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Thermo Scientific Portable XRF Analyzers

Latest Developments in PMI Tools, alloy verification and new applications

Mark Lessard

Business Development Manager

The world leader in serving science

Analytical Capabilities

“**Ferrous**” Metals
Iron-based matrix

- **Iron and C-steels**
- **Low alloy steels (LAS)**
- **Cr-Mo Steels (Cr-Mo)**
- **High alloy steels (HAS)**
  - Stainless steels (SS)
  - Duplex & Super Duplex
  - Tool steels (TS)
  - Specialty steels

“**Non-Ferrous**”
Metals
Non iron matrix

- **Superalloys**
  - Ni alloys
  - Ni-Co alloys
  - Co alloys
- **Ti alloys**
- **Al & Mg alloys (“white” metal)**
- **Exotic alloys (W, Ta, Hf, Zr)**
- **Precious metals (Au, Ag)**
- **Cu alloys**
  - Brass, Bronze, Cupro-nickels
  - “Red” & “Yellow” metals

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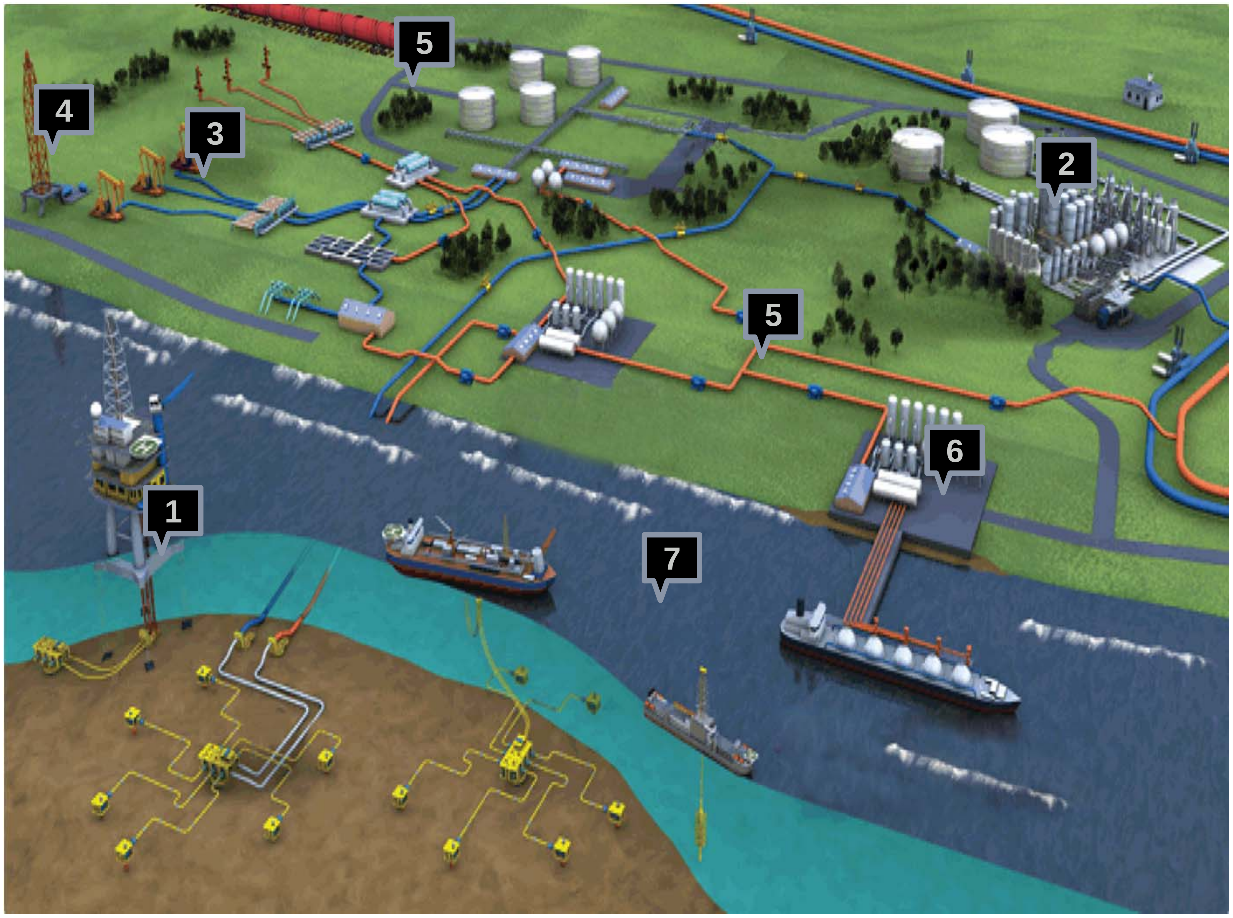
PMI Alloy verification

