

Panel Discussion on Water Monitoring for Combined Cycle Plants

THORNTON
Leading Pure Water Analytics



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METTLER TOLEDO Thornton
Billerica, MA USA

METTLER TOLEDO

THORNTON – Leading Pure Water Analytics



- 1964 Dr. Richard Thornton, an MIT professor, founded Thornton Associates near Boston in USA.
- 2001 Acquired by METTLER TOLEDO and integrated into Process Analytics Division

- Developed first resistivity / conductivity instrumentation for ultrapure water treatment in the semiconductor industry.
- Technology leader actively engaged in international organizations such as EPRI, VGB, ASTM, ASME
- Known as a leading supplier of resistivity/conductivity and TOC instrumentation plus sodium, silica, dissolved oxygen, ozone, pH/ORP and flow for pure and ultrapure water treatment.

Industry Participation



METTLER TOLEDO Thornton personnel actively participate in many power industry organizations:

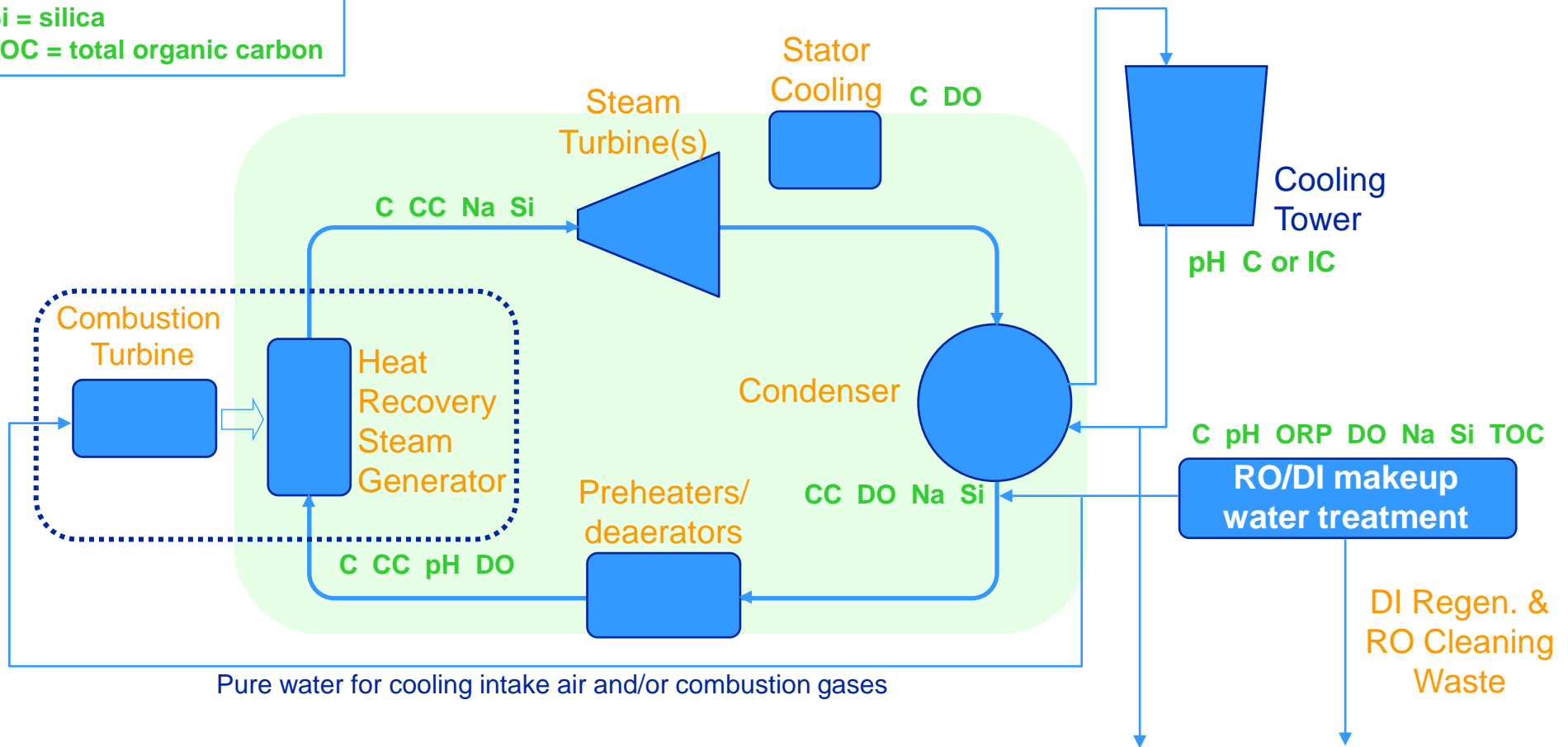
- Chairing task groups on the ASTM D19 Water Committee
- Presenting at industry conferences
 - EPRI conferences (Electric Power Research Institute)
 - VGB conferences (Germany)
 - Eskom conferences (South Africa)
 - Electric Utility Chemistry Workshops (University of Illinois, USA)
 - Southwest Chemistry Workshops (Western USA)
 - IWC (International Water Conference)
- Publishing technical papers
 - *PowerPlant Chemistry*
 - *Ultrapure Water Journal*
- Participating in IAPWS (International Association for the Properties of Water and Steam)
- Reviewing standards for TPRI (Thermal Power Research Institute, China)
- Contributing to ASME Performance Test Code



Combined Cycle On-Line Measurements



C = specific conductivity
CC = cation conductivity
DO = dissolved oxygen
ORP = redox
pH = pH
Na = sodium
Si = silica
TOC = total organic carbon



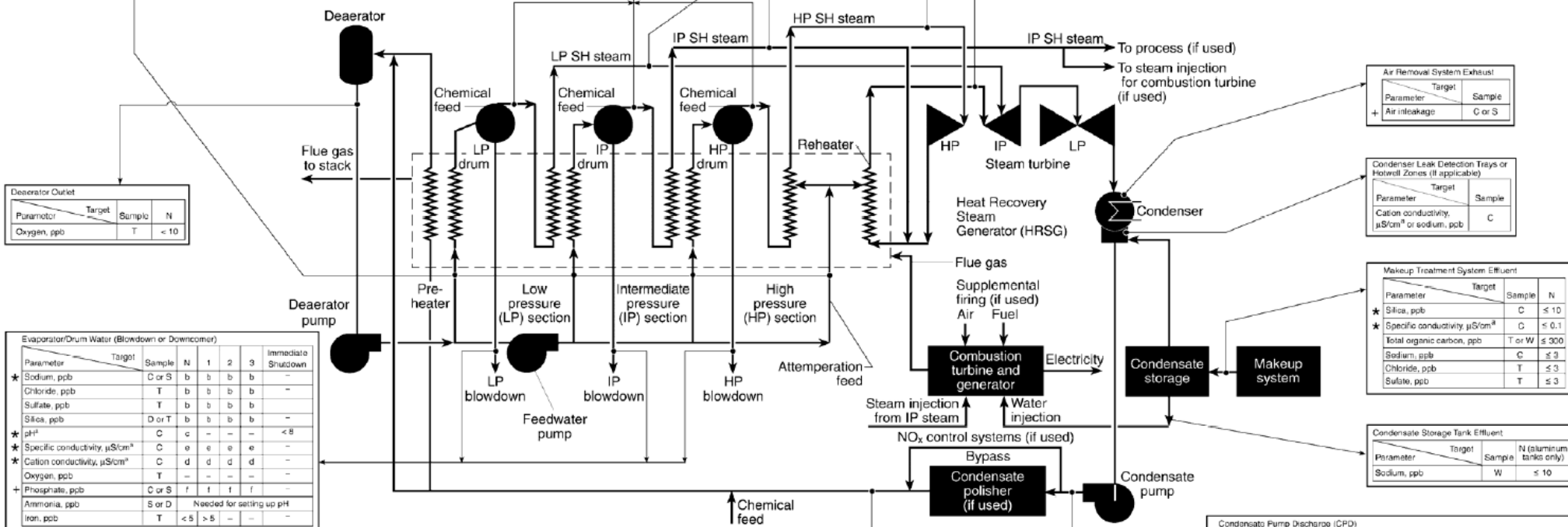
Drum HRSG on Phosphate Treatment



Parameter	Target	Sample	N	1	2	3
* Cation conductivity, $\mu\text{S}/\text{cm}^2$	C	≤ 0.2	≤ 0.4	≤ 0.8	> 0.8	
pH ^a	C	9.2-9.6	< 9.2	> 9.6		
Ammonia, ppb	D or T	Consistent with pH				
Specific conductivity, $\mu\text{S}/\text{cm}^3$	C					
Copper, ppb	T	≤ 2	> 2			
Iron, ppb	T	≤ 2	> 2			
* Sodium, ppb	C	≤ 3	≤ 6	≤ 12	> 12	
* Oxygen, ppb	C	1-10	≤ 15	≤ 20	> 20	

