Automated corrosion sensors for on-line real time monitoring of indoor and outdoor atmospheres

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Air control in museums and archives

- Inevitable for protection of objects of cultural heritage
- Aim: Limit as much as possible objects' degradation
- Feedback often missing or limited

Protection is either inadequate or excessive (too costly)

Real time monitoring of the air aggressiveness for particular object / group of objects

→

Operators could take immediate counter measures when the air aggressiveness is elevated

… ventilation parameters, replacement of filters, reduction of the number of visitors, increase of temperature …

Corrosion of metals in the atmosphere

Affected by many parameters:

- Temperature
- Time of wetness (relative humidity)
- Concentration of pollutants
- Dust particles, surface contamination
- Metal composition
- Heat transfer, etc.

Relationship between climatic parameters and the corrosion rate of metals (or degradation of other materials) is rather complicated

→ **It is more appropriate to measure corrosivity of air directly on metal sensors**

Monitoring of air quality using metal sensors

- Most appropriate for protection of metal objects
- Applicable also for other materials by selecting metal sensitive to particular pollutant

Measurement of metal corrosion rate

Cumulative

- Mass gain
- Mass loss
- Coulometric reduction

Long time to respond

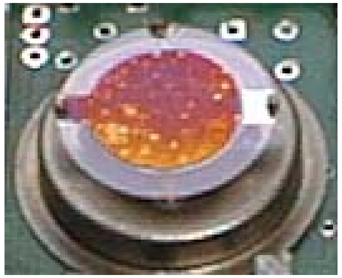
Continuous

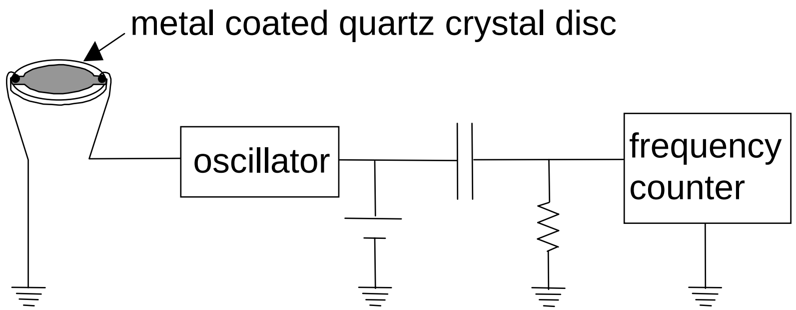
- Electrochemical monitoring

Only for aqueous media

- Quartz crystal microbalance
- Electrical resistance sensors

Quartz crystal microbalance



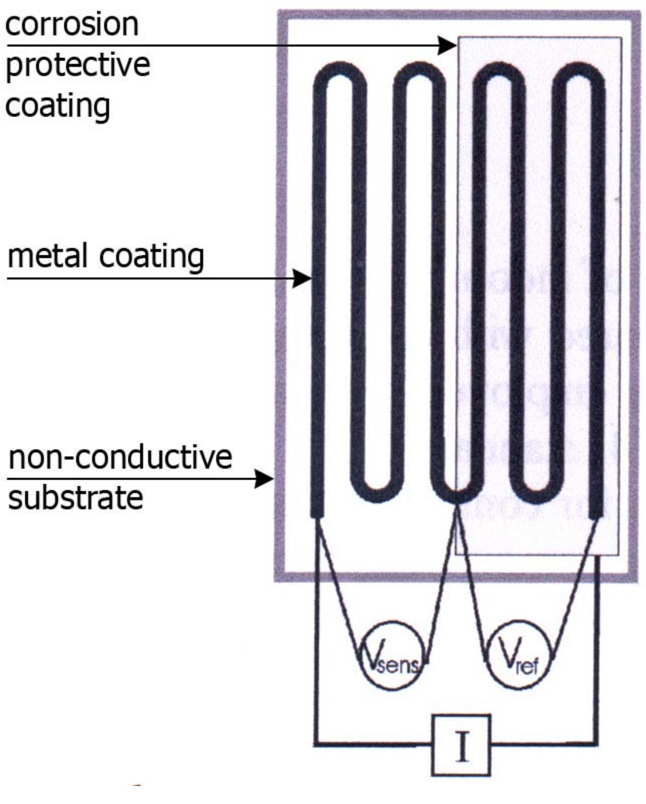


$$\Delta f = -\left(\frac{f_0^{\,2}}{N \cdot \rho_q}\right) \cdot \Delta m$$

Δf	Change in frequency, resonance frequency
N	Frequency constant
ρ	Density
Δm	Mass change/area, assuming film growth on one side of the crystal

