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APLICAÇÕES EM FABRICAS DE CLORO







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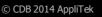
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O2 em H2-Segurança do Processo O2 em Cl2-Qualidade do Produto Analisador a laser



- Resposta Rapida- <2 Segundos
- Estável- Calibração Anual
- Resistente- Sem contato com amostra
- In Situ Sem contato com amostra
- Pouca manutenção





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H2 em Cl2-Qualidade do Produto



2500 HCI + Conversor UV

- H2 + C12 = 2HC1, 2HC1/2 = H2
- Estável- interferençia cruzada =0
- Resistente-Ø contato com amostracelula de Hastelloy
- Resposta Rapida-Melhor do que com TC (termocondutividade)

Nova Solução





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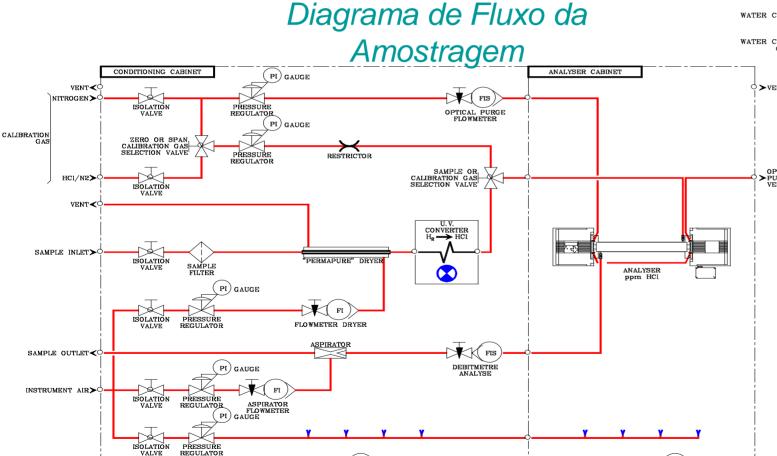
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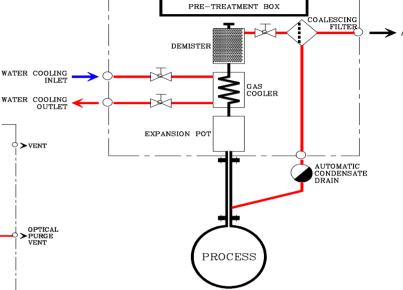
Solução

H2 em Cl2-Qualidade do Produto

TS

TS





Ponto de Amostragem

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H20 em Cl2-Qualidade do Produto

Nova Tecnología



- Resposta Rapida-<2 Segundos
- Estável-Calibração Anual
- Resistente- Sem contato com amostra
- Sistema não extrativo-IN SITU
- SEM SISTEMA DE AMOSTRAGEM
 - Baixo limite de deteção-0.03ppm

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Solução H2O em Cl2-Qualidade do Produto ENCL. ENVIRONM. PURGE VENT FICV1 SAMPLE SET ~ 6L/m CL2 WIRING SEE DWG ASWD-2413 (50% SCALE) VENT HEADER US10125SYS02 US0105-3510A-1 PRESSURE REDUCTION STATION FICV3 SET ~ I FICV2 SET ~ |-CUSTOMER PROCESS SEE TABLE C-351A VENT PR SET ~ 15 PSIG VENT SPAN FROM PERMEATION MOISTURE GAS GENERATOR US10125SYS02 US0105-3510A-2 PRESSURE REDUCTION STATION CUSTOMER PROCESS SEE TABLE C-351B VENT X 8 E ZERO GAS IN AT 30 PSIG SAMPLE PROBE & TRANSPORT TUBING BY OTHERS US10125SYS02 US0105-3510A-3 PRESSURE REDUCTION STATION CUSTOMER PROCESS SEE TABLE RELIEF VENT C-351C VENT SAMPLE TRANSPORT TUBING BY OTHERS ELECTRICAL CONNECTIONS (DIRECT BY OTHERS) FICV4 INSTRUMENT AIR IN AT 80-100PSIG ~ 100 SCFH SET ~ 100 SCFH JB1 PIFR 110-120VA 60Hz POWER NITROGEN IN TRENDS







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HCI- Emissoes no Incinerador



2900

- Resposta Rapida-<2 Segundos
- Estável-Calibração Anual
- In-Situ-Sem Sistema de Amostragem
- Baixa Limite de Deteção-0.05ppm
- Relatorio em Base Seca (CONAMA)-Medição Opcional H2O

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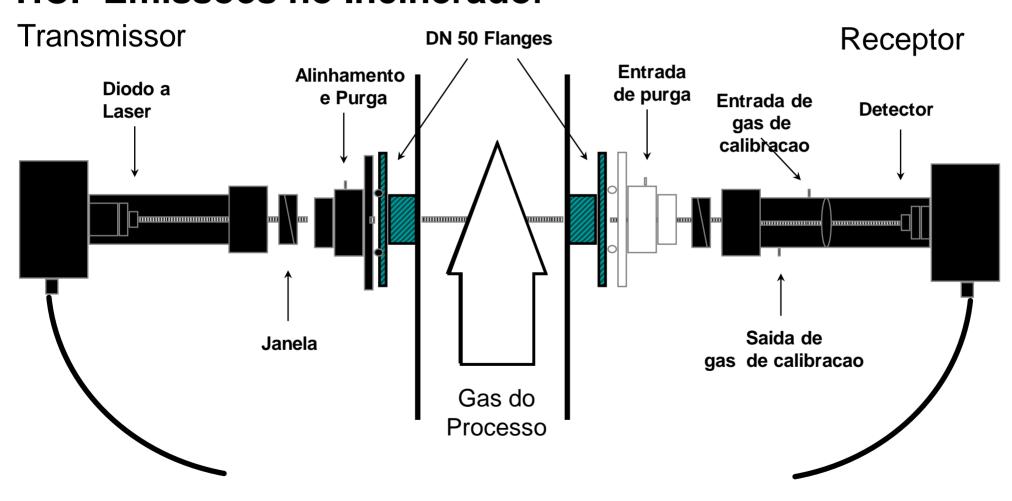
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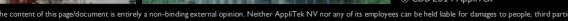
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Instalação

HCI- Emissoes no Incinerador







- •LINHA APPLITEK- analisadores diversos de gases e liquidos
- Analisadores de Oxigenio
- •Analisadores de diversos gases em Processo e CEMS
- Analisadores de umidade (dew point)
- Analisadores de Combustão
- •Detectores fixos e portateis de cloro para proteção da área



RLD chlorine council

Safety Workshop: Process Safety Management (PSM)





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TONI® special (Total Ammonia)

Medição on-line de <u>Total Amonia</u>[amonia (NH₃)+monocloramina (NH₂Cl) + dicloramina (NHCl₂)] em <u>Ultra-Purified brine</u>



- Early Warning
- ⇒ Evita formação de nitrogen trichloride (NCl₃)
- ⇒ Evita Explosão do nitrogen trichloride (NCl₃)

Medição on-line FAST do hidrogenio (H2) em cloro ÚMIDO (Cl2) using Multi Wavelength InfraRed (IR) Technology



- MARNING ⇒ Early Warning
 - ⇒ Avoid hydrogen (H₂) explosion



by: Chris Du Bois



WHY & Quality CONTROL as Chromatography











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by Alternating Pressure Paramagnetic analyzer













ACIDIFICATION

6



WHY & SAFETY CRITICAL

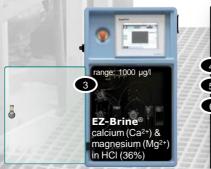
Œ

⇒ PROTECT Plant against hydrogen Explosion

by mu<mark>lti</mark> wavelength **INFRARED**

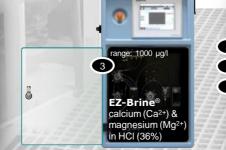
nydrogen (H₂) in DRY chlorine (Cl₂)

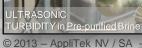




Pre-Purified Brine

SETTLING









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Leading supplier of Safety Critical (Life Saving) on-line hydrogen analyzer systems



"Works good, Looks Good"











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TONI® special (Total Ammonia)

on-line Total Ammonia [ammonia (NH₃) + monochloramine (NH₂Cl) + dichloramine (NHCl₂)] in <u>Ultra-Purified brine</u>



- Early Warning
- ⇒ Prevent formation of nitrogen trichloride (NCl₃)
- ⇒ Avoid nitrogen trichloride (NCl₃) explosion





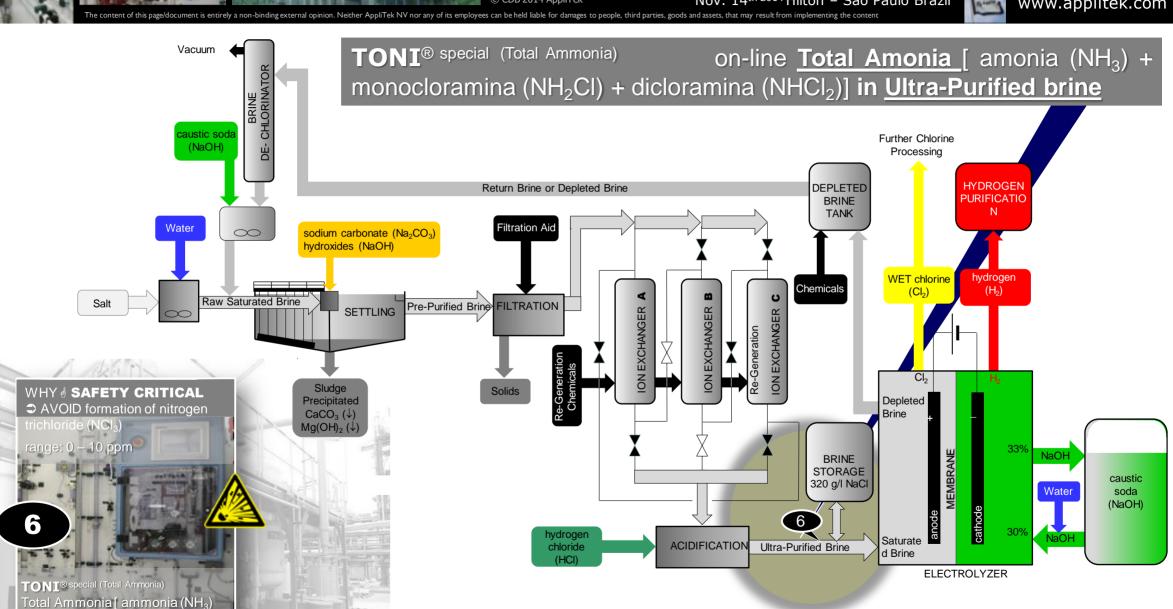


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+ monochloramine (NH2Cl)

+ dichloramine (NHCl₂)]

WHERE?