Parameter	Target	Sample
Sodium, ppb	T	
Silica, ppb	D or T	
+ Carryover	T	

Parameter	Target	Sample	N	1	2	3
* Sodium, ppb	C	≤ 2	≤ 4	≤ 8	> 8	
* Cation conductivity, $\mu\text{S}/\text{cm}^3$	C	≤ 0.2	≤ 0.4	≤ 0.8	> 0.8	
Silica, ppb	D or T	≤ 10	≤ 20	≤ 40	> 40	
Chloride, ppb	T	≤ 2	≤ 4	≤ 8	> 8	
Sulfate, ppb	T	≤ 2	≤ 4	≤ 8	> 8	
Total organic carbon, ppb	I	≤ 100	> 100			
Specific conductivity, $\mu\text{S}/\text{cm}^3$	T					



Parameter	Target	Sample	N
Oxygen, ppb	T		< 10

Parameter	Target	Sample	N	1	2	3	Immediate Shutdown	
* Sodium, ppb	C or S	b	b	b	b			
Chloride, ppb	T	b	b	b	b			
Sulfate, ppb	T	b	b	b	b			
Silica, ppb	D or T	b	b	b	b			
pH ^a	C	c				< 8		
* Specific conductivity, $\mu\text{S}/\text{cm}^3$	C	e	e	e	e			
* Cation conductivity, $\mu\text{S}/\text{cm}^3$	C	d	d	d	d			
Oxygen, ppb	T							
+ Phosphate, ppb	C or S	f	f	f	f			
Ammonia, ppb	S or D	Needed for setting up pH						
Iron, ppb	T	< 5	> 5					

Targets	Cumulative Hours per Year	
	Base Load	Cycling
N (Normal)		
1 (Action Level 1)	330 (2 weeks)	672 (4 weeks)
2 (Action Level 2)	48 (2 days)	96 (4 days)
3 (Action Level 3)	8	16
Immediate Shutdown	1	2

Sample Frequency	Target Values
C = continuous	N = Normal
S = grab, once per shift	1 = Action Level 1
D = grab, once per day	2 = Action Level 2
W = grab, weekly	3 = Action Level 3
T = troubleshooting and commissioning	

a = Conductivity and pH measured at 25° C
b = See curves of maximum allowable concentration versus pressure
c = Must be determined
d = See curves of allowable cation conductivity vs pressure
e = See curves of allowable specific conductivity vs pressure
f = See curves of allowable phosphate vs pressure

* = "Core" parameter alarmed in control room
▶ = Continuous samples
◀ = Chemical feed
+ = "Core parameter"

Parameter	Target	Sample	N	1	2	3
* Sodium, ppb	C	< 3	< 6	< 12	> 12	
* Cation conductivity, $\mu\text{S}/\text{cm}^3$	C	≤ 0.2	> 0.2			
Silica, ppb	C	≤ 10	> 10			

Parameter	Target	Sample	N	1	2	3
* Cation conductivity, $\mu\text{S}/\text{cm}^3$	Plants with polisher Plants without polisher	C	≤ 0.3	> 0.3		
* Oxygen, ppb (switchable with EI)		C	≤ 10	≤ 20	> 20	
Sodium, ppb	Plants with polisher Plants without polisher	C	≤ 6	> 6		
Chloride, ppb		C	≤ 3	≤ 6	≤ 12	> 12
Sulfate, ppb		T	≤ 200	> 200		