- Used in practice
- Sufficiently sensitive for indicating changes
- Mechanically vulnerable
- Affected by temperature
- Affected by humidity
- Affected by dust etc.
- Signal disturbances
- High cost

Electrical resistance technique



$$CD = t_{init}\left(1 - \frac{R_{ref}}{R_{sens}}\frac{R_{sens,init}}{R_{ref,init}}\right)$$

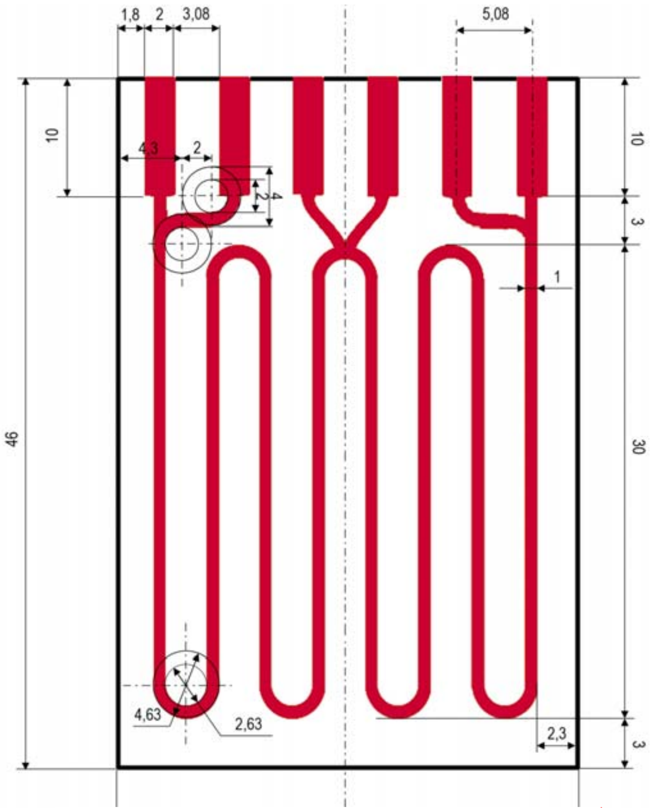
corrosion depth

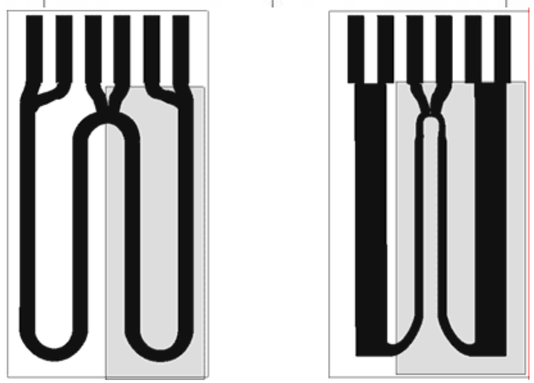
t_{init}	Initial metal track thickness
R_{sens}	Resistance of the sensor track
R_{ref}	Resistance of the reference track
$R_{sens,init}$, $R_{ref, init}$	Initial resistance

- Mechanically non-vulnerable
- Unaffected by humidity
- Unaffected by dust etc.
- Less sensitive
  (longer time to respond)