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TONI^{® special (Total Ammonia)} on-line **Total Ammonia** [ammonia (NH₃) + monochloramine (NH₂Cl) + dichloramine (NHCl₂)] in **Ultra-Purified brine**

WHY? d EARLY WARNING:

Prevent formation of Nitrogen trichloride (NCl₃) | avoid explosion

- ➡ Most Chlorine (Cl₂) is produced by electrolysis of brine generated by dissolving Sodium Chloride (NaCl) or Potassium Chloride (KCl) in water (H₂O). Side reactions with the Nitrogen impurities in the salt can lead to the formation of Nitrogen trichloride (NCl₃) during the Chlorine process.
- ⇒ Nitrogen compounds present in the BRINE are the main source for the formation of Nitrogen trichloride (NCl₃).
- □ In certain parts of the Chlorine production, the Chlorine is either liquefied or evaporated.
 Due to its lower volatility, the NCl₃ accumulates in liquid Chlorine.
- Traces of Ammonia (NH₃) and other Nitrogen compounds in BRINE can produce NCl₃ in Chlorine.





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TONI® special (Total Ammonia) on-line <u>Total Ammonia</u> [ammonia (NH₃) + monochloramine

(NH₂Cl) + dichloramine (NHCl₂)] in <u>Ultra-Purified brine</u>

WHY? d EARLY WARNING:

Prevent formation of Nitrogen trichloride (NCl₃) | avoid explosion

Prevention of Nitrogen trichloride (NCl₃) formation:

- ⇒ Approximately 25% of Nitrogen trichloride (NCl₃) formed in cells enters the chlorine process (1)
- → Ammonia in cell feed brine is the major source (1)

Learning from incidents:

Nitrogen trichlorinde incident @ Orica, Yarraville – 30 July 1998 (1)
One of the conclusions after investigation was: "Inaccurate method and inadequate frequency of analysis for ammonia in brine"

"Managing Risks Nitrogen Trichloride" by Shane Fast - Vice President The Chlorine Institute @ the WORLD chlorine council meeting.

N-compounds



CI₂

 \rightarrow

NCI₃





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TONI® special (Total Ammonia) on-line <u>Total Ammonia</u> [ammonia (NH₃) + monochloramine (NH₂Cl) + dichloramine (NHCl₂)] in <u>Ultra-Purified brine</u>

HOW?

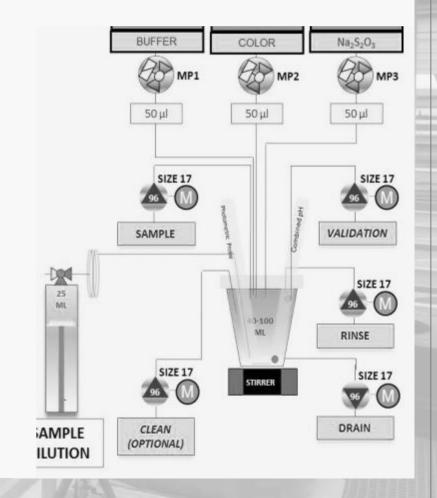
Measuring Principle TONI® special (Total Ammonia)

by Colorimetric analysis (Adapted Berthelot method conform ASTM 4500-NH₃ F)

To determine the total amount of $NH_{3,}$ $NH_{2}CI$ and $NHCI_{2,}$ $NH_{2}CI$ and $NHCI_{2}$ they have to be converted to $NH_{3,}$ This is done by adding thiosulphate.

Reactions:

 $4 \text{ NH}_2\text{Cl} + \text{Na}_2\text{S}_2\text{O}_3 + 5 \text{ H}_2\text{O} \rightarrow 2 \text{ NaHSO}_4 + 4 \text{ NH}_3 + 4 \text{ HCl}$ $2 \text{ NHCl}_2 + \text{Na}_2\text{S}_2\text{O}_3 + 5 \text{ H}_2\text{O} \rightarrow 2 \text{ NaHSO}_4 + 2 \text{ NH}_3 + 4 \text{ HCl}$







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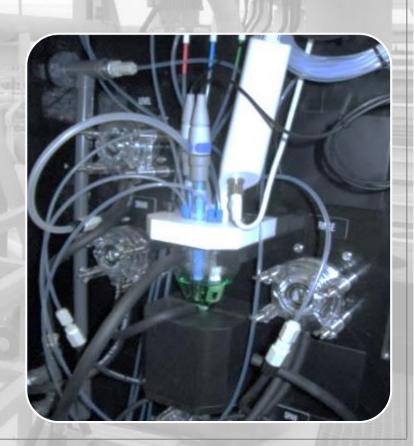
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TONI^{® special (Total Ammonia)} on-line **Total Ammonia** [ammonia (NH₃) + monochloramine (NH₂Cl) + dichloramine (NHCl₂)] in **Ultra-Purified brine**

HOW?

Measuring Principle TONI® special (Total Ammonia)

- ⇒ injection of BRINE sample in analyzer
- ⇒ addition of buffer
 → Alkaline
- \Box Initial absorbance value is measured at (λ) 630 nm (ABS 1)
- addition of color solution
- \supset Final Absorbance value is measured at (λ) 630 nm (ABS 2)
- ⇒ calculation of result: Lambert Beer's Law ABS = €.b. C
 - **c** = molar absorptivity (I. cm-1. mol-1)
 - **b** = path length (cm)
 - concentration (mol/liter)







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TONI® special (Total Ammonia) on-line **Total Ammonia** [ammonia (NH₃) + monochloramine (NH₂Cl) + dichloramine (NHCl₂)] in <u>Ultra-Purified brine</u>

HOW?

methodology: colorimetric measurement using

adapted Berthelot method

conforms to: ASTM 4500-NH₃ F

 $\underline{\lambda}_{\mathsf{LED}}$: 630 nm

range: 0 - 2 mg/l NH₃

 $(0 - 10 \text{ mg/l NH}_3 \text{ by Sample dilution}) \sim 0 - 50 \text{ mg/l N-NH}_3$

higher range by Sample dilution*

detection limit: $\leq 100 \mu g/l \text{ (for 0-1 mg/l NH}_3)$

<u>precision</u>: < 2% full scale range for standard test solutions

<u>cycle time</u>: 1 cycle/25 minutes

stream selection: 1 stream (up to 3 streams optional)









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TONI® special (Total Ammonia) on-line <u>Total Ammonia</u> [ammonia (NH₃) + monochloramine (NH₂Cl) + dichloramine (NHCl₂)] in <u>Ultra-Purified brine</u> **Field Example**









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TONI® special (Total Ammonia) on-line <u>Total Ammonia</u> [ammonia (NH₃) + monochloramine (NH₂Cl) + dichloramine (NHCl₂)] in <u>Ultra-Purified brine</u> **Field Example**



WRLD chlorine council

Safety Workshop: Process Safety Management (PSM)

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Early Warning!





Eliminating the risk of hydrogen explosions in chlor-alkali plants

on-line FAST determination of hydrogen (H₂) in WET chlorine (Cl₂) by Multi-Wavelength INFRARED







Explosion risk



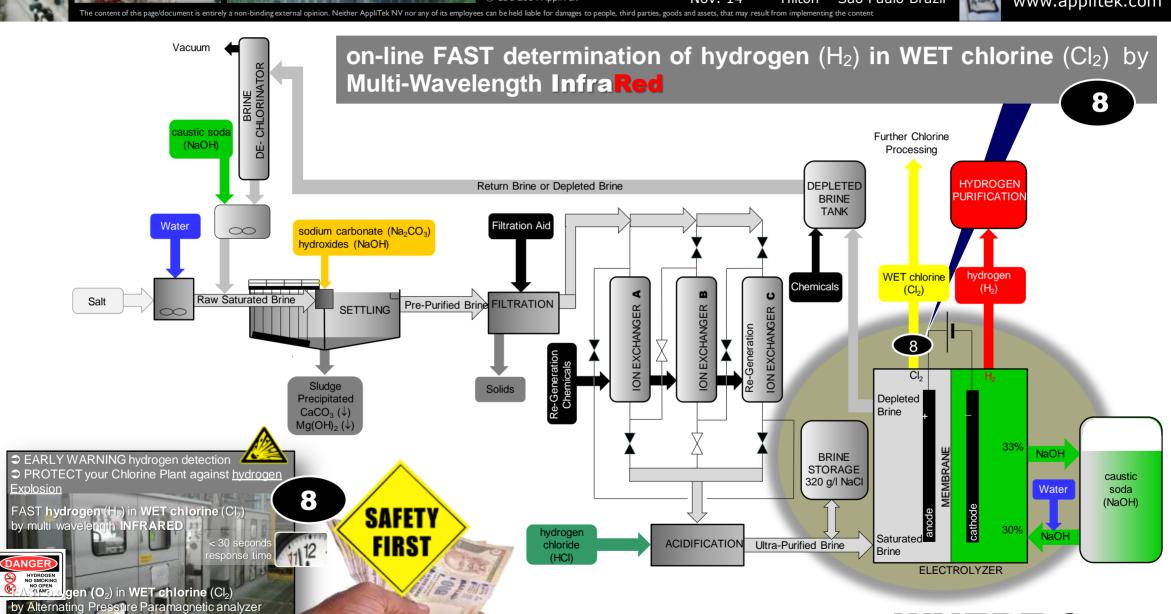


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Safety is not Expensive

It is Priceless

WHERE?