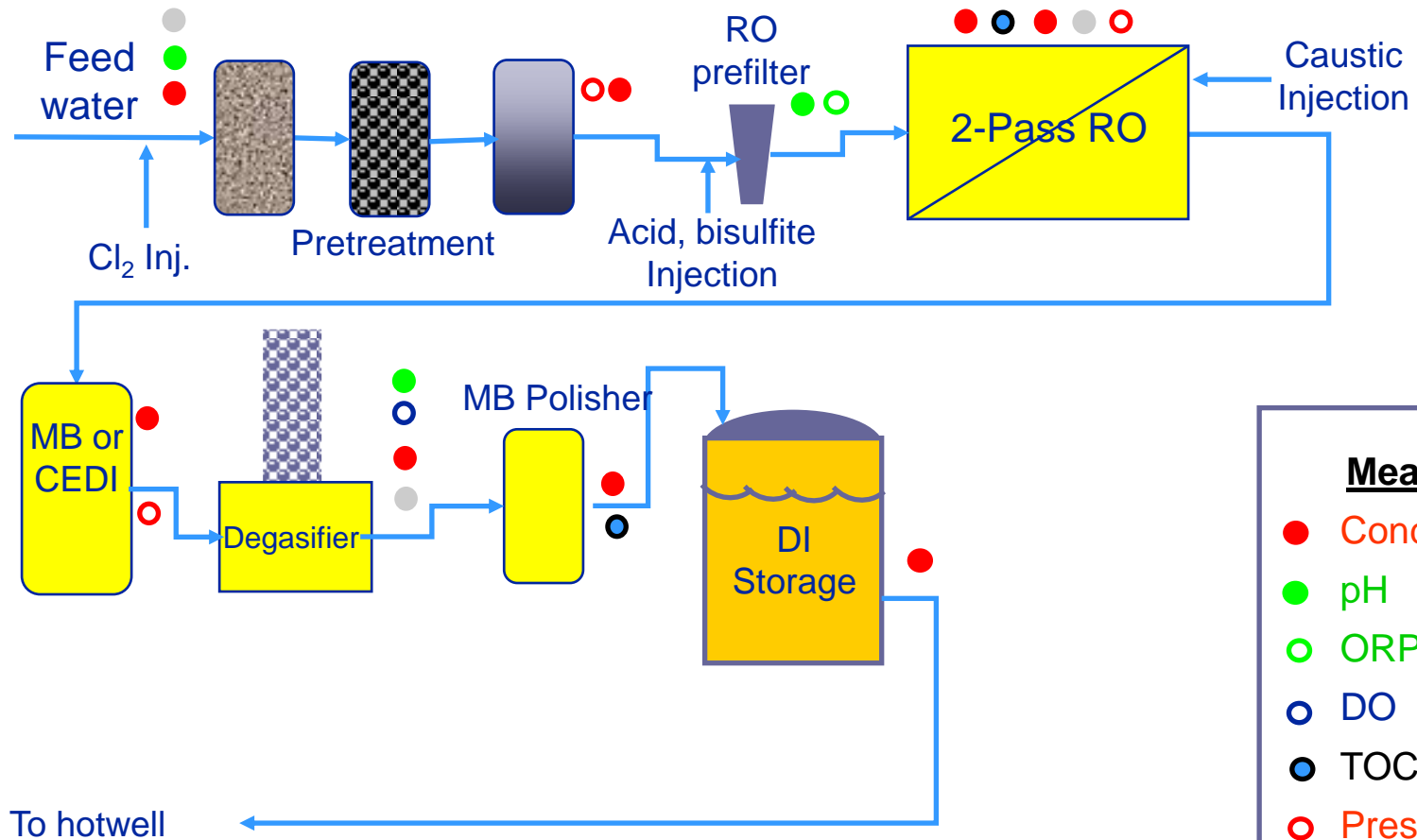
Cycle Chemistry Monitoring



Cogeneration Monitoring Condensate Return



Make-up Water Treatment



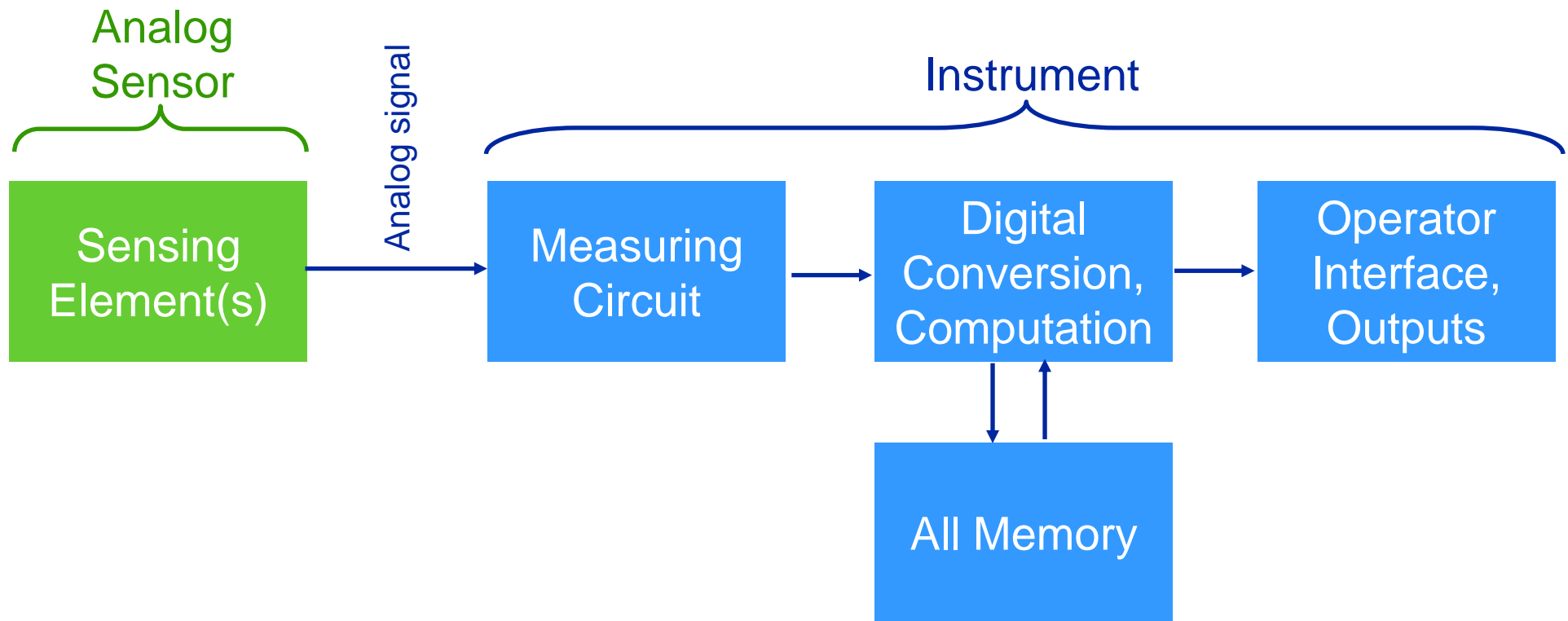
<u>Measurements</u>	
●	Conductivity
●	pH
○	ORP
○	DO
●	TOC
○	Pressure
●	Flow

Makeup Water Treatment



Zero Discharge Plant - CA

Measurement Functions—Traditional Sensor

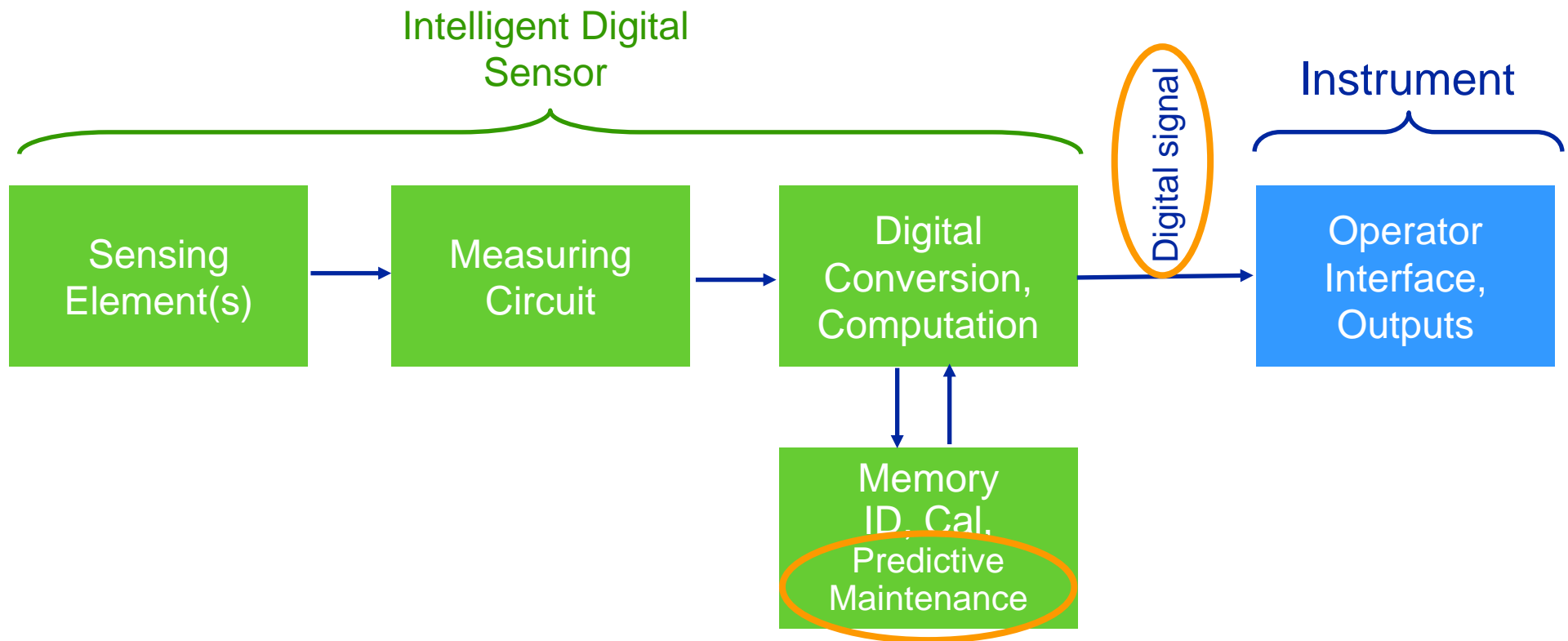


Measurement Functions—Digital Sensor



Intelligent Sensor Management

ISM[®]



Leading performance and diagnostics are achieved by locating more signal handling and intelligence within the sensor

Intelligent Digital Sensors



- What is Intelligent Sensor Management®?
 - Digital sensors with ISM store their identification, calibration and diagnostic data in integral memory
 - Sensors with ISM include on-board measurement and analog to digital signal conversion circuitry
- What does ISM do for the user?
 - Provides Plug & Measure simplicity
 - Improves accuracy with “system” calibration—the sensing element cannot be separated from the measuring circuit or stored calibration data
 - Eliminates signal transmission errors
 - Eliminates operator error
 - Enables remote calibration in the lab
 - Simplifies wiring
 - Enables enhanced, predictive diagnostics
 - Reduces maintenance and spare parts



Dissolved oxygen / Conductivity / pH/ORP

Sodium



- 2300Na Specifically for power applications
 - Makeup water deionization monitoring—cation resin
 - Cycle chemistry—feedwater, steam and condensate
- High performance capabilities
 - Automatic, unattended calibration for operator time savings
 - Optimum DIPA reagent for lowest level detection
 - pH check on reagent delivery for reliability
 - Convenient grab sample measurement
 - Analog outputs (0/4-20 mA) for sodium, adjusted pH, sample temperature for complete data acquisition
 - Choice of protective enclosures to meet installation requirements
 - Range: 0.001 to 100,000 ppb





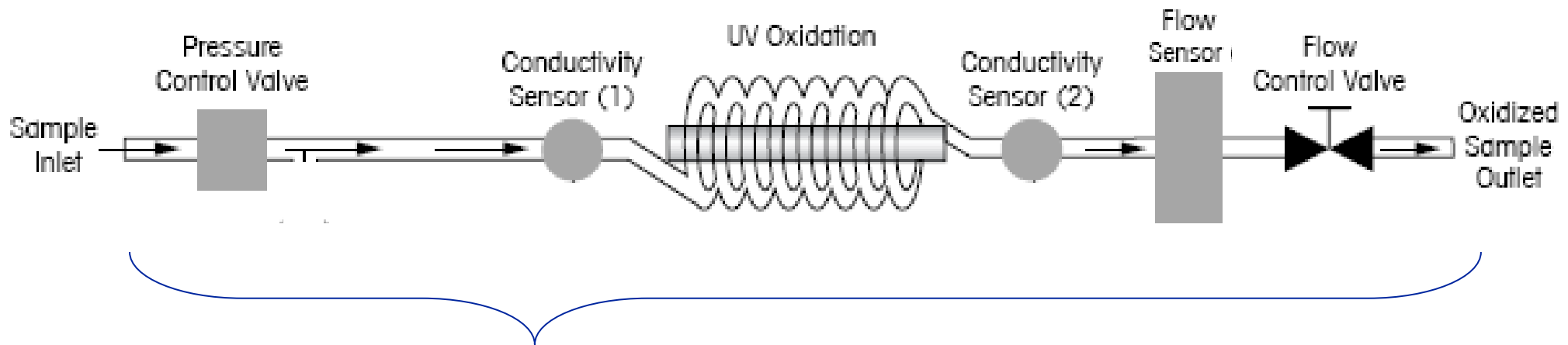
- Specifically for power applications
 - Makeup water deionization monitoring—**anion resin**
 - Cycle chemistry—**feedwater, steam and condensate**
- The 2800Si Silica Analyzer provides
 - Automatic zero calibration with each measurement
 - Automatic, unattended span calibration
 - User configurable measurement time and calibration interval to optimize operation
 - Reaction chamber temperature monitoring for reliable measurement
 - Large reagent capacity for long maintenance interval
 - High sensitivity
 - Convenient grab sample measurement
 - Protective, lockable enclosure
 - Range 0-2,000 ppb



