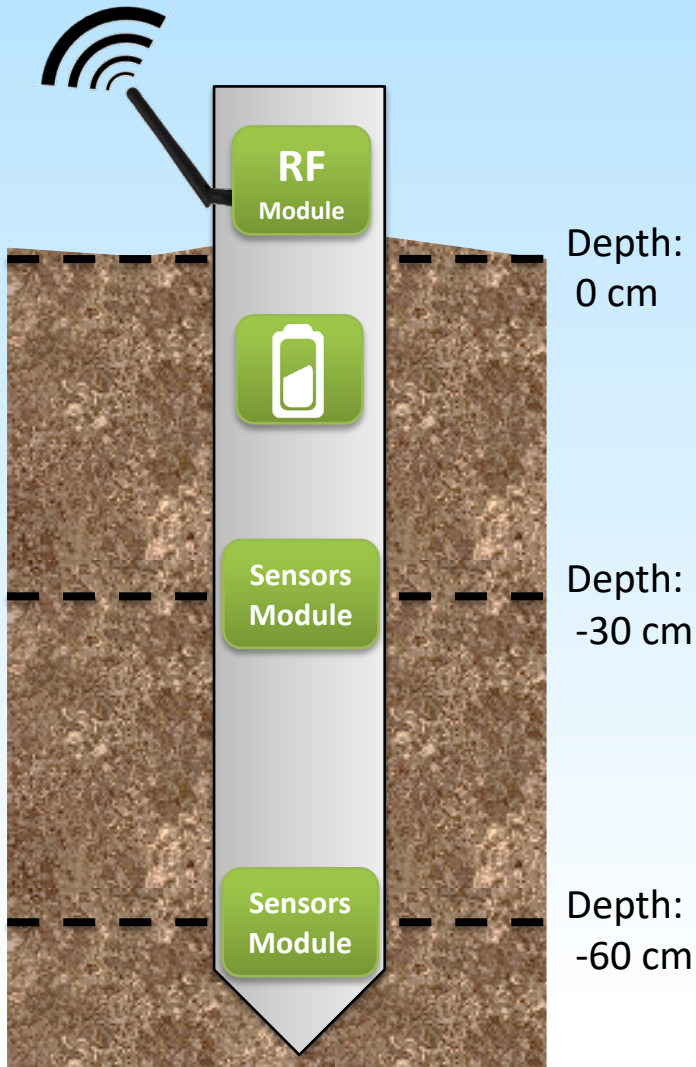
Team “Microsystems for Analysis”:

- Electrochemical and optical sensors in liquid and gas phase in the fields of environment, health, biology or security

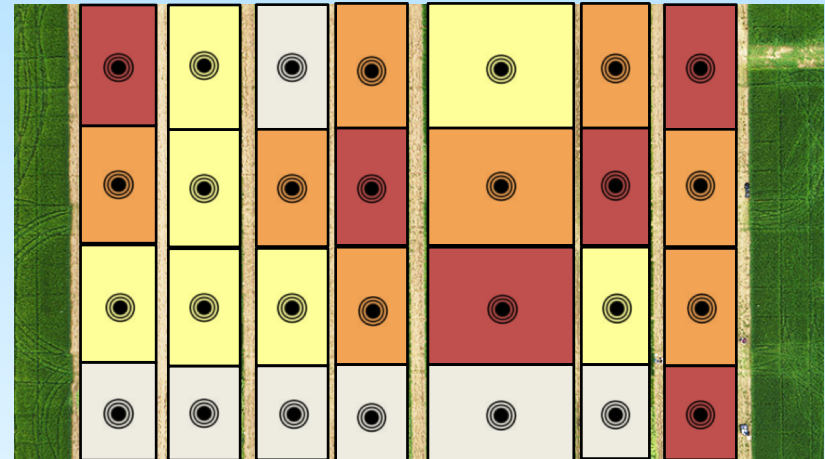
- A medium-sized company specialized in plant nutrition



Goal: Improve nitrogen fertilizer efficiency with a time & site-specific tool



A wireless sensors network:

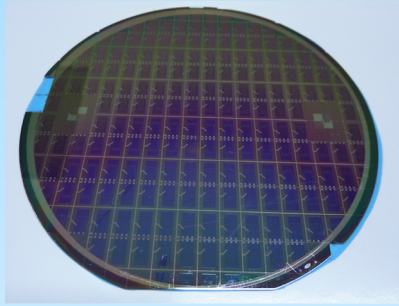


Each Micro-Sensors module measures:

- Soil pH
- Soil Nitrate (NO_3^-) concentration
- Soil Ammonium (NH_4^+) concentration
- Soil Temperature
- Soil Ionic Conductivity

Ion-Sensitive Field Effect Transistor (ISFET) Technology

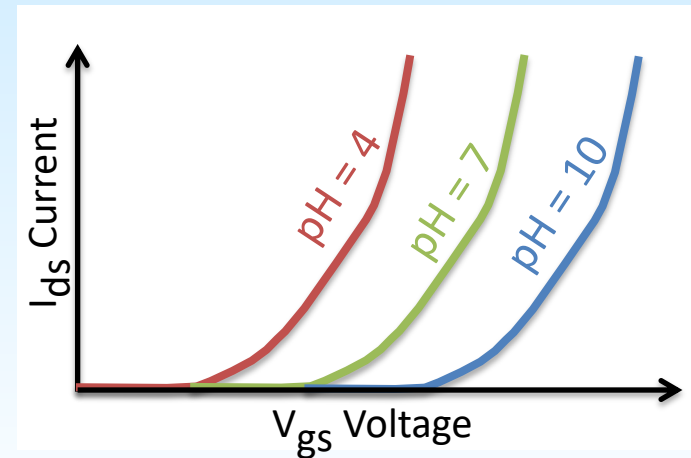
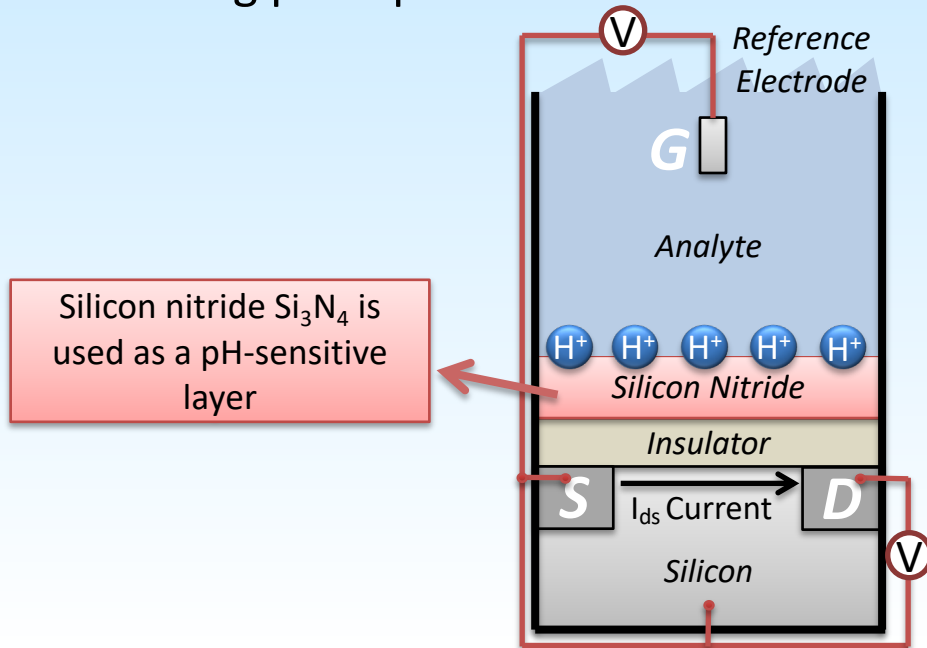
□ **pH-ISFET** microsensors are fabricated in a clean room using silicon technology



Advantages vs. pH glass electrodes:

- Non-glass body → Rugged, no broken glass problem
- No electrolyte → Can be stored dried
- Fast response
- Low-cost

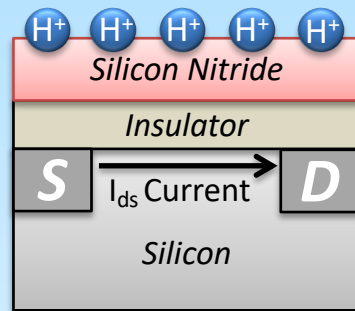
□ Working principle:



ISFET's Sensitivity > 50 mV/pH

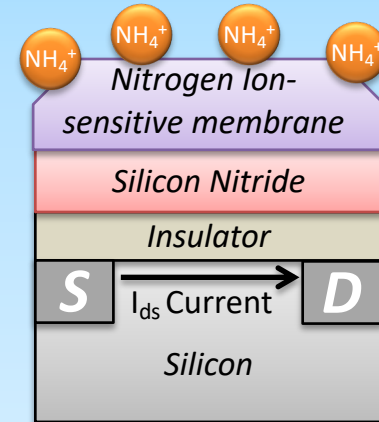
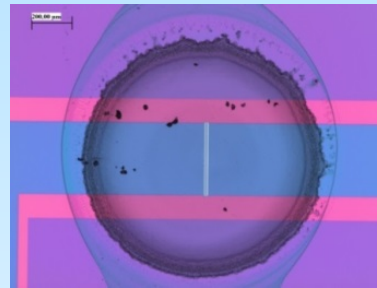
Ion-Sensitive Field Effect Transistor (ISFET) Technology

- pH-ISFET functionalization to Nitrate and Ammonium detection by adding an ion-sensitive membrane



pH-ISFET

Membrane drop-casting



pNO3-ISFET / pNH4 ISFET

- Challenges of using ISFET for monitoring in agriculture:
 - Lifetime of ISFET must be long (> 5 months) in a complex environment
 - Use of a sensor technology dedicated to liquid phase measurement in non-liquid soil



In-situ soil measurements with pH-ISFET

Effect of soil moisture on ISFET's detection capability:

Soil moisture given in % of maximum soil water holding capacity

Soil moisture	30%	40%	50%	60%	70%	80%	90%	100%
Silty Clay	✓	🐢	🐢	✓	✓	✓	✓	✓
Sand	🐢	🐢	✗	✓	🐢	✓	🐢	✓

✓ Quick response

🐢 Slow response

✗ No response



➤ ISFET's sensitive area must be in fine contact with soil paste

Conclusions:

- ✓ ISFET measurement is compatible with typical water contents during wheat growth

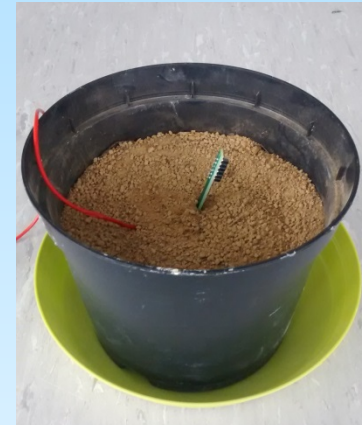
In-situ soil measurements with pH-ISFET

□ pH-ISFET measurements compared to standard laboratory method:

- In a silty-clay soil of pH 4,7
 - In a silty-clay soil of pH 8,4
- } Soil moisture \approx 75% of maximum water holding capacity



Quick 3-points calibration of ISFET in buffer pH solutions



N° Measurement	1	2	3	4	5	Average	Standard deviation	Measurement Error
Soil pH = 4,7	4,99	4,75	5,35	5,5	5,19	5,15	0,26	0,45
Soil pH = 8,4	7,98	8,40	8,04	8,06	8,45	8,19	0,19	0,21

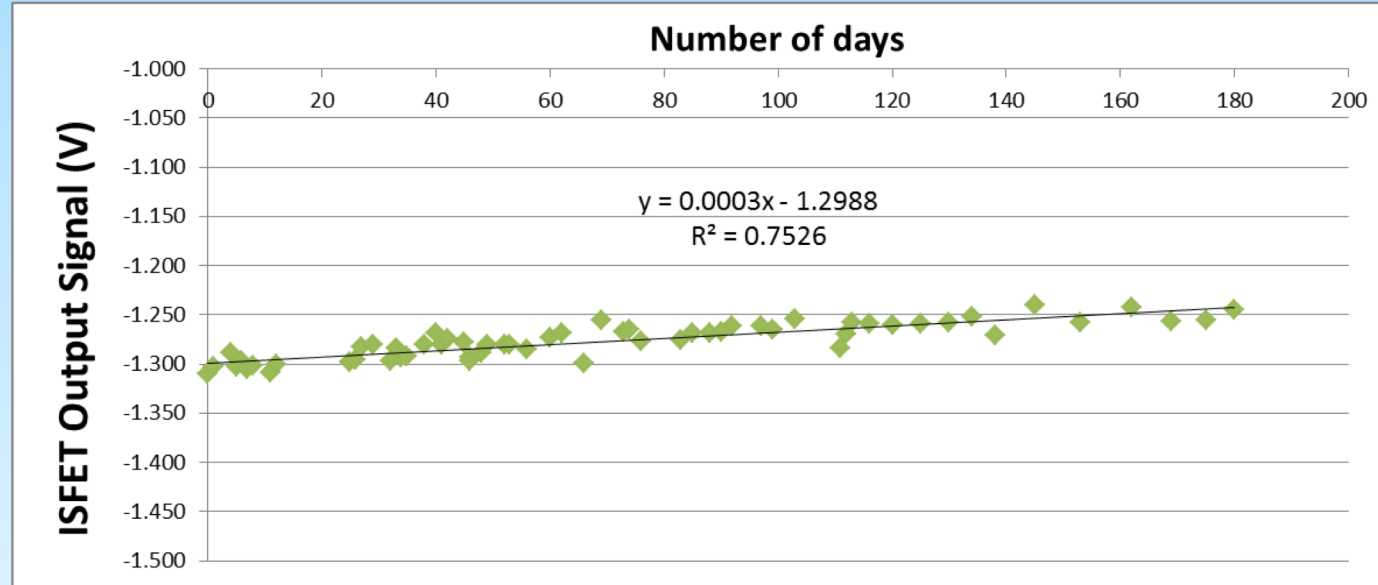
Conclusions:

- ✓ Rapid in-situ pH-measurement in acid and basic soils leads to values in good accordance with standard laboratory results

In-situ soil measurements with pH-ISFET

- Study of ISFET and reference electrode potential drift and lifetime in a silty clay soil

LAAS ISFET



- ISFET drift is little and predictive: Loss of 1 pH unit after 6 months

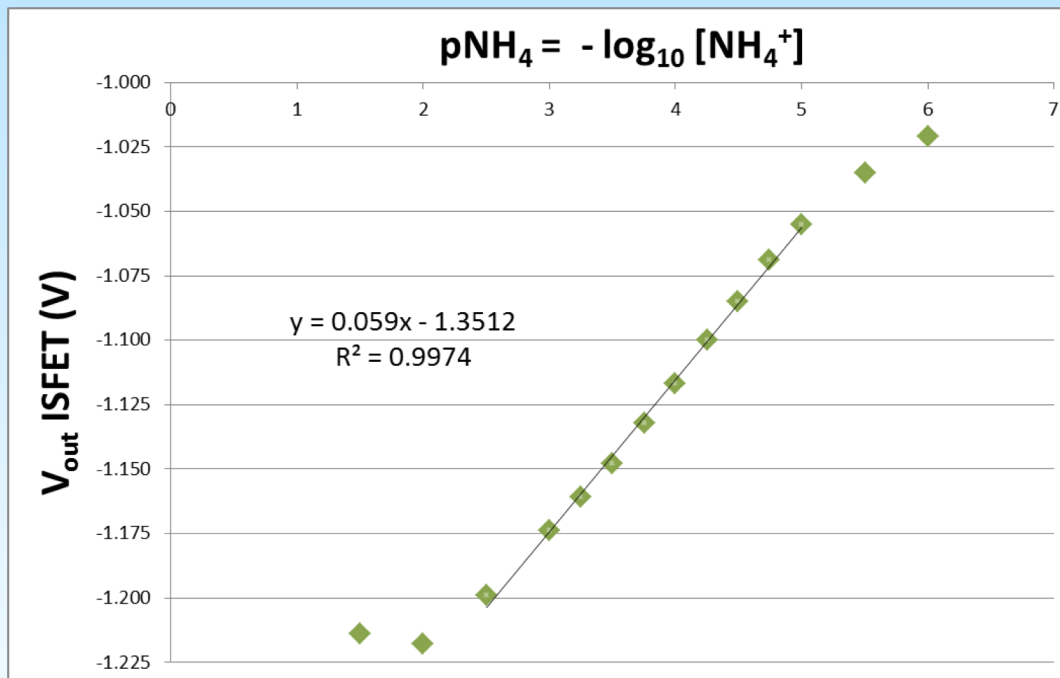
Conclusions:

- ✓ pH-ISFET technology could allow the monitoring of soil-pH during all wheat growth stages

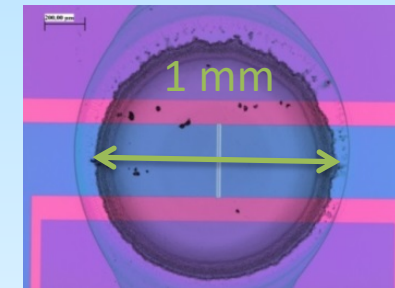
From the pH-ISFET to mineral nitrogen detection

- Functionalization of pH-ISFET : Casting of a sensitive membrane based on a fluoropolysiloxane matrix with ionophores.