Concept of corrosion logger

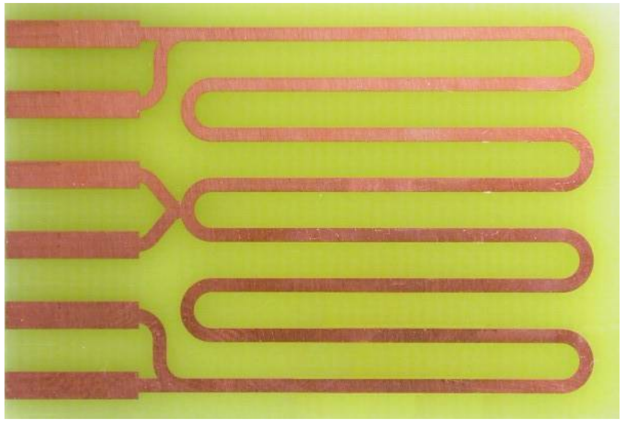
- Electrical resistance measurement
- Good sensitivity and reliability
- Wider range of metal sensors at different sensitivity (indoor/outdoor) – Iron, zinc, copper, silver, nickel
- Small, battery driven device
- Non-contact data reading
- Optional GPRS data transfer
- Exchangeable sensors
- Simple operation demanding no special skills
- Reasonable price



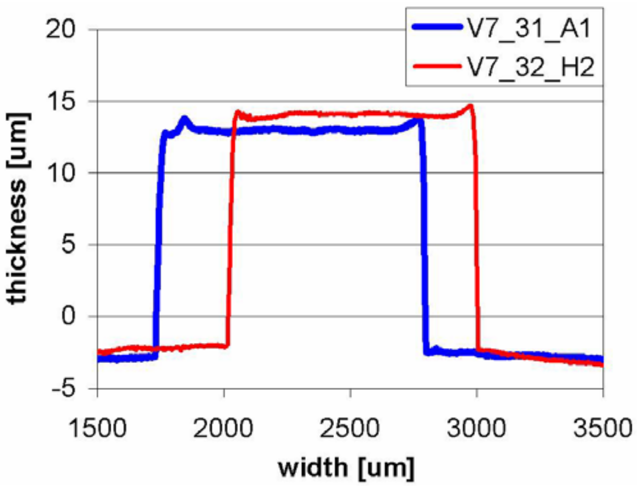


Metal sensors

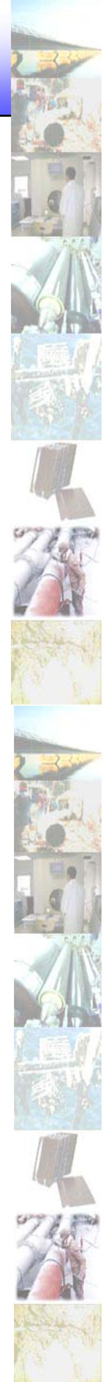
- Thin, precise metal tracks deposited on an insulating material (glass, ABS, laminate)
- Metal deposition: electrodeposition, printed circuit board (PCB) technique, physical vapor deposition (PVD)
- Testing: Profilometry, chemical composition
- Corrosion properties – comparison to metal coupons (corrosion rate, uniformity, composition of corrosion products)
- Protective lacquer and substrate stability – UV, weathering