Total Organic Carbon



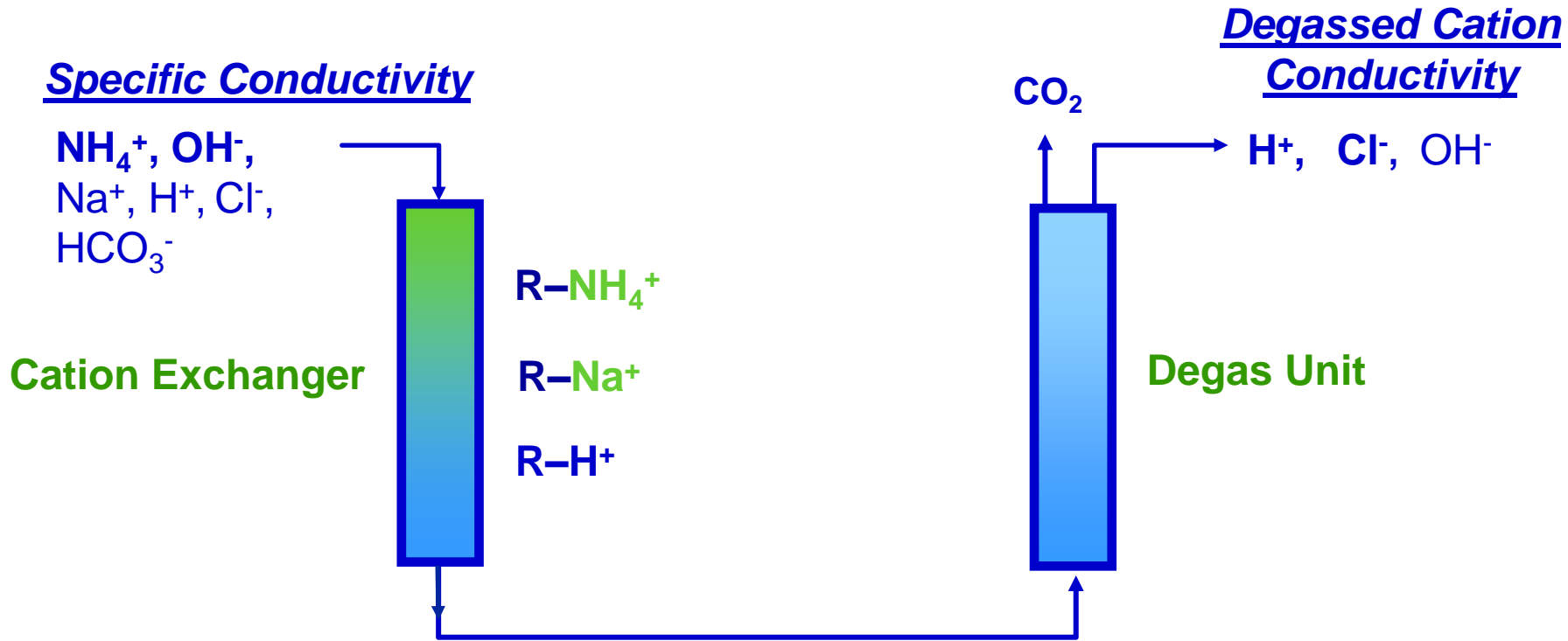
- Detects organics in makeup water treatment to prevent fouling of anion exchange resin
- In cogeneration processes, detects organic contamination of condensate return from the process



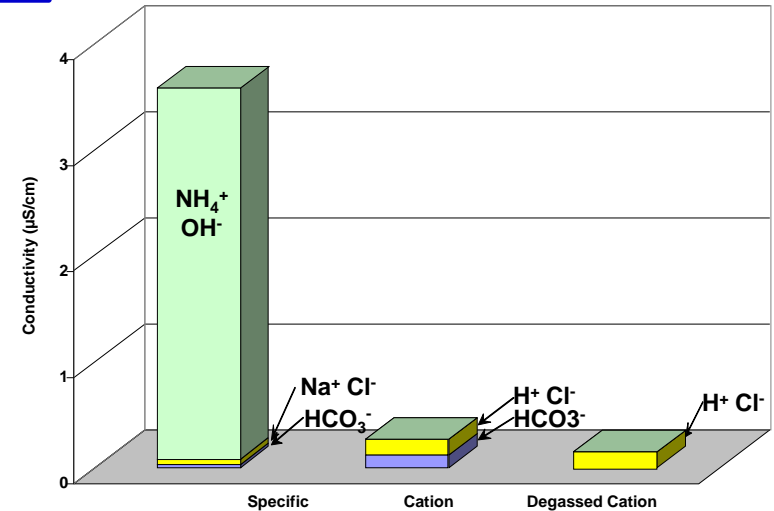
Backup slides for possible questions



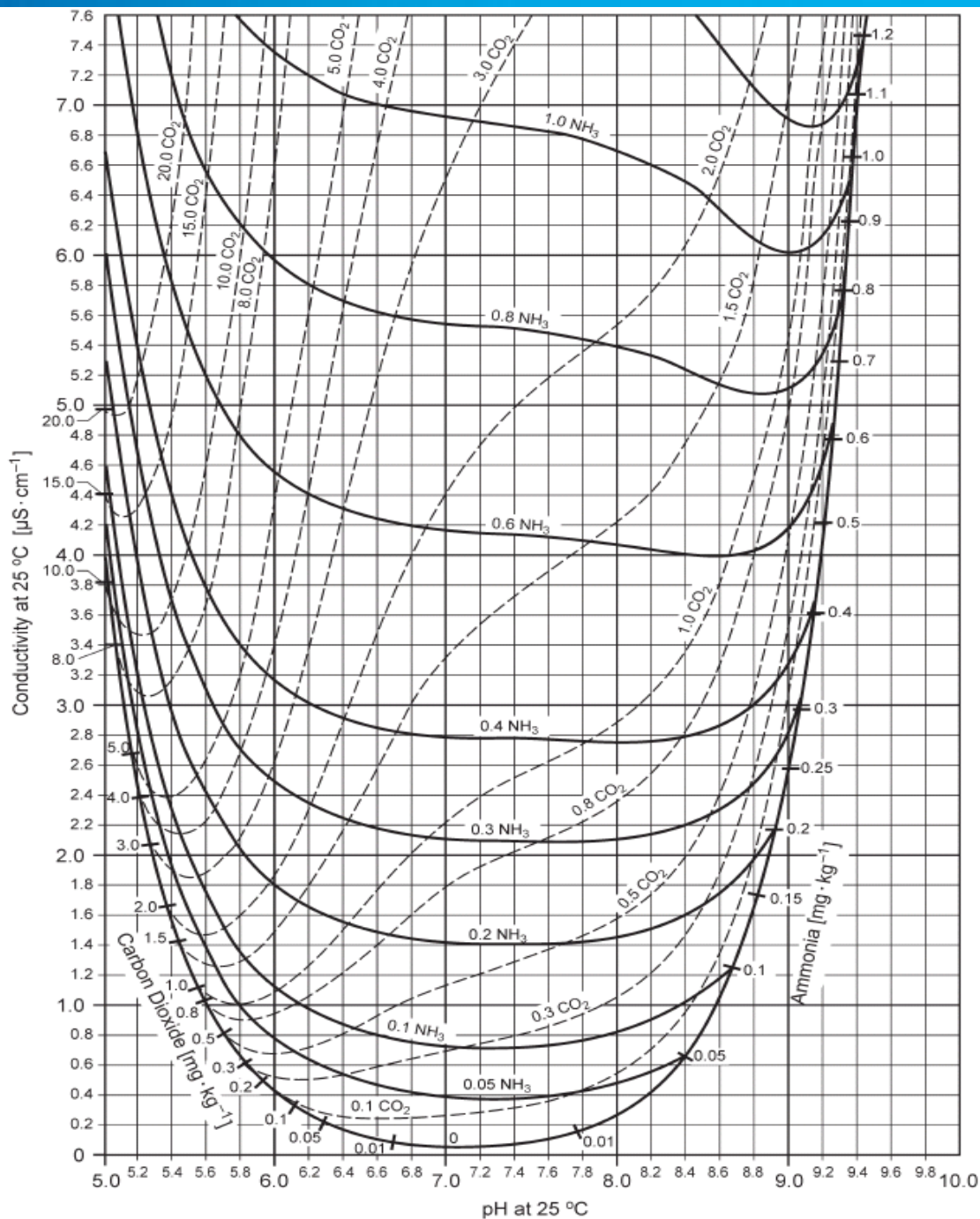
Specific, Cation, Degassed Conductivity



Cation Conductivity
 H^+ , Cl^- , CO_2 , HCO_3^- , OH^-



Conductivity vs. pH of CO₂ & NH₃



Calculated pH from Conductivity



Specific conductivity at 25°C →

- Represents ammonia/amines (ppm)
- Dominates the calculation

Cation conductivity at 25°C →

- Represents salts and acids (ppb) e.g. chlorides, sulfates, bicarbonates, formates, acetates
- Trims the calculation