Characterization in aqueous solution with ammonium nitrate concentrations ranging from 10^{-6} to 10^{-1} mol/L



Membrane composition:
FPSX + Nonactine + KT-4-CIPB



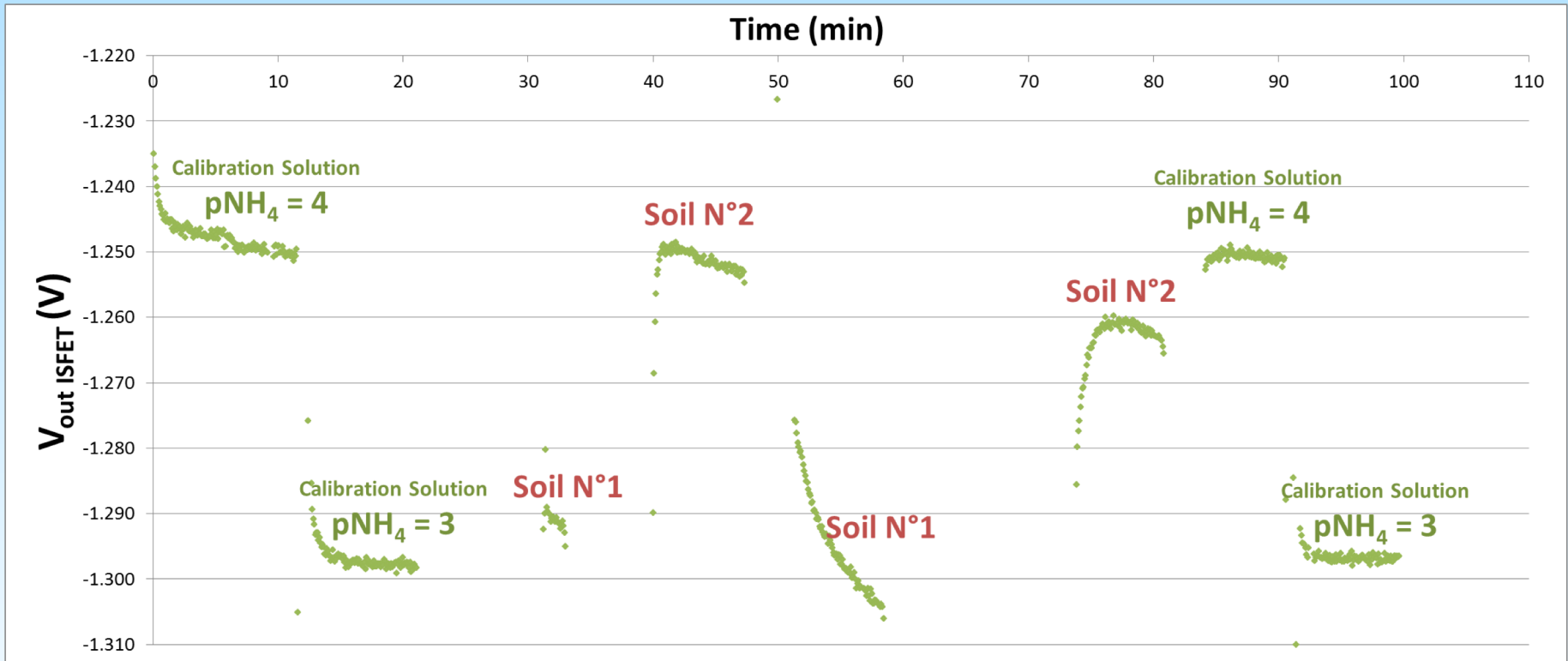
Slope (mV/ pNH_4^+)	59,0
Linear Range (pNH_4^+)	[2,5 – 5]
Detection limit (pNH_4^+)	> 5,5

Conclusions:

- ✓ Functionalized ISFET exhibit sensitivity and detection limit in liquid phase in accordance with standard values in field conditions

Soil ammonium sensing with pNH₄-ISFET

- Soil N°1: Nitrogen mineralization stimulated by high temperature (38°C) for 1 month
- Soil N°2: Nitrogen mineralization inhibited by low temperature (4°C) for 1 month



Conclusions:

- ✓ An increase of NH₄ concentration from pNH₄ = 4 to pNH₄ = 3 was highlighted by pNH₄-ISFET in silty-clay

Conclusion and prospects

- ✓ pH-ISFET are suitable for an easy and long-term pH analysis in soil
- ✓ pNH_4 and pNO_3 -ISFET already showed promising results in soil nitrogen sensing
 - ...but some properties still need to be validated in soil:
 - Lifetime of the ion sensitive membrane
 - Selectivity
 - Integration of a stable reference electrode



Acknowledgements

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Thank you

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