Cu / PCB technique



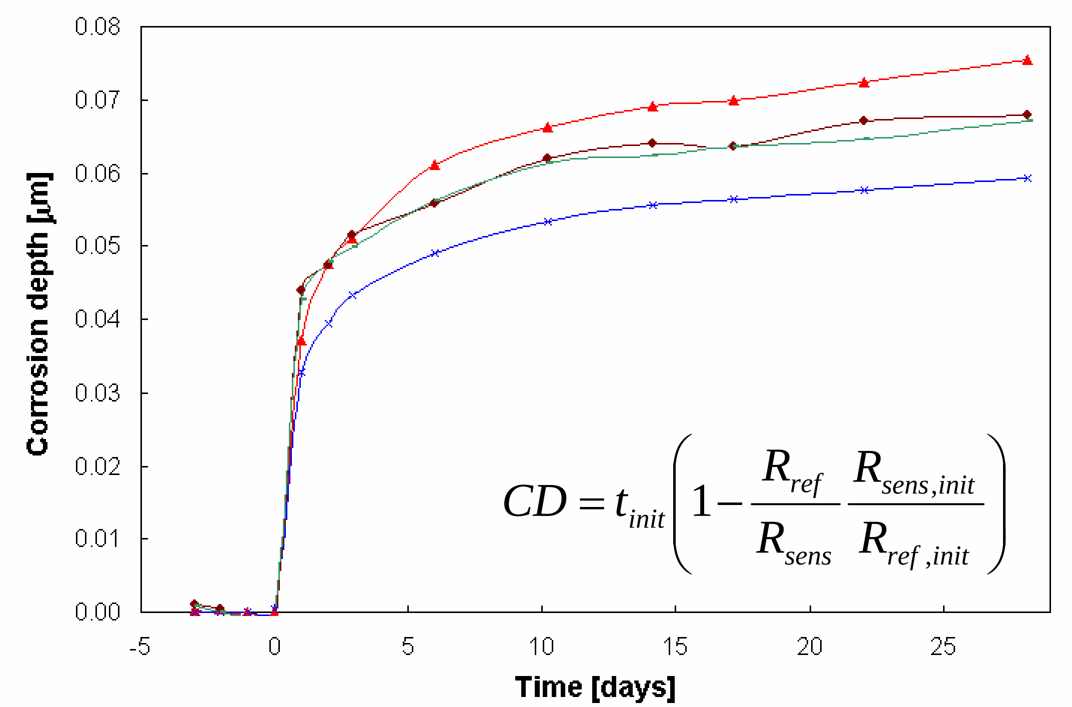
Track profile



Metal sensors – Corrosion tests

- Masking of reference track with tape
- Application of NaCl to accelerate corrosion
- Exposure in a chamber at 20 ºC and 80 % relative humidity for 28 days
- Coupons of zinc and galvanized steel