W RLD chlorine council

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WHY?

Low voltage

4

High Current = High Energy

High Electrical Current → NO electrical Ex Proof Technology possible

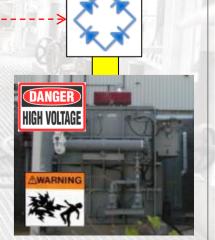
▲ Chlorine Electrolysis Process

on-line Hydrogen Analyzer system

FAST on-line analysis of Hydrogen (H₂) in WET Chlorine gas to keep the gas matrix within the flammability limits.

SAFETY FIRST

- ➡ Field Proven Technology
- **⇒ FAST Response** (T90 = 15 seconds)
- GOOD results during start-up CELL ROOM
- HAZOP approved



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Misconceptions!







Explosion risk

NO RISK

- ⇒ hydrogen is a light gas
- hydrogen is not an hydrocarbon NORISK

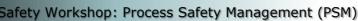
one of your ONLY protections is to have an



May 6, 1937 Lakehurst, New Jersey

SAFETY FIRST

on-line hydrogen (H₂) in WET chlorine (Cl₂) by Multi-Wavelength Infra Rec







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on-line analyzer system for the <u>FAST</u> determination of <u>hydrogen</u> (H₂) in <u>WET chlorine</u> (Cl₂)



hydrogen is not waiting to ignite until you are ready with analysis!!!

Every second counts!!!

Response time of < 35 seconds T90

Do not install an analyzer systems that needs minutes to show results

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presented by Jean-Pol Debelle (Technical Director Eurochlor)

@ WCC Global Safety Team meeting in Dubai, UAE

October 24th 2013



The 10 WCC Cardinal Rules

- 1. Remain in safe concentration range for hydrogen in chlorine
- 2. Use titanium only with wet enough chlorine
- 3. Insure low moisture content for dry chlorine handling and uses
- 4. Control chlorine maximum temperature to avoid iron fire
- 5. Avoid contact between chlorine and organics
- 6. Avoid formation/concentration of nitrogen trichloride
- 7. Write operating procedures/Manage the changes
- 8. Insure sufficient training/information of all personnel
- 9. Prepare and test emergency response plans
- 10. Do not forget incidents investigation and experience sharing



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presented by Jean-Pol Debelle (Technical Director Eurochlor)

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Remain in safe concentration range for hydrogen in chlorine



- Explosion risk if hydrogen concentration in chlorine between about 4 and 93 % (precise values vary in function of pressure, temperature, presence of other constituents ...)
- Additionally to preventative actions, monitoring (on-line analysers) is mandatory:
 - Some hydrogen is produced in the cells, but quantity can increase (bad brine quality) and there can be some mixing with chlorine (damaged membrane or diaphragm ...)
 - concentration of hydrogen increases also when chlorine is liquefied ...
- Hydrogen can also be produced downstream, by steel corrosion ...







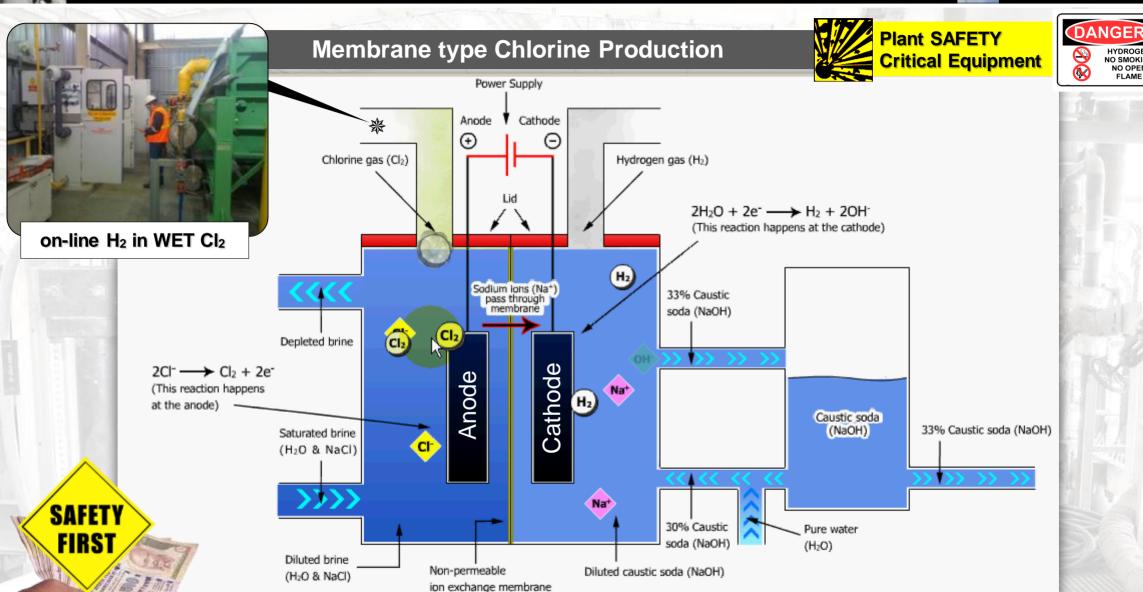
HYDROGEN NO SMOKING

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Safety Workshop: Process Safety Management (PSM)

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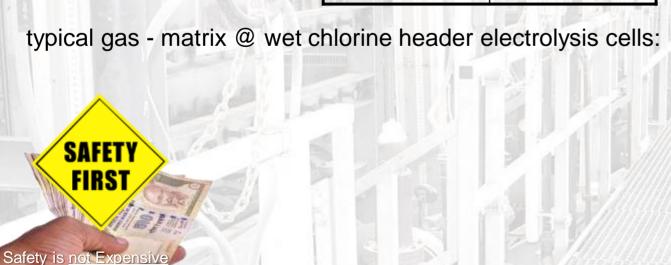
Protect Your plant against HYDROGEN Explosions

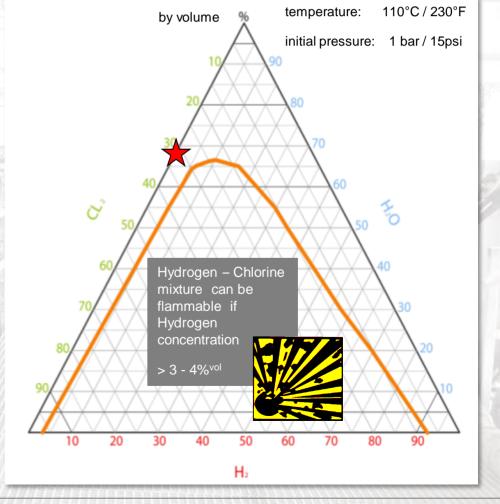
DANGER NO OPEN Hydrogen – Chlorine mixture can be flammable if Hydrogen > 4% (v/v)

WHY?

It is Priceless!

Gas	Chlorine Cell gas		
Chlorine	31% ^{vol}		
Hydrogen			
Water vapor	68.2% ^{vol}		
Inerts	0.6% ^{vol}		





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Protect Your plant against HYDROGEN Explosions

typical chlorine gas travel time = 2,5min.

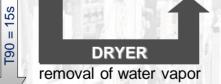
Hydrogen – Chlorine mixture can be flammable if Hydrogen > 4% (v/v)

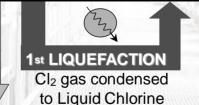


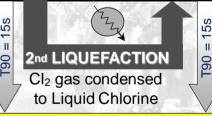
WHY?

Course to the Street St	The State of the Control of the Cont		1202		
Gas	chlorine cell gas	outlet compressor	50% liquefaction	90% liquefaction	
Chlorine	31% ^{vol}	97,5% ^{vol}	48.7% ^{vol}	9.7% ^{vol}	
Hydrogen	0.2% ^{vol}	0.6% ^{vol}	> 1.2% ^{vol}	5%vol DANGE	
water vapor	68.2% ^{vol}				
Inerts	0.6% ^{vol}	1.9% ^{vol}	50.1% ^{vol}	85.3% ^{vol}	

footnotemark Eiquefaction is a Dynamic process. Dry Air, Nitrogen or even in some cases CO_2 are injected to keep the mixture H_2 - Cl_2 outside the flammable limits







SAFETY FIRST

Double system for Safety

on-line H₂ in WET Cl₂





Safety is <u>not Expensive</u>

It is Priceless!