Calculated pH at 25°C

(Similar to Siemens-Westinghouse, VGB, EPRI, ASME algorithms and software)

Requirements for calculating pH

- pH > 7.5
- Specific Conductivity >> Cation Conductivity
- No phosphates

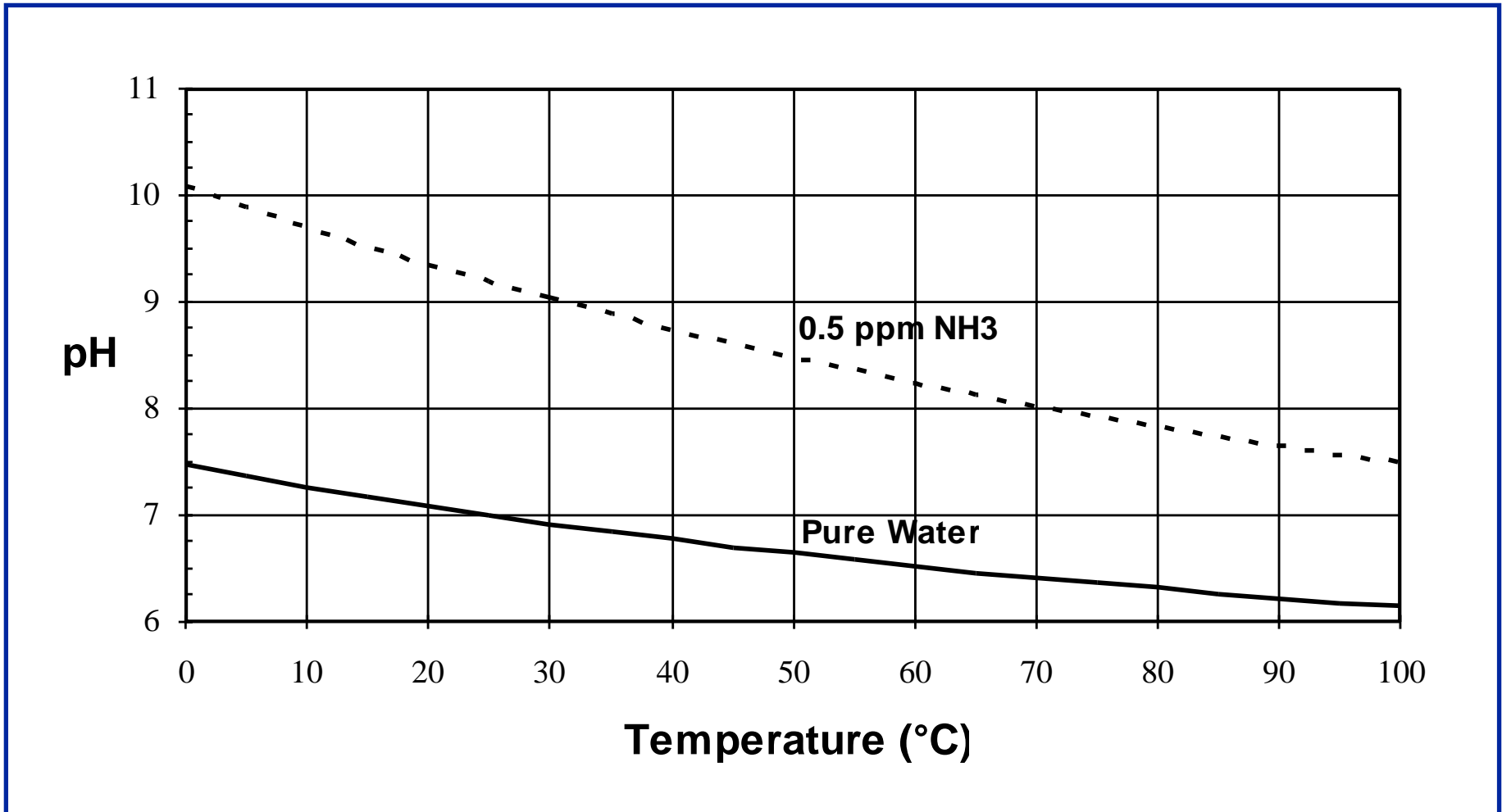
Calculated pH from Conductivity



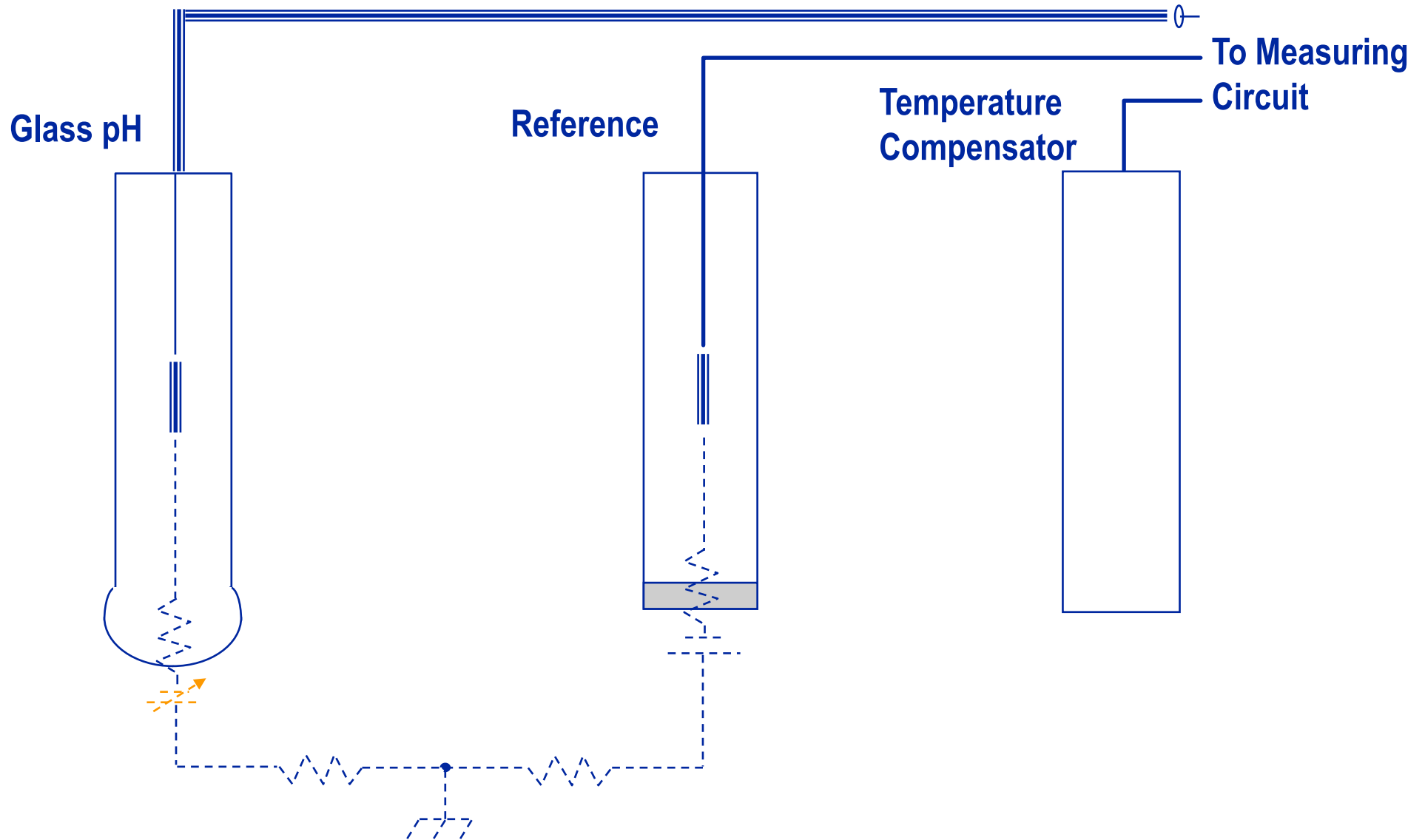
- Four channel transmitter offers unique advantages
- Simultaneous display of:
 - Specific conductivity
 - Cation conductivity
 - Calculated pH
 - Electrode pH—for backup if conditions go outside calculation parameters
 - Dissolved Oxygen
 - Sample temperature
- Alarm on the difference between calculated pH and electrode pH