Positive **M**aterial **I**dentification

Portable XRF Analyzers in Oil & Gas

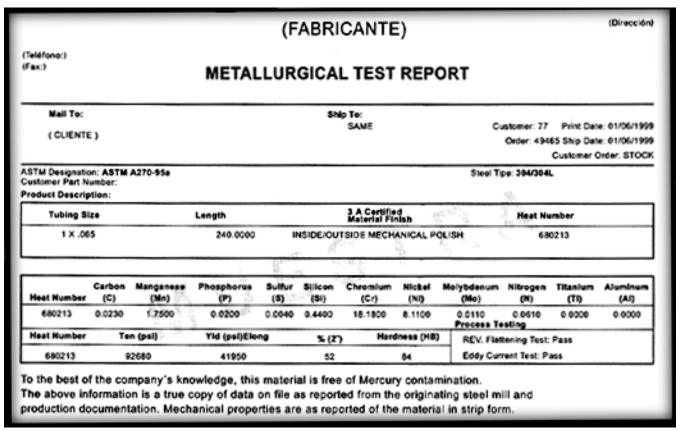
1. Offshore oil
2. Refinery & Petrochem plants
3. On-shore production: traditional
4. On-shore production: hydraulic fracturing
5. Midstream: Pipelines, Valves & Rail
6. Liquid Natural Gas: Processing, Condensing & Import/Export
7. Tankers: Oil & Gas



New Construction: Do Not Rely Solely on Supplier MTRs

- Experience has shown that you cannot rely on material test reports (MTRs) alone; there can be significant errors.
- One customer site survey revealed that as much as 40% of MTRs did not match actual chemistry. They also tend to lose the reports. They get separated from the existing material.

"Trust but verify" – This is what PMI does !!!



(FABRICANTE) (Dirección)

(Teléfono:)
(Fax:)

METALLURGICAL TEST REPORT

Mail To:
(CLIENTE)

Ship To:
SAME

Customer: 77 Print Date: 01/06/1999
Order: 49465 Ship Date: 01/06/1999
Customer Order: STOCK

ASTM Designation: **ASTM A270-95a**
Customer Part Number:
Product Description:

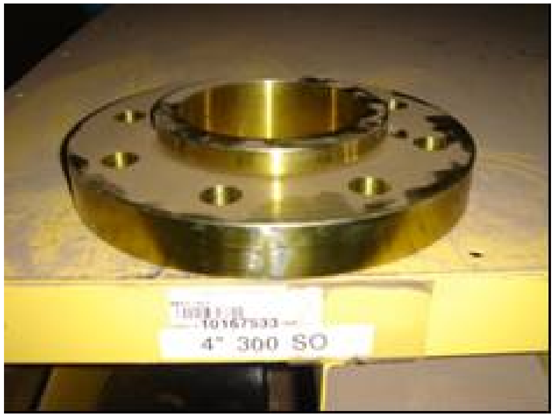
Steel Tipe: **304/304L**

Tubing Size	Length	3 A Certified Material Finish	Heat Number
1 X .065	240.0000	INSIDE/OUTSIDE MECHANICAL POLISH	680213