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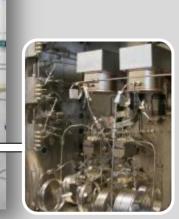
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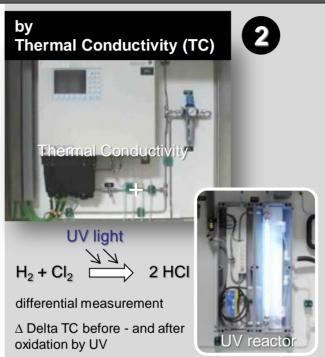
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on-line analyzer system for the <u>FAST</u> determination of <u>hydrogen</u> (H₂) in <u>WET chlorine</u> (Cl₂)

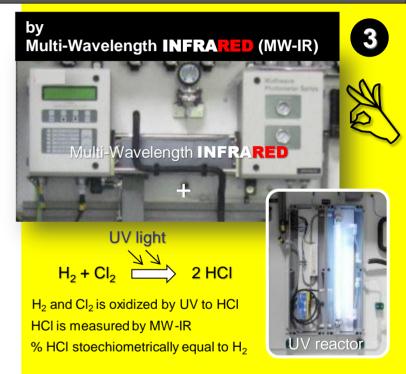
by Gas-Chromatograph (GC)



- Discontinuous measurement
- Long analysis time (several min.!)
- Can only be used for Quality Control
- Cannot be used for Process Control
- Cannot be used for SAFETY
- Complex Technology
- High Maintenance
- Low Up-time

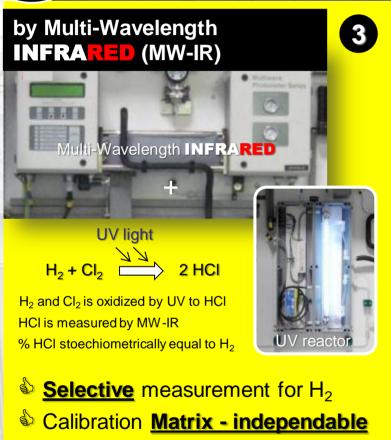


- Not Selective measurement for H₂
- Calibration Matrix dependable
- Does not react first 6 − 12 min. after Plant Start-up
- Cannot be used for SAFETY during Plant Start-up

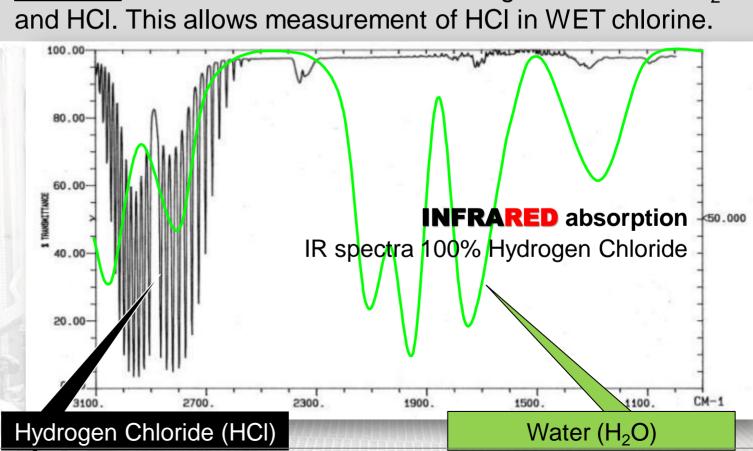


- Selective measurement for H₂
- Calibration Matrix independable
- Fast Response (T90 < 20 seconds)
- Shows Good results @ Plant Start-up
- **Best Available Technology**
- Field Proven High Up-time





- **Fast Response** (T90 < 20 seconds)
- Shows Good results @ Plant Start-up
- Best Available Technology
- Field Proven High Up-time



Support

W RLD chlorine council

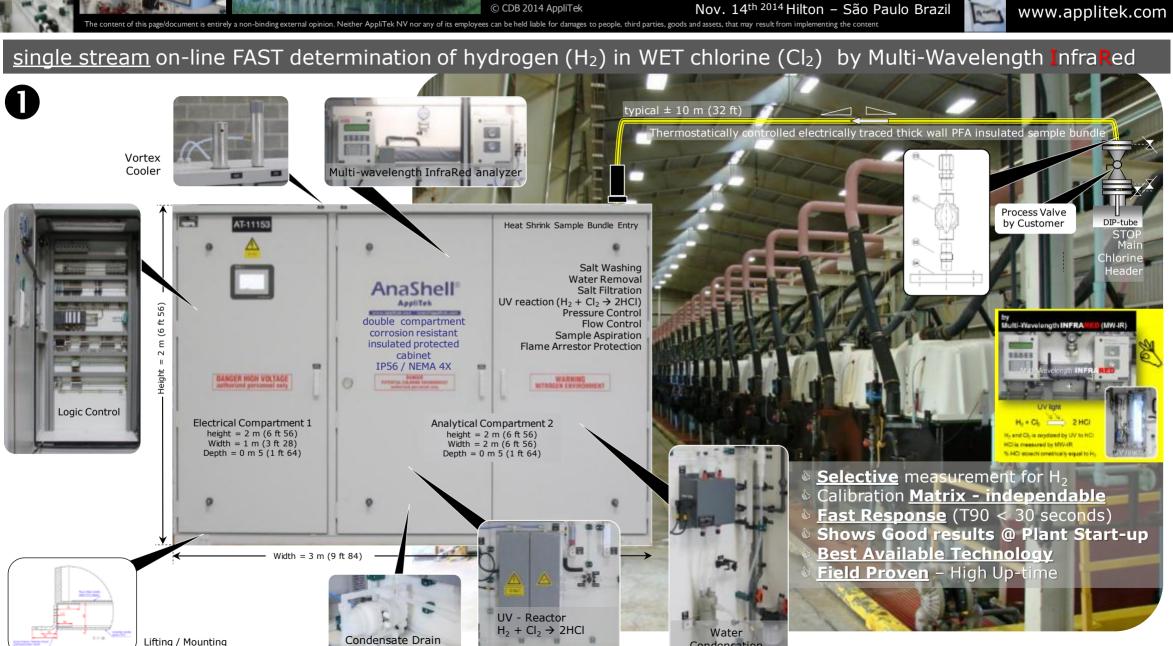
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Condensation

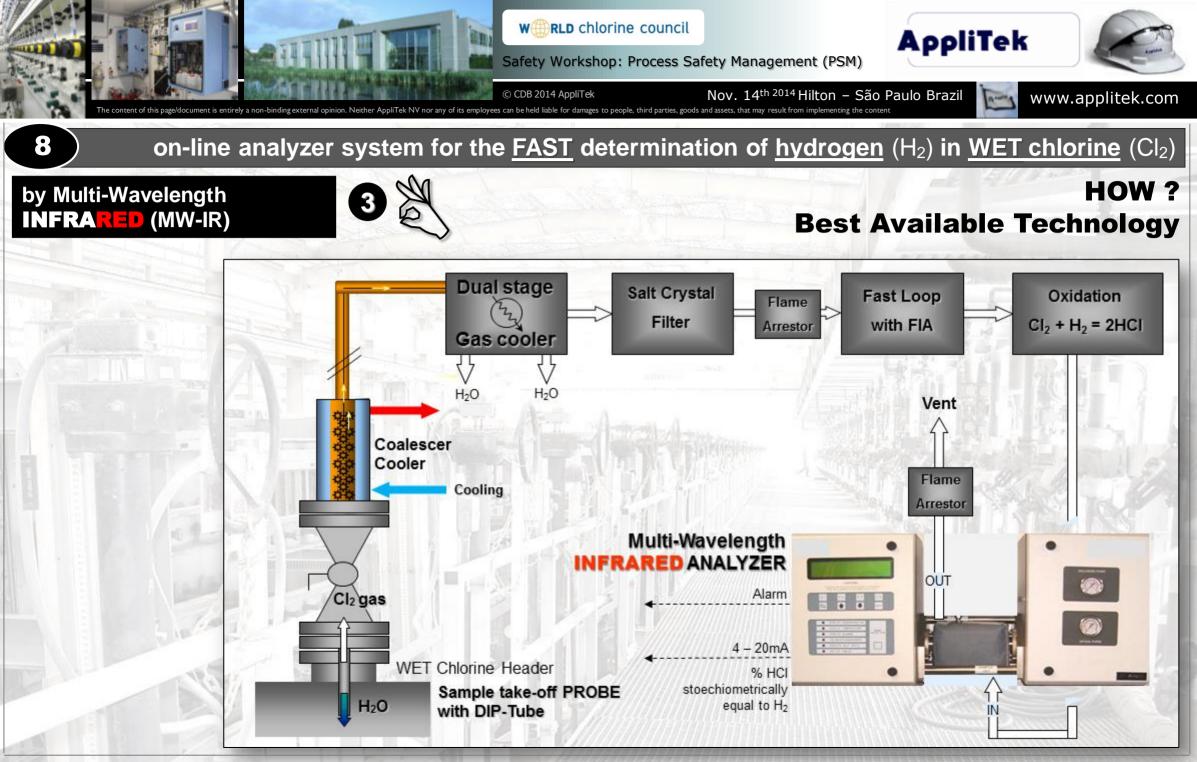








Pump







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HOW?