Zinc sensor / electrodeposition / about 2 μm



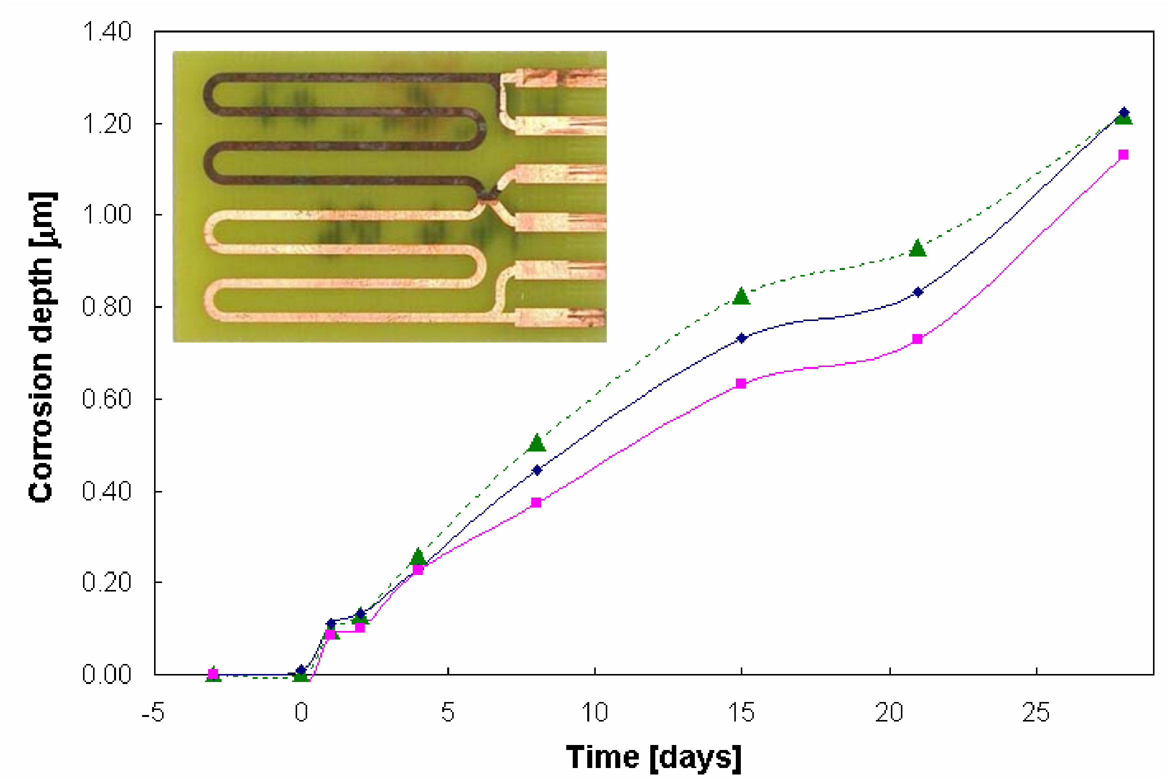
CD = 66 ± 8 nm

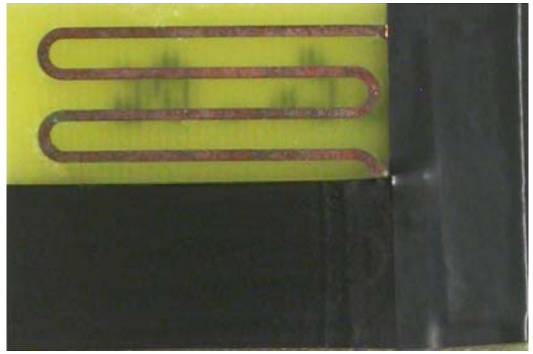
Coupons: CD = 63 nm (both zinc and galvanized steel)

Detection limit: nanometers

Metal sensors – Corrosion tests

- Masking of reference track with tape
- Exposure in Renault ECC1 test (35 °C, wet/dry cycles, salt fog once a day)
- Coupons of copper