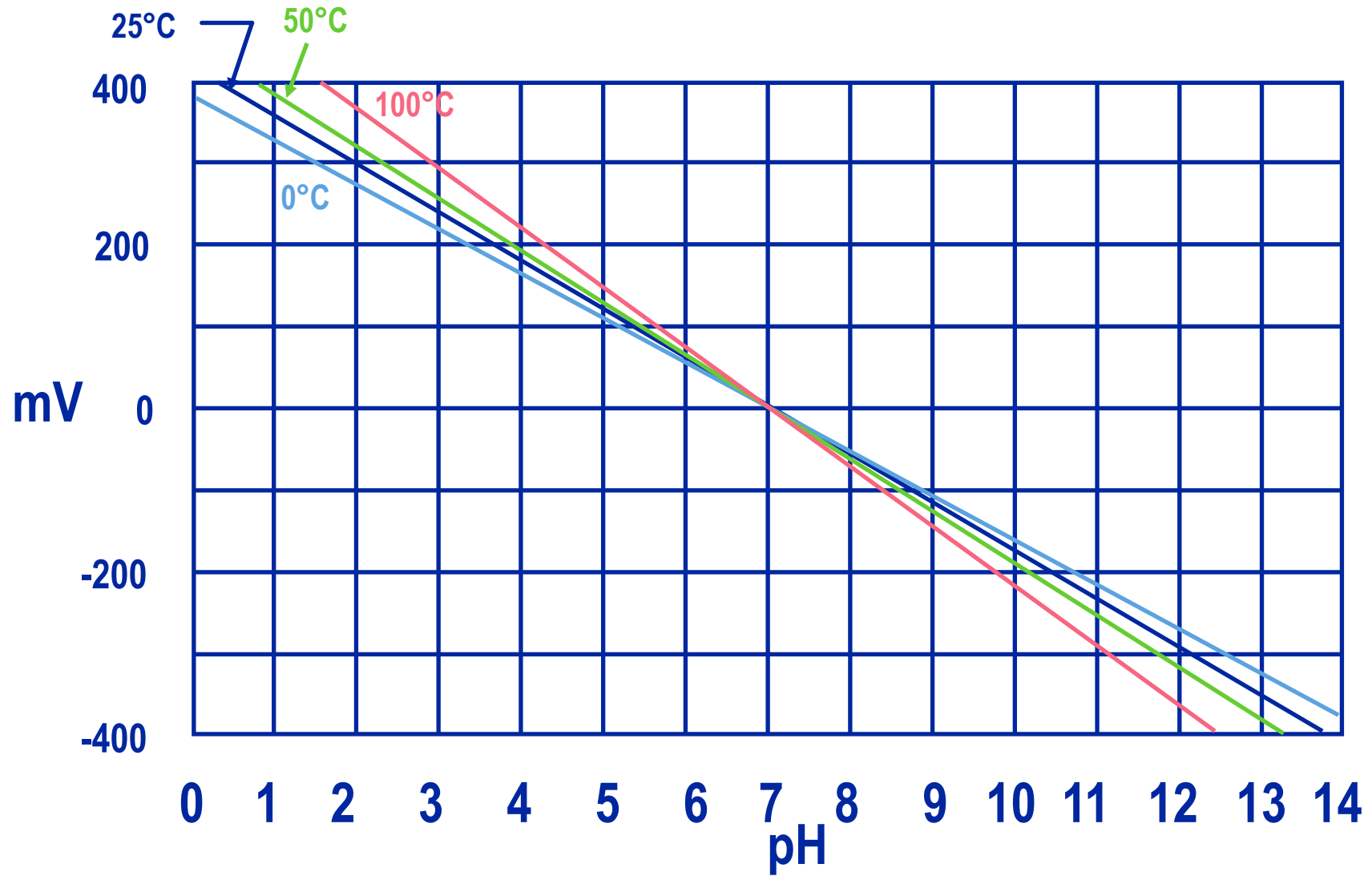
pH vs. Temperature for Pure Waters



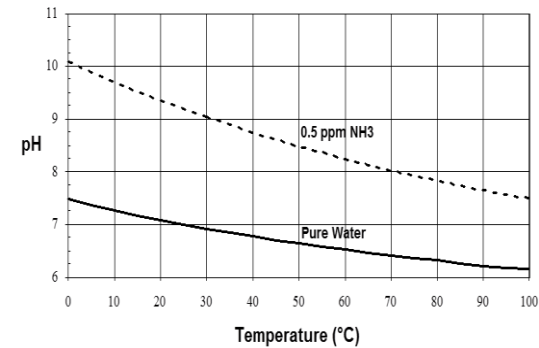
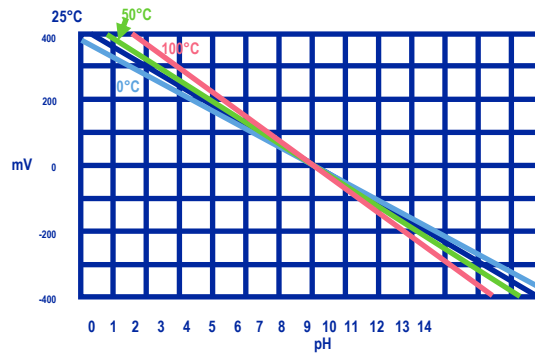
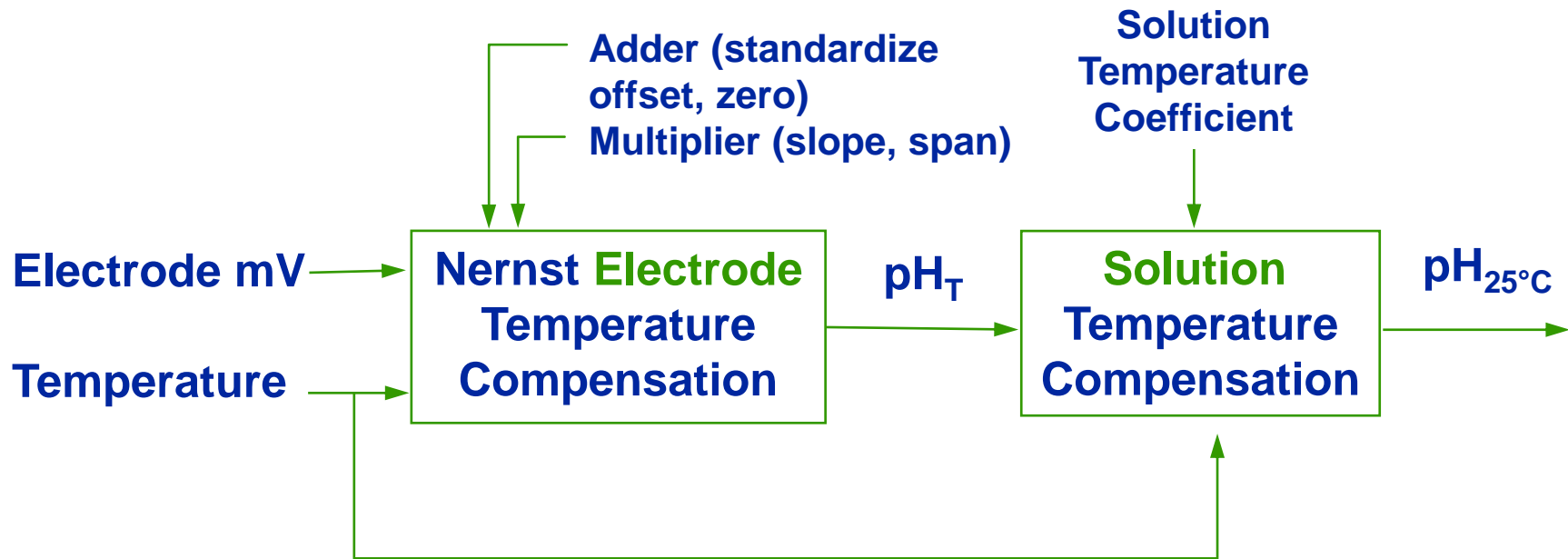
pH Electrode System