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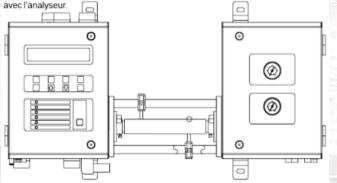


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8

on-line analyzer system for the <u>FAST</u> determination of <u>hydrogen</u> (H₂) in <u>WET chlorine</u> (Cl₂)

by Multi-Wavelength INFRARED (MW-IR) vecl'analyseur.

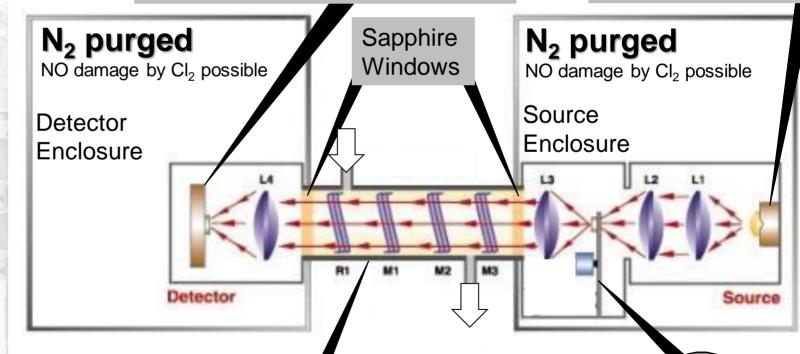




Pyro Electric Lithium Tantalite solid-state **INFRARED** Detector (FET transistor) with Medium Sensitivity but High stability.

Broadband (Pt)

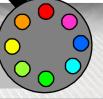
INFRARED source

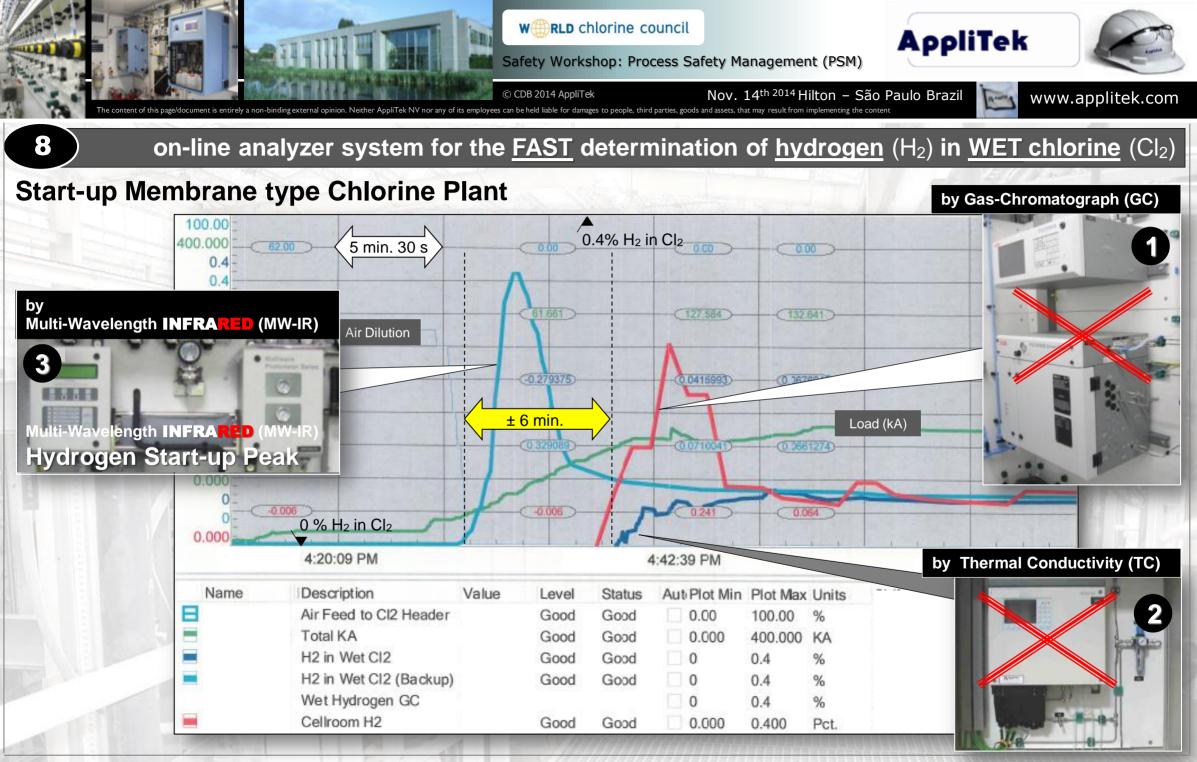


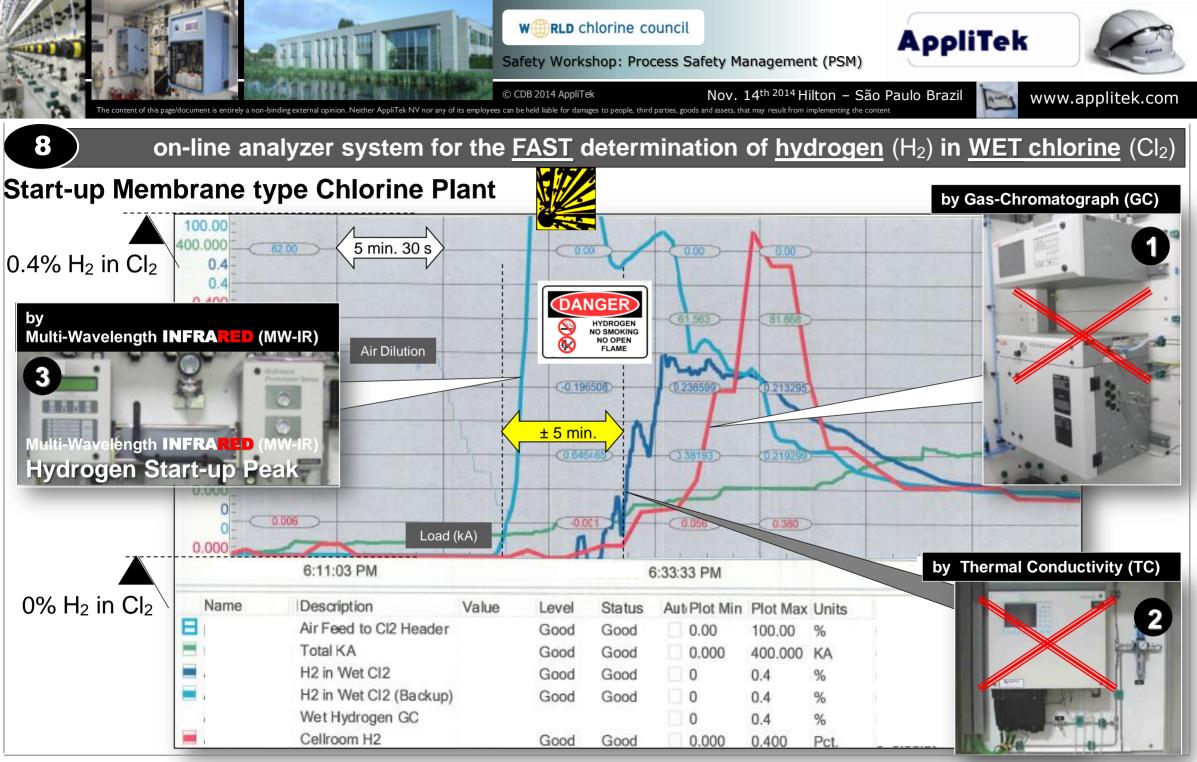
Best Available Technology

Heated Hastelloy-C Sample Cell up to 34 bar (510psi)

Rotating Optical Filter













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on-line analyzer system for the <u>FAST</u> determination of <u>hydrogen</u> (H₂) in <u>WET chlorine</u> (Cl₂)

Hydrogen (H₂) peak during Start-up Membrane type Chlorine Plant

Migration of hydrogen from the cathode compartment to the anode compartment is caused by <u>small holes in the membrane</u>. This hydrogen flow is mainly depending on the <u>pressure difference</u> of the two compartments, the pressure in the cathode compartment is higher than in the anode compartment. This pressure difference is kept constant. Consequently, the flow of hydrogen to the anode compartment is more or less independent of the cell load.

During start up of the cell, there is hardly any chlorine flow, and consequently, you achieve a rather high hydrogen concentration. With increasing chlorine production, this hydrogen is diluted, and the hydrogen concentration decreases.