Heat Number	Carbon (C)	Manganese (Mn)	Phosphorus (P)	Sulfur (S)	Silicon (Si)	Chromium (Cr)	Nickel (Ni)	Molybdenum (Mo)	Nitrogen (N)	Titanium (Ti)	Aluminum (Al)
680213	0.0230	1.7500	0.0200	0.0040	0.4400	18.1800	8.1100	0.0110	0.0610	0.0000	0.0000

Heat Number	Ten (psi)	Yld (psi)Elong	% (2")	Hardness (HB)	Process Testing
					REV. Flattening Test: Pass
680213	92680	41950	52	84	Eddy Current Test: Pass

To the best of the company's knowledge, this material is free of Mercury contamination.
The above information is a true copy of data on file as reported from the originating steel mill and production documentation. Mechanical properties are as reported of the material in strip form.



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Residual Element Analysis

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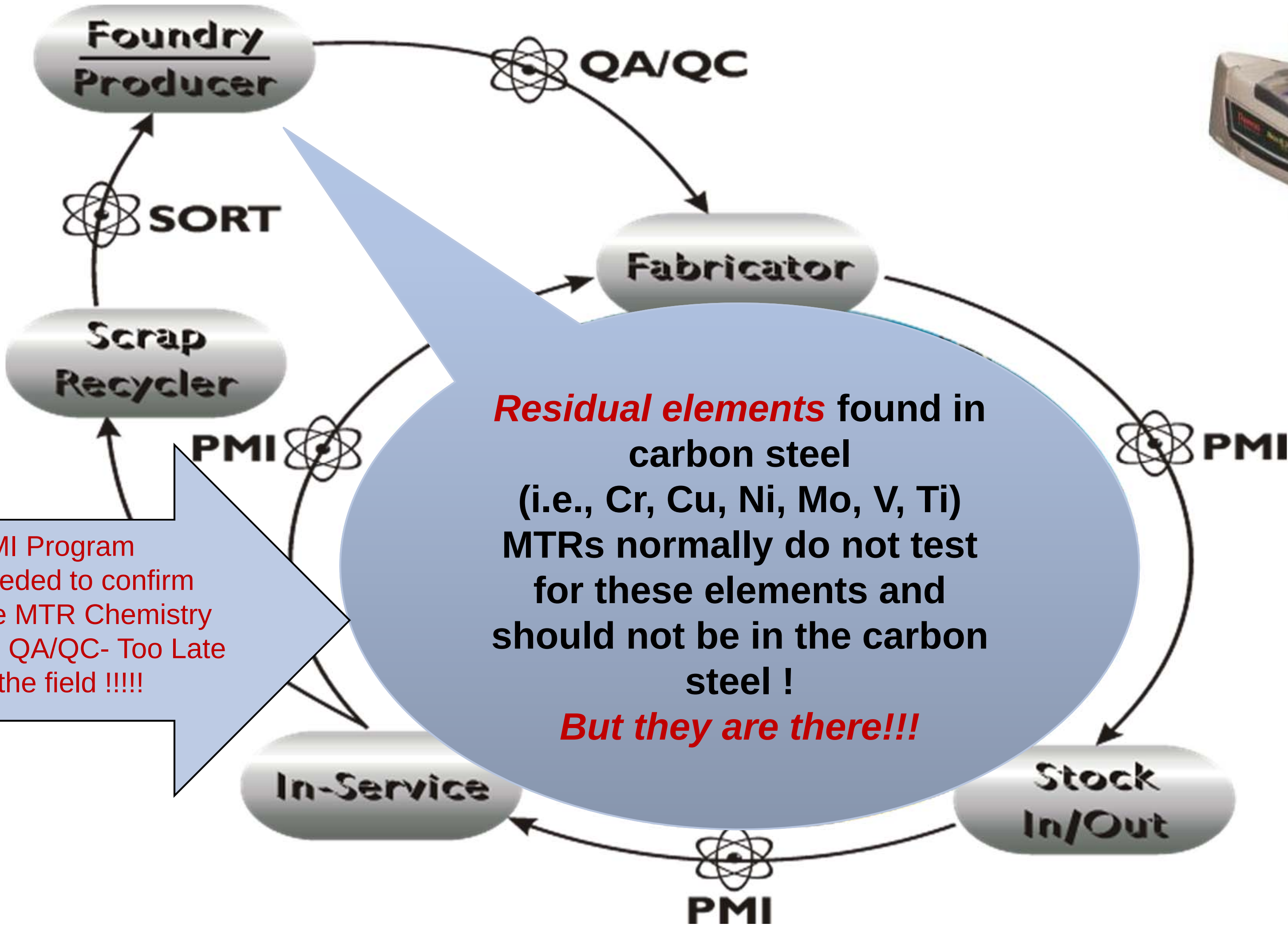
New Construction: PMI Cycle Overview – Renewed & Now Required Emphasis