pH Electrode Output Signal



pH Temperature Compensation

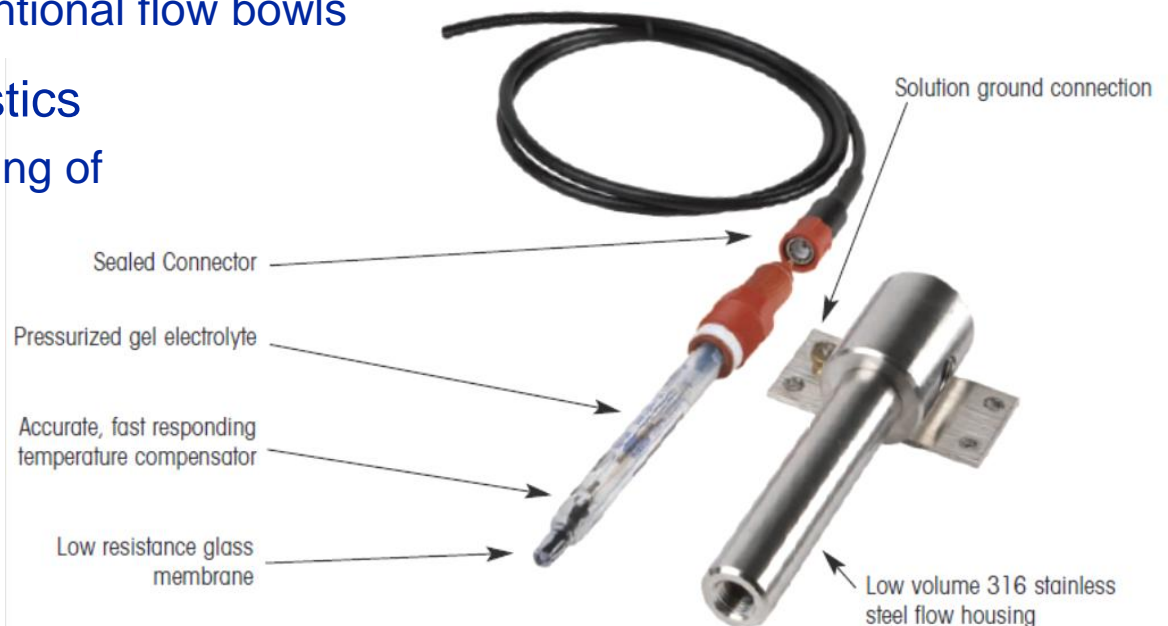




■ pH and ORP measurement with ISM

- Improves signal integrity
 - ▶ High impedance signal is completely encapsulated
 - ▶ Digital conversion provides a robust signal
- Enables pH and ORP measurement from a single sensor
- Improves response
 - ▶ The Thornton pHure Sensor™ flow housing maintains high flow velocity, pushing corrosion particles to the drain instead of letting them settle as in conventional flow bowls
- Improves sensor diagnostics
 - ▶ Enabled by close coupling of measuring circuit
 - ▶ Increased reliability

ISM®



Intelligent Liquid Electrolyte High Purity pH Sensor



Liquid electrolyte reference system
maximizes calibration accuracy

Integrated measuring circuit, memory &
digital signal conversion

Accessible electrolyte fill port

Visible liquid electrolyte level

Protective cover

Buffer solution containers

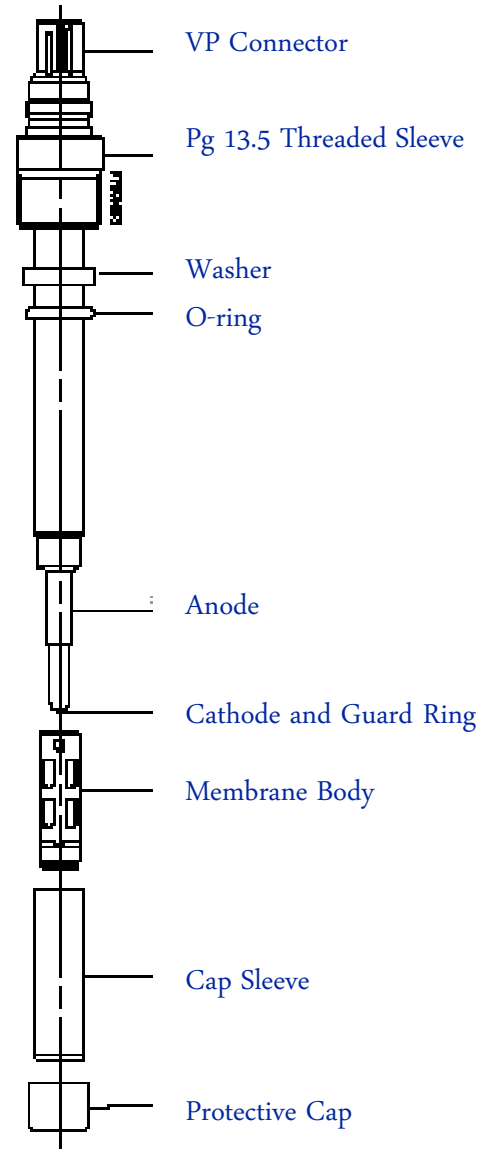
Low-volume housing prevents particles
and sludge from accumulating and
slowing response

Most other sensors require 3 electrodes
in a flow bowl for this measurement

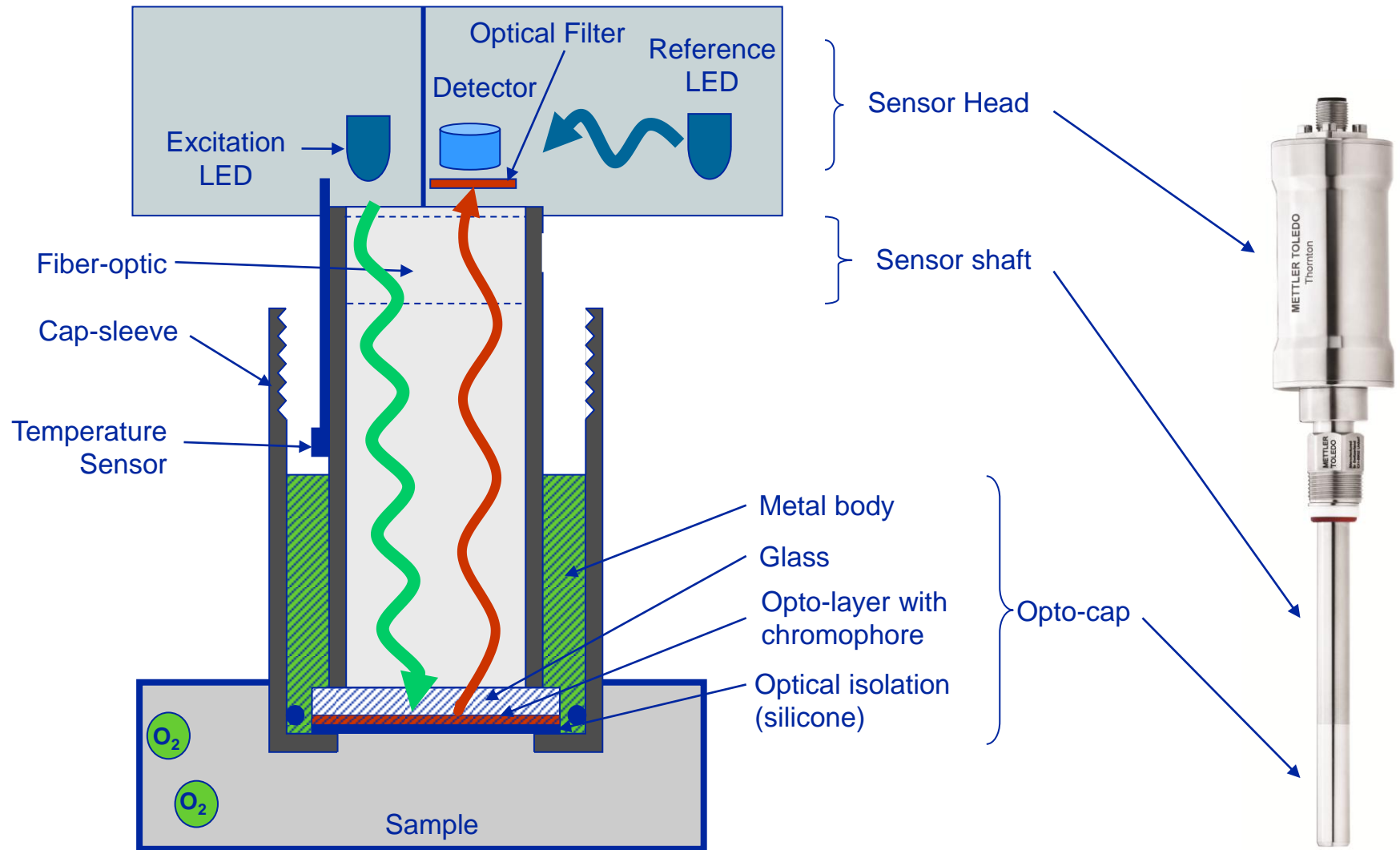


- Measuring electrode
- Reference electrode
- Temp. compensator
- ORP electrode/
Solution ground