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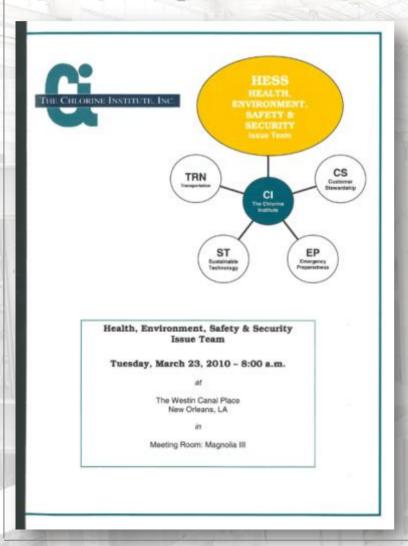
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on-line analyzer system for the <u>FAST</u> determination of <u>hydrogen</u> (H₂) in <u>WET chlorine</u> (Cl₂)

vees can be held liable for damages to people, third parties, goods and assets, that may result from imp

Hydrogen (H₂) peak during Start-up Membrane type Chlorine Plant



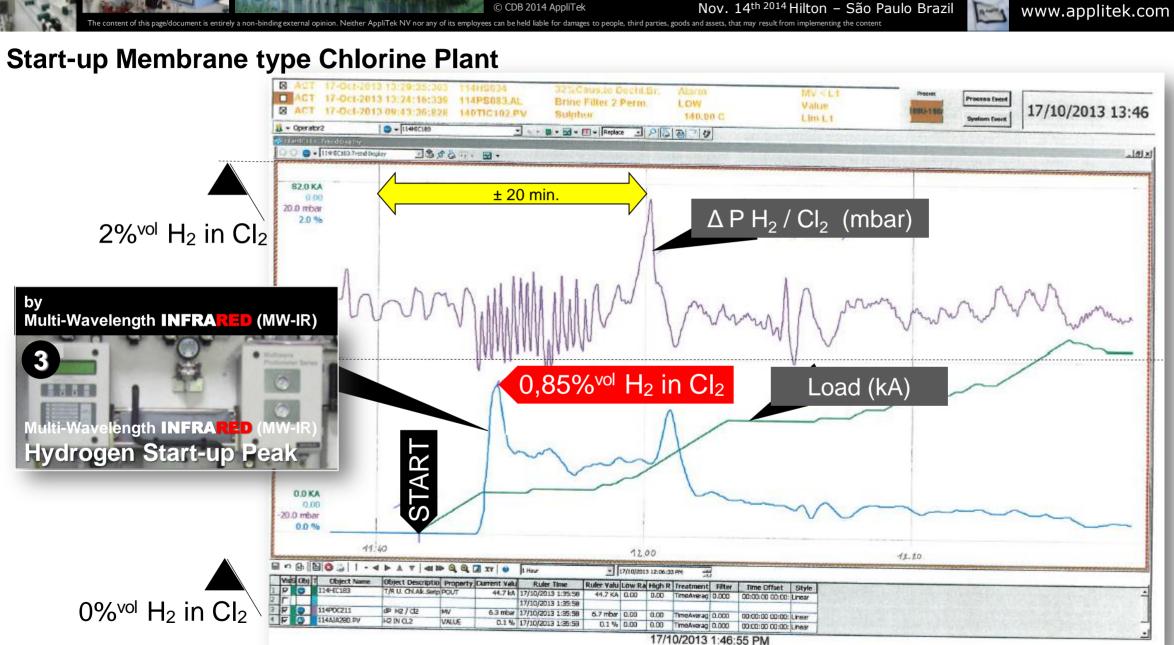
Hydrogen in Wet Chlorine

The issue of excessive hydrogen concentrations on the chlorine side of a membrane cell during start-up has been raised. The peak concentrations can be dangerously high depending on the speed at which the facility goes trough the start up procedure. The Issue team discussed the issue and agreed that the phenomenon was generally understood by all producers















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PRECONDITIONING

FIELD proven preconditioning @ Sample Take Off Point (STOP)

- ⇒ Sample Probe with DIP-tube
 - ⇒ Sample Cooler / Coalescer















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on-line hydrogen (H₂) in WET chlorine (Cl₂)

PRECONDITIONING

measures the sample after oxidation

 $(H_2 + Cl_2 \rightarrow 2HCl)$

H₂ and Cl₂ is Oxidized by UV to HCl and is measured by the INFRARED analyzer









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on-line hydrogen (H₂) in WET chlorine (Cl₂)

PRECONDITIONING



- **FIELD** proven preconditioning **⇒** Salt Filtration
- Water removal
- \bigcirc UV reactor (H₂ + Cl₂ \rightarrow 2HCl)
- ⇒ Flow & Pressure Control





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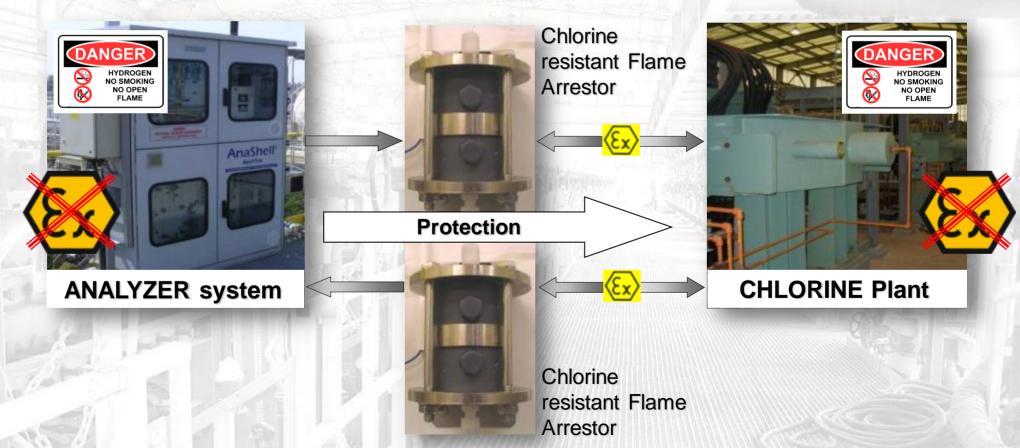


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Protect Your plant against HYDROGEN Explosions

of its employees can be held liable for damages to people, third parties, goods and assets, that may result from impl

Due to high electrical currents a Chlorine Production Plant is defined as **General Purpose zone** → **Need** for Flame Arrestors



Your Analyzer system can be a source of explosion for your plant!







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on-line FAST determination of hydrogen (H₂) in WET chlorine (Cl₂) by Multi-Wavelength INFRARED

FIELD Example















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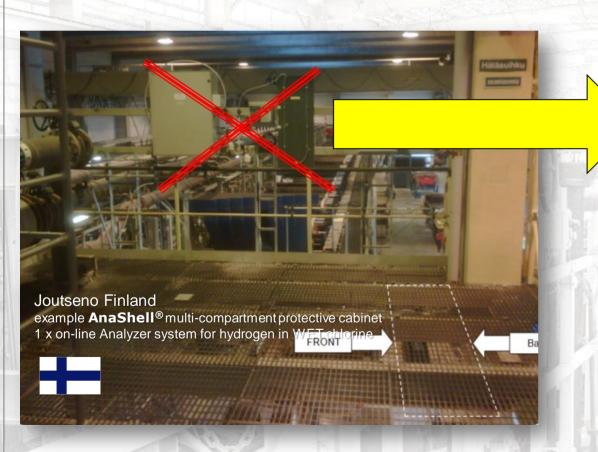
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on-line FAST determination of hydrogen (H₂) in WET chlorine (Cl₂) by Multi-Wavelength InfraRed Field Example











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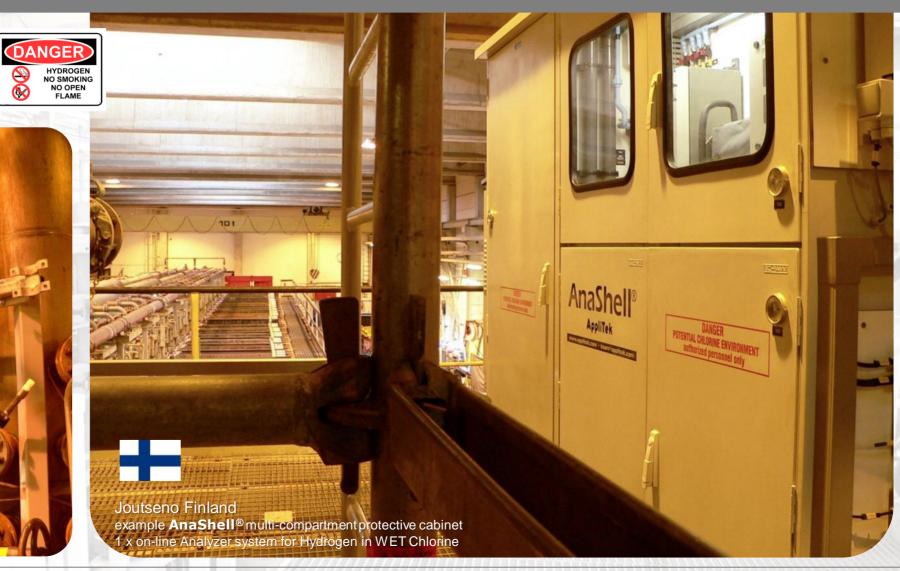


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on-line FAST determination of hydrogen (H₂) in WET chlorine (Cl₂) by Multi-Wavelength InfraRed **Field Example**



Plant SAFETY









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Joutseno Finland

example AnaShell® multi-compartment protective cabinet 1 x on-line Analyzer system for Hydrogen in WET Chlorine





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on-line FAST determination of Hydrogen (H₂) in WET Chlorine (Cl₂) by Multi-Wavelength INFRARED

The bitterness of poor quality remains long after the sweetness of low price is forgotten, especially for life saving, safety critical equipment

You can only apply Best Available Technology

Safety is not expensive, it is priceless











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on-line FAST determination of hydrogen (H₂) in WET chlorine (Cl₂) by Multi-Wavelength InfraRed Field Example





Yokkaichi, Japan example **AnaShell**® multi-compartment protective cabinet 1 x on-line Analyzer system for Hydrogen in WET Chlorine



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on-line FAST determination of hydrogen (H₂) in WET chlorine (Cl₂) by Multi-Wavelength InfraRed **Field Example Repeat Order**







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on-line FAST determination of hydrogen (H₂) in WET chlorine (Cl₂) by Multi-Wavelength InfraRed **Repeat Order Field Example**