PMI Program needed to confirm the MTR Chemistry for QA/QC- Too Late in the field !!!!!

Residual elements **found in carbon steel**
(i.e., Cr, Cu, Ni, Mo, V, Ti)
MTRs normally do not test for these elements and should not be in the carbon steel !
But they are there!!!

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The world of Oil&Gas is Changing.
Why is it important to analyze for residual elements?

- Unlike the old days when we mined ore from the earth to create our metals, today most all of our metals come from recycled scrap metal.
  - When mills melt down a lot of scrap metal (molten heat) it's difficult for them to insure that they are keeping the undesirables out of the melt
  - The mills do provide some kind of MTR for their customers, though those MTR's list the majors elements and not the minor elements (tramps).

- Today's crude oil's (and natural gas) have often different chemistries that can now interact with the Tramps and Residuals in the alloy compositions.
  - Higher levels of S and contaminants with thicker viscosities require higher pressures/ higher temperatures to transport and refine these oils.

What are the Residual/Tramp & Micro alloying elements?

- Cr, Ni, Cu residual elements
  - The Niton XL5t can measure Cr, Ni, and Cu at extremely low levels at petroleum refineries.
  - Cr+Ni+Cu must be less than 0.2%/2000 ppm…LOD for sum is 0.06%%/600 ppm at 5 sec per filter

- Si in C Steel for sulfidation corrosion (RP-939-C)
  - Si can be tested to assure levels above 0.1%

- Flow accelerated corrosion
- Cr > 0.1%, Cu, Mo

- Pipelines, Chemical composition of PSL 1
  - Cu < 0.5%
  - Ni < 0.5%
  - Cr < 0.5%
  - Mo < 0.15%
  - Nb + V < 0.06%
  - Nb + V + Ti < 0.15%