High Performance DO Sensor Components



Optical DO Measurement



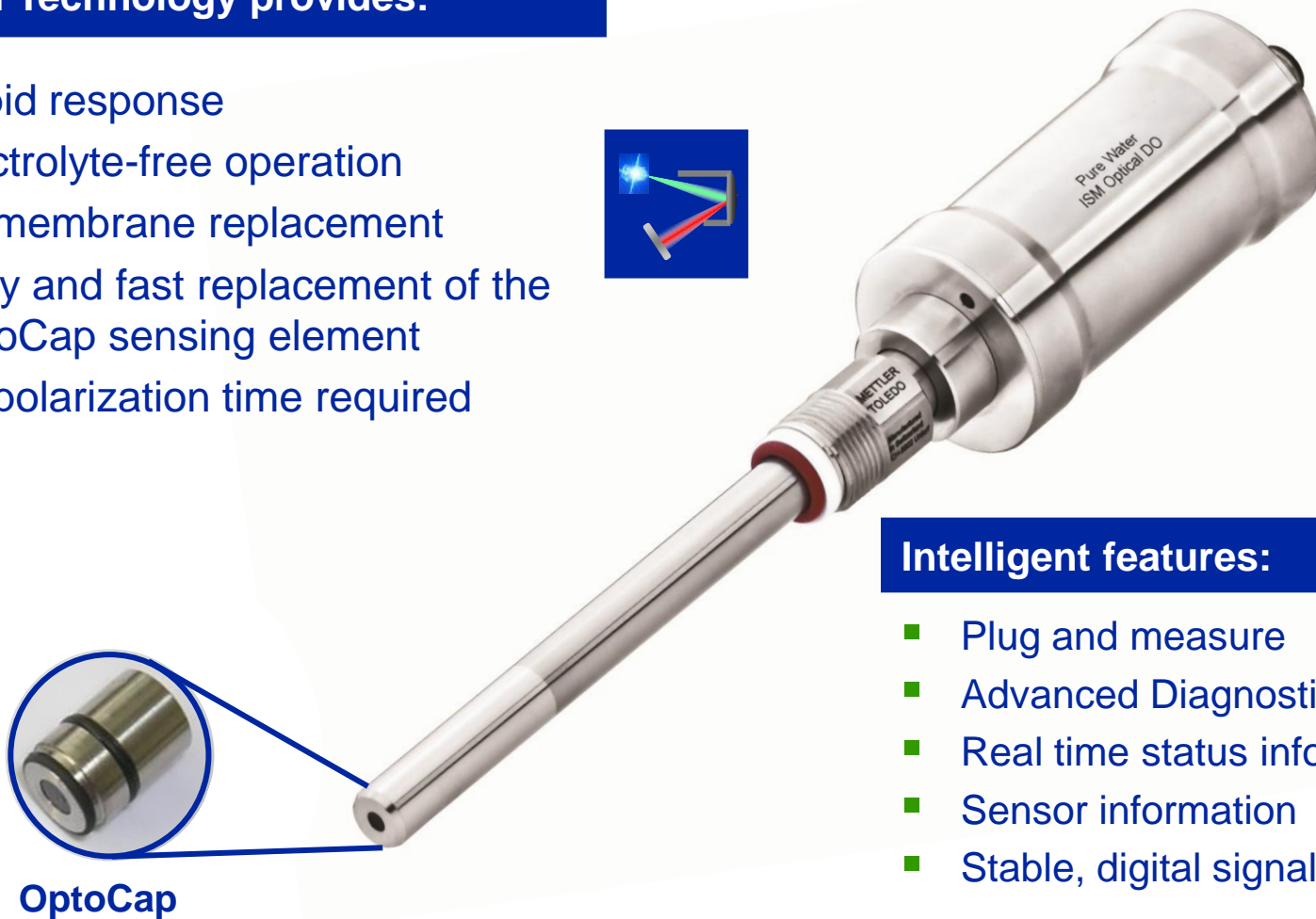
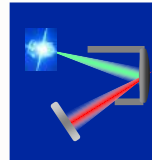
The presence of oxygen “quenches” the fluorescence → smaller light intensity and shorter duration

Optical DO Measurement



Optical Technology provides:

- Rapid response
- Electrolyte-free operation
- No membrane replacement
- Easy and fast replacement of the OptoCap sensing element
- No polarization time required



Intelligent features:

- Plug and measure
- Advanced Diagnostics
- Real time status information
- Sensor information
- Stable, digital signal

Optical technology offers faster measurement response and less downtime for maintenance

Optical vs. Polarographic Technology



Optical technology

- Fast response time
- Innovative technology
- Electrolyte-free
- Easy to maintain
- Extended maintenance intervals
- No polarization time
- No flow required
- No hydrogen interference – suitable for stator cooling



Amperometric technology

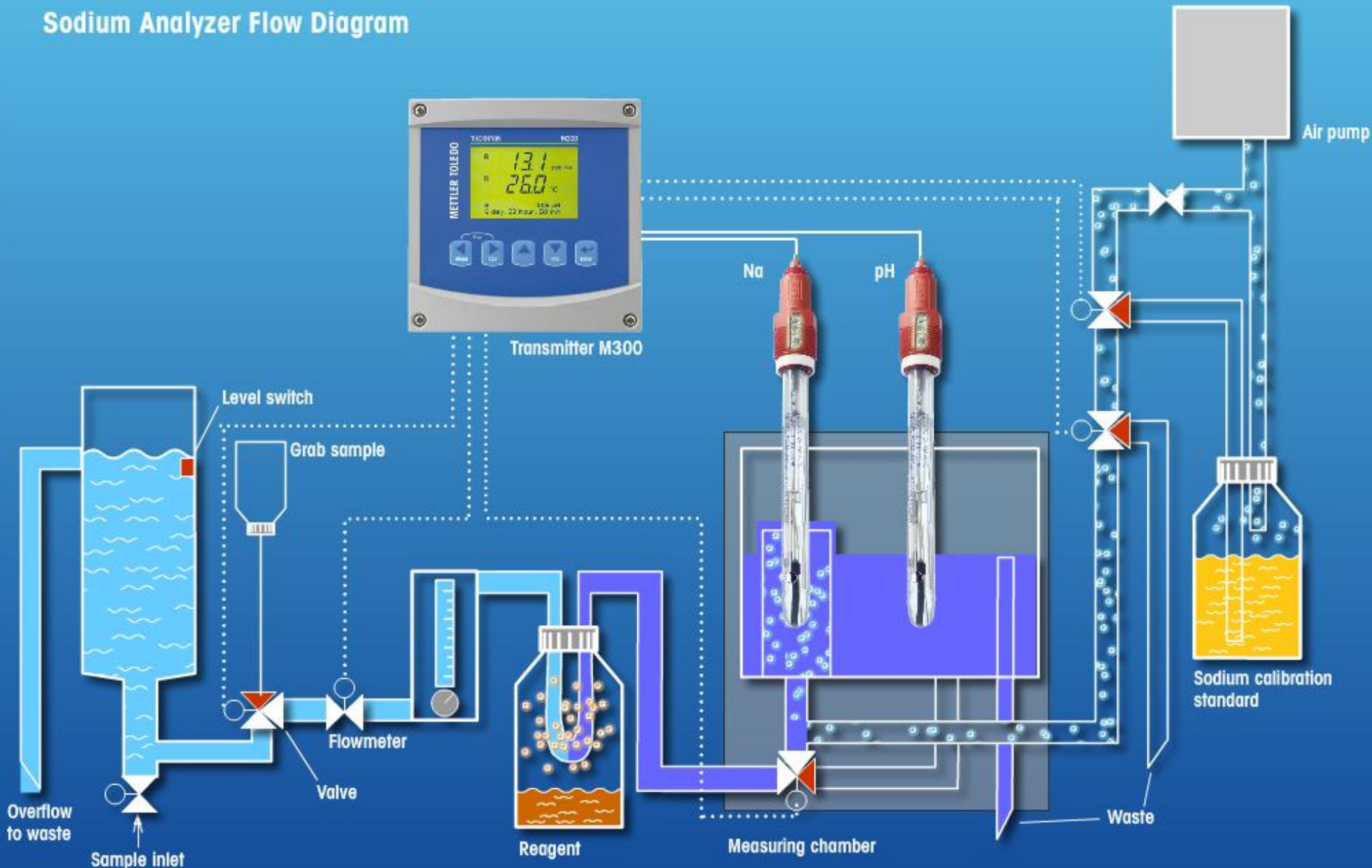
- Proven, reliable technology
- Rugged system
- Measurement to lowest concentrations
- Broad application coverage
- Susceptible to hydrogen interference

Optical DO measurement is an attractive alternative to traditional sensing with added value of faster response and reduced service

Sodium Analyzer



Sodium Analyzer Flow Diagram



2800Si Silica



Silica Analyzer Flow Diagram