AnaShell® multi compartment protective cabinet

1 x on-line Analyzer system for Hydrogen in WET Chlorine

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on-line FAST determination of hydrogen (H₂) in WET chlorine (Cl₂) by Multi-Wavelength InfraRed **Field Example**









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on-line FAST determination of hydrogen (H₂) in WET chlorine (Cl₂) by Multi-Wavelength InfraRed **Field Example**







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on-line FAST determination of hydrogen (H₂) in WET chlorine (Cl₂) by Multi-Wavelength InfraRed **Repeat Order Field Example**







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on-line FAST determination of hydrogen (H₂) in WET chlorine (Cl₂) by Multi-Wavelength InfraRed **Field Example Repeat Order**









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on-line FAST determination of hydrogen (H₂) in WET chlorine (Cl₂) by Multi-Wavelength InfraRed **Field Example Repeat Order**



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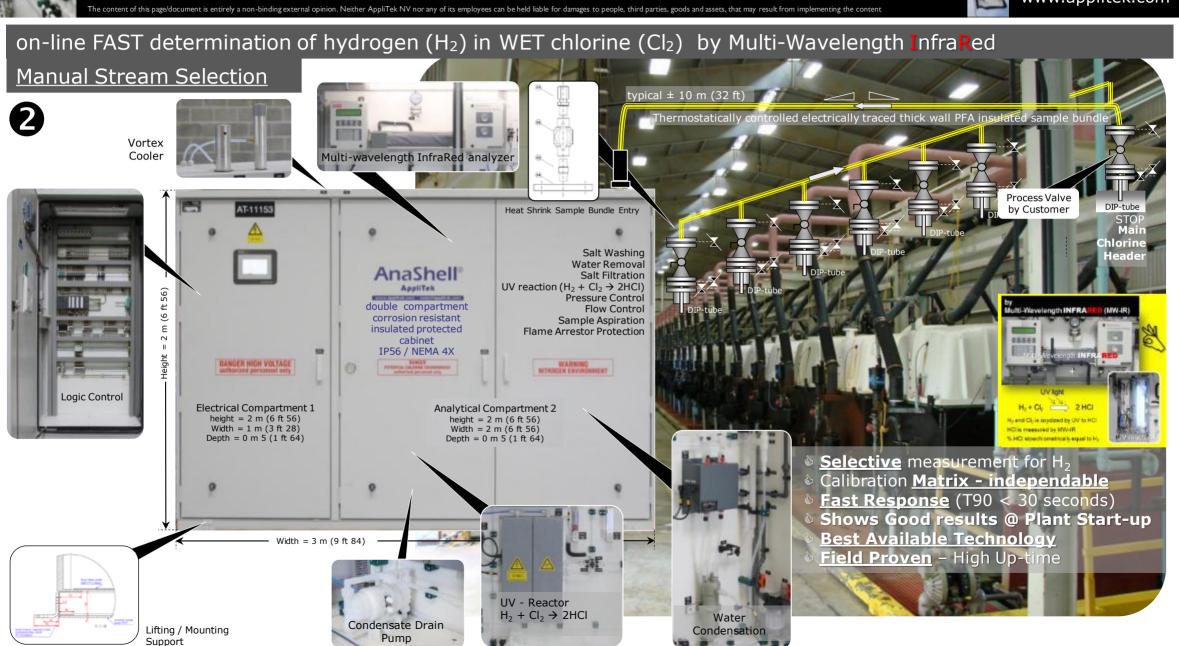


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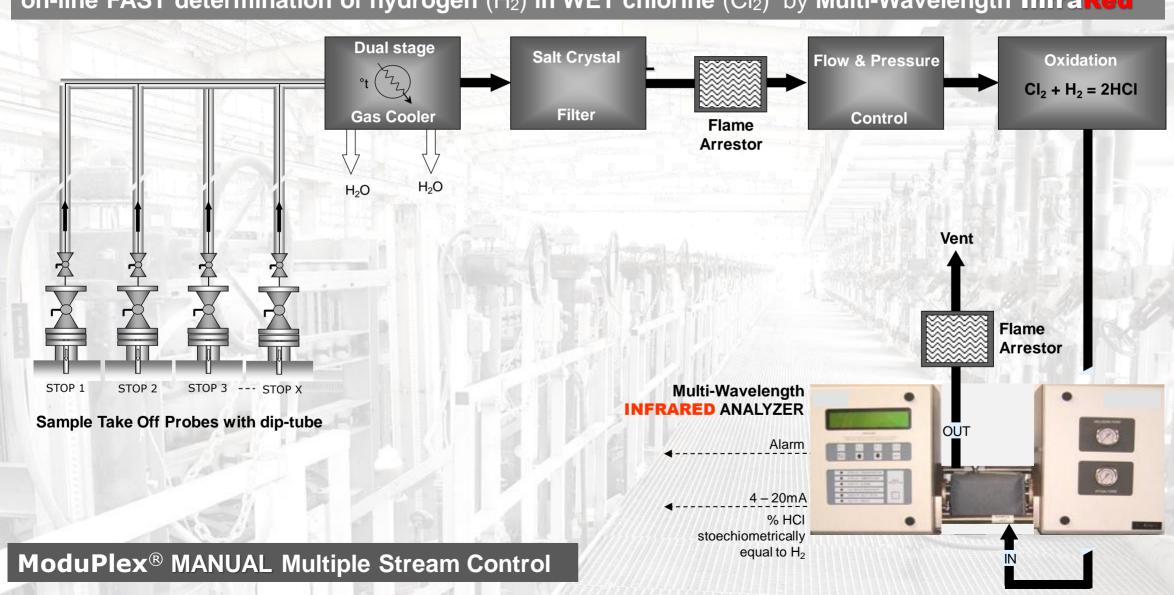
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on-line FAST determination of hydrogen (H₂) in WET chlorine (Cl₂) by Multi-Wavelength InfraRed



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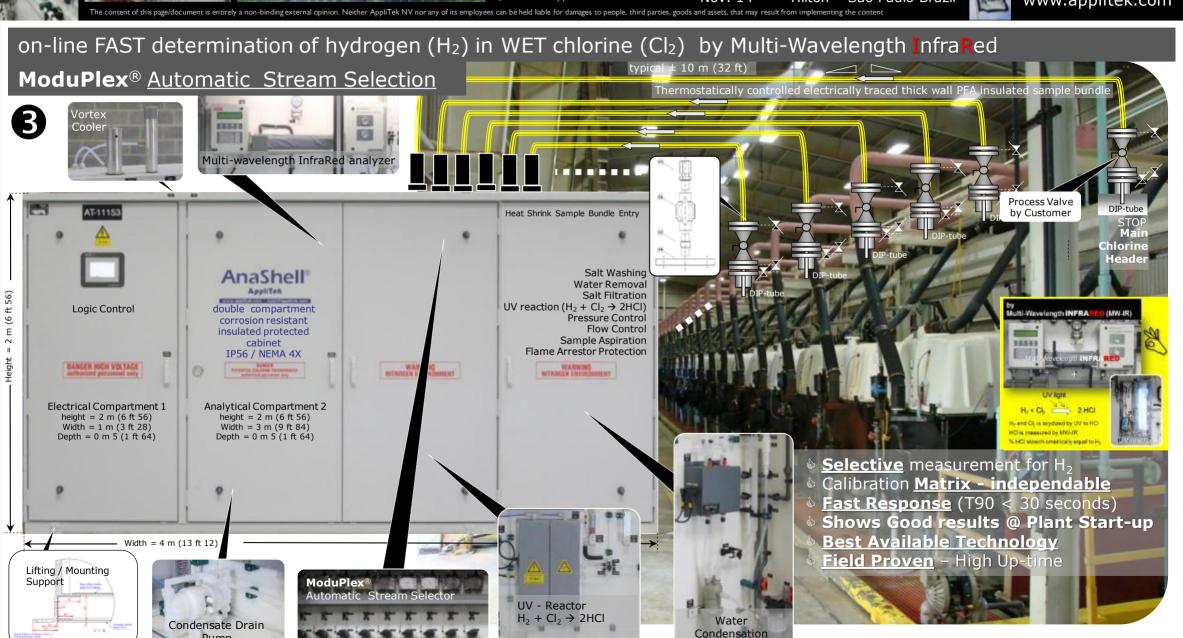