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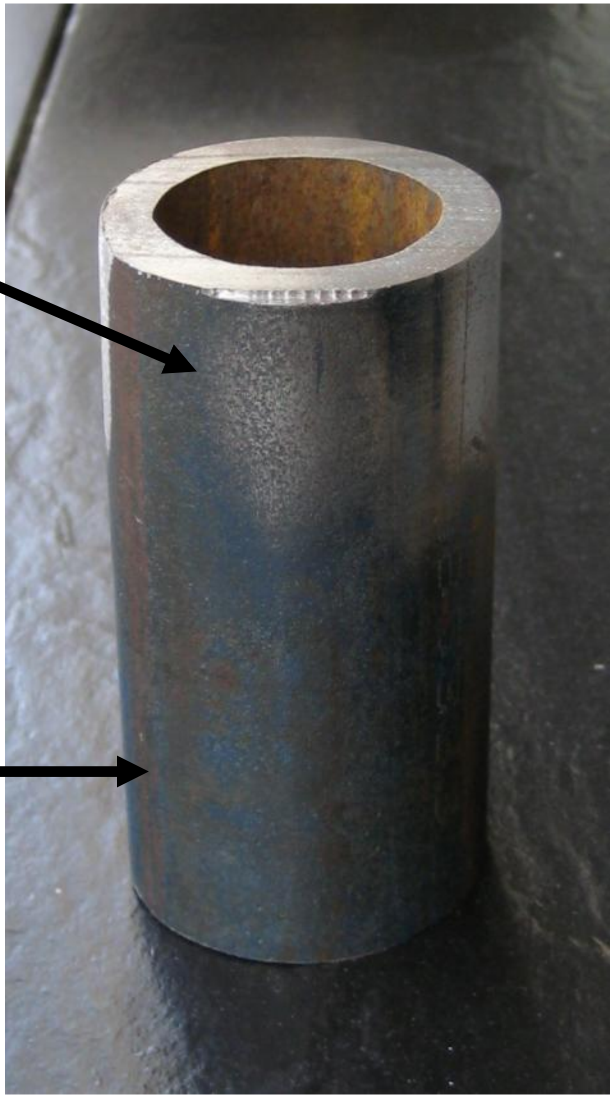
Residual Element Testing
HF Piping, C Steel Material from Warehouse

Hand 'ground' with diamond paper

Cu	Ni	Cr	RE Sum
0.313	0.124	0.082	0.519

Unprepared, light oxidation

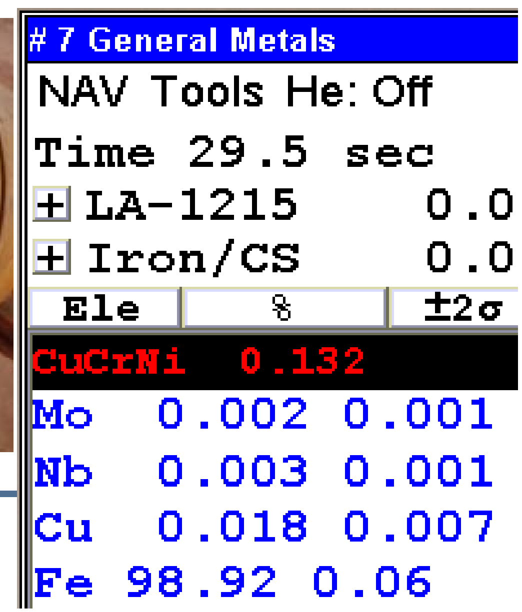
Cu	Ni	Cr	RE Sum
0.655	0.228	0.097	0.981



- When testing HF Alkylation system piping, achieving high accuracy at low concentrations is critical. As such, sample preparation is very important.
- Objective is to discern whether the material contains Residual Element (RE) Sum (Cu+Ni+Cr) less than 2000 ppm (0.2%).
- RE Sum above that level can be an indicator of accelerated corrosion susceptibility.
- Inspectors want to ensure RE Sum levels are less than 2000 ppm to avoid excessive FAC and possible system failure.

Existing Piping Systems (Retroactive PMI) Programs

- ***Priority for API 578 3rd Edition:***
- **Residual Elements in Carbon Steels in Hydrofluoric Acid Alkylation Units –** Note: Carbon steels in HF acid service have been reported to suffer increased corrosion rates based on the residual elements (RE) in steels.
- In general, it has been reported that steels with a high RE content are likely to suffer enhanced corrosion attack. Operators should review the potential impact of this in HF service.
- A guideline is that for base metal of <u>*C> 0.18% wt% and Cu + Ni + Cr, 0.15% wt % is optimum*</u>. These values are critical as the type and concentrations to be measured will directly affect the analytical methods operations need to adopt.
- API RP 571 **–** Pages 12,38