Copper sensor / PCB technique / about 17 µm

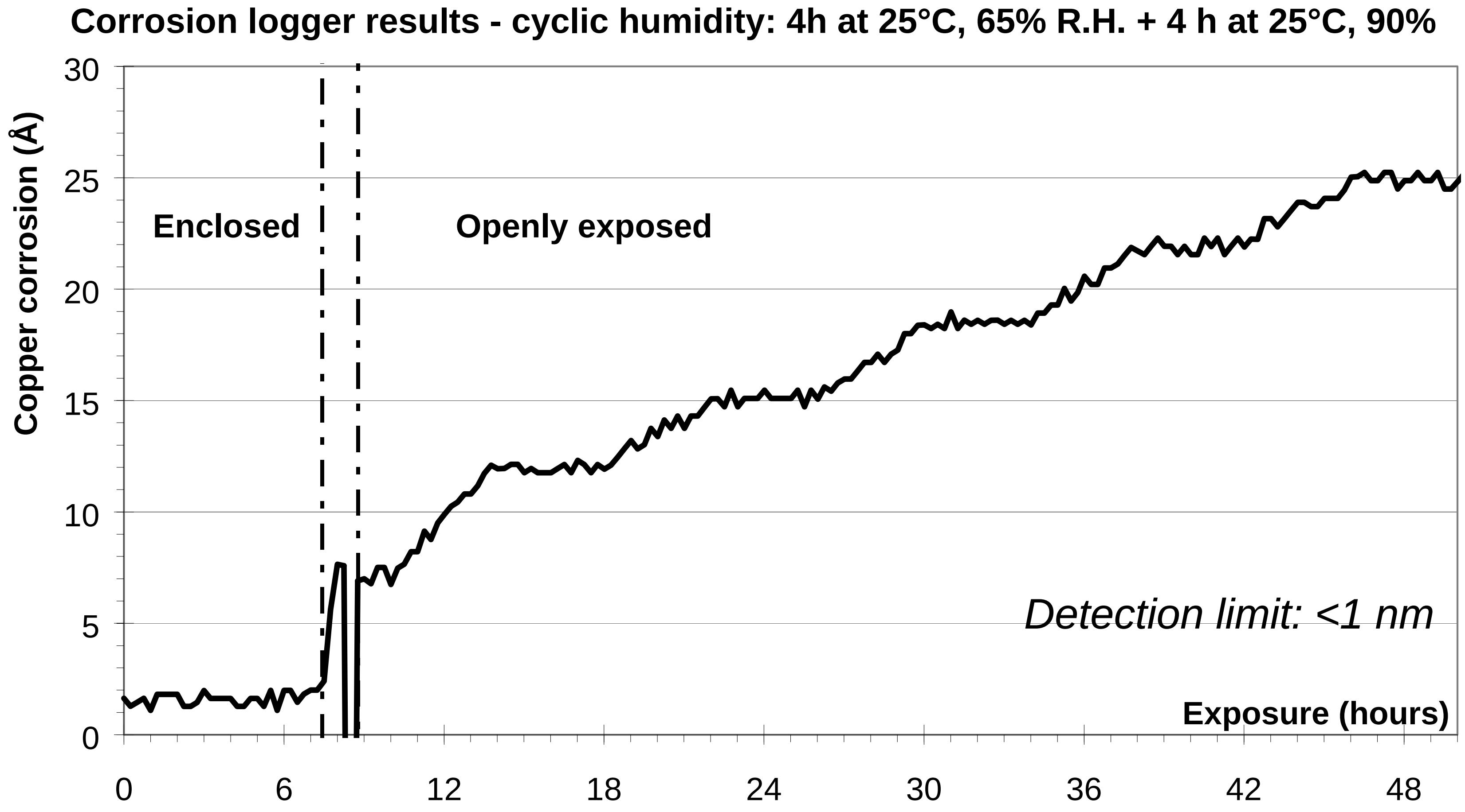
CD = 1190 ± 30 nm

Coupons:
CD = 725 ± 33 nm

Detection limit: 100 nm

Metal sensors – Corrosion tests

- Copper sensor, PVD technique, 0.5 µm



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Metal sensors – Conclusions

- Uniform metal distribution
- **Acceptable reproducibility** of measurement of the corrosion rate; better for sensors produced with printed board technique than electrodeposited
- **Good correlation of the corrosion rate** measured with sensors and metal coupons (somewhat higher corrosion rate is acceptable)
- The same composition of corrosion products
- **Uniform corrosion**
- Good adherence of sensing track to substrate
- **High enough sensitivity for real time monitoring**
- **Continuous monitoring** is important for high reliability of the measurement

Metal sensors

Metal	*Application*	*Thickness*	*Method*	*Substrate*	*Status*
Zinc	Indoor	5 µm	ED	ABS	for testing
Zinc	Outdoor	20 µm	ED	ABS	for testing
Zinc	Indoor	2.5 µm	PCB	Glass-fiber	under development
Zinc	Outdoor	25 µm	PCB	Glass-fiber	for testing
Iron	Indoor	25 µm	PCB	Glass-fiber	for testing
Iron	Outdoor	100 µm	PCB	Glass-fiber	under development
Nickel	Indoor	2 µm	ED	ABS	final
Copper	Indoor	1 µm	ED	ABS	final
Copper	Outdoor	5 µm	PCB	Glass-fiber	for testing
Silver	Indoor	1 µm	ED	ABS	under development

Corrosion rate logger – Characteristics

- Electrical resistance measurement at high sensitivity with the accuracy of <0.1 %
- Size 98 x 64 x 38 mm, weight up to 100 g
- Non-contact inductive reading
- LED signaling trespassing corrosion depth threshold
- Full autonomy up to 3 years
- Exchangeable battery
- Exchangeable sensors (waterproof connector)
- Optional GPRS reading

End-users testing

Objectives:

- Verification of reliability and application limits in conditions of real applications
- Improvement of user-friendliness of the products

→ Feedback for the final stage of logger development

Selection of partners
↓
Tailor-made test plans
↓
Presentation of the technique
↓
Exposure & monitoring
↓
Data processing, feedback

- Museum of Louvre, Paris
- Prague Castle
- Jewish Museum of Prague
- National Museum of Denmark
- …

Start: Beginning of 2007

Conclusions

- Monitoring of the air quality using metal sensors is the most appropriate for protection of metal objects
- Small, battery driven device was developed for continuous measuring of the corrosion rate of metal sensors
- Electrical resistance technique is suitable for real time monitoring
- Non-contact data reading, optional GPRS access
- Silver, copper, nickel, iron, and zinc sensors are under development
- Corrosion behavior correlates well to that of traditional metal coupons
- Sensitivity of measurement: ~1 nm
- Availability: 2007

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