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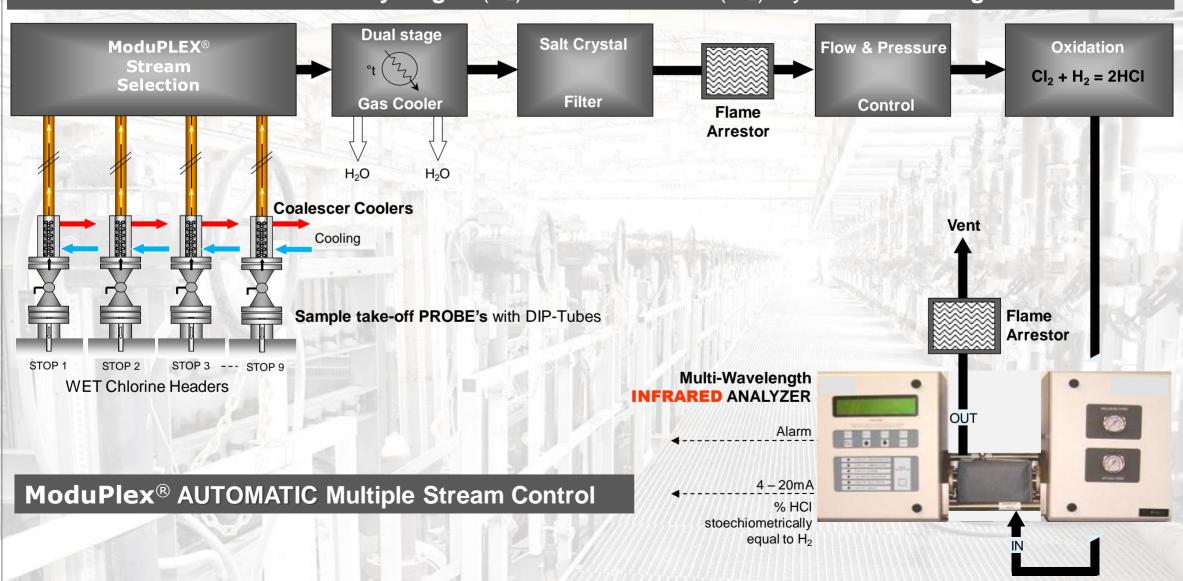
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on-line FAST determination of hydrogen (H₂) in WET chlorine (Cl₂) by Multi-Wavelength INFRARED









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on-line FAST determination of hydrogen (H₂) in WET chlorine (Cl₂) by Multi-Wavelength Infra Red **Field Example**











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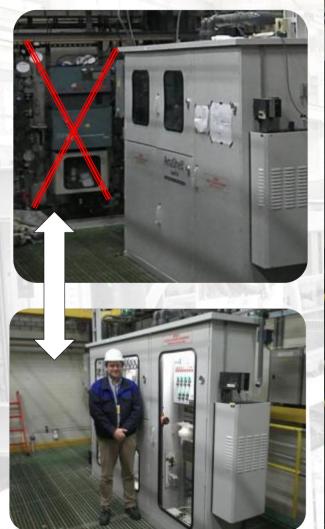
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on-line FAST determination of hydrogen (H₂) in WET chlorine (Cl₂) by Multi-Wavelength InfraRed Field Example

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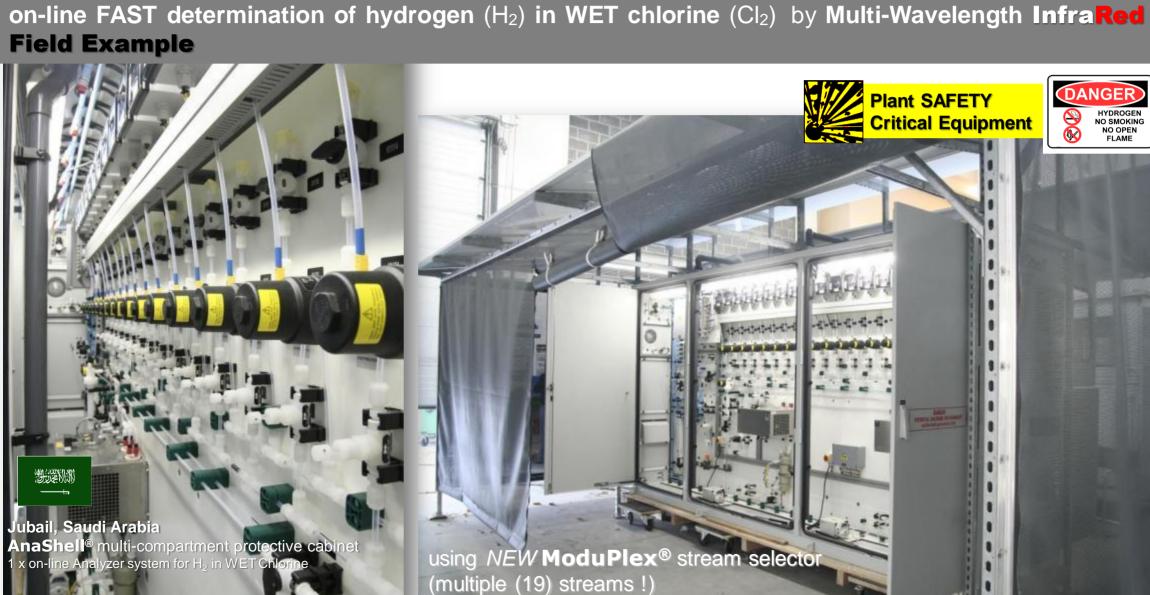


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on-line FAST determination of hydrogen (H₂) in WET chlorine (Cl₂) by Multi-Wavelength Infra Red

Field Example





Jubail, Saudi Arabia AnaShell® multi-compartment protective cabinet 1 x on-line Analyzer system for H₂ in WET Chlorine

using NEW ModuPlex® stream selector (multiple (19) streams!)

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David Laurier, CEO AppliTek









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- In-house feasibility studies
- Application development.
- Danger Assessment Studies
- ⇒ In-house customer & product training

Application & Feasibility







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Process Analyzers:

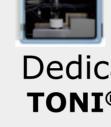
- titration
- ionometry
- colorimetry

Single <u>Parameter</u> series Analyzers





















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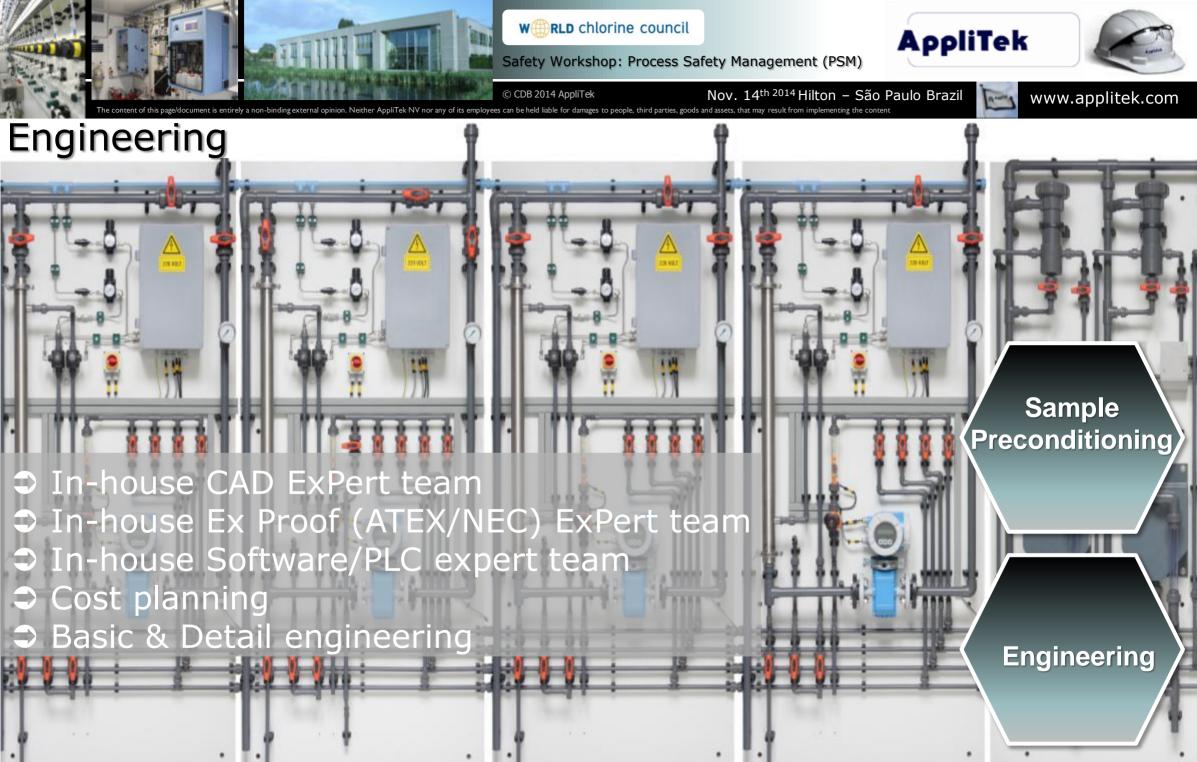


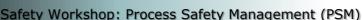


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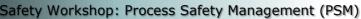
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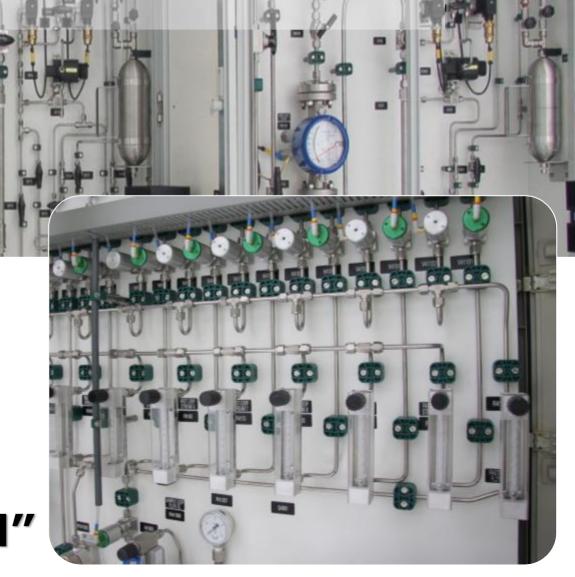
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- ⇒ Site Acceptance Test (SAT)
- ⇒ Start up / Test runs
- Operator / Product training
- Maintenance (contracts)
- Periodic preventive checks

Commissioning / After Sales Service



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