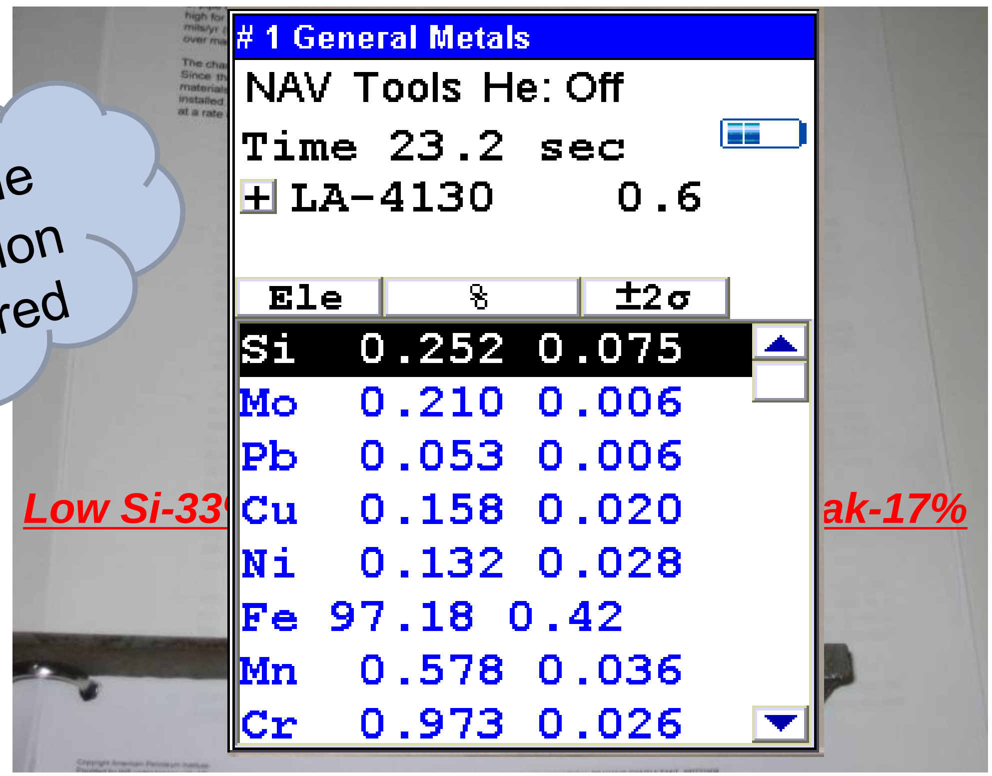


Existing Piping Systems (Retroactive PMI) Programs

Priority for API RP 578 2nd Edition – <u>"High Temperature Sulfidic Corrosion – API RP 939-C"</u>

- Process units susceptible to sulfidation:
  - Carbon steels with low silicon (0.10%) content can corrode at an accelerated rate
  - Assets at risk from this type of degradation should apply PMI control to determine silicon levels. *<u>(Retroactive PMI is suggested and to follow API 578.)</u>*
  - See API 571 and API RP 939-C
  - See Section 7.1.4 & 5

Sample preparation is required



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Carbon Equivalent

Inspection Program – Pipeline Material Compatibility when Welding

- API 5L-Line Pipe inspection for *chemical elements* for weld pre-heat and post heat treatment (PWHT-Stress Relief). Elements affect the *hardenability*, which affects the depth & distribution of hardness induced by quenching. The heat affected zone (HAZ). Leads to delayed hydrogen cracking, and loss in ductility and toughness.
  - PSL 1 Welded Pipe-API 5L Table 4 (X42 to X70 Welded Pipe)
  - PSL 2 Welded Pipe-API 5L Table 5 (X42M to X120M Welded Pipe)
- Maximum Carbon Equivalency-Table 5 (two formulas)

$$CE_{Pcm} = C + \frac{Si}{30} + \frac{Mn}{20} + \frac{Cu}{20} + \frac{Ni}{60} + \frac{Cr}{20} + \frac{Mo}{15} + \frac{V}{10} + 5B$$

Use when "Carbon Mass Fraction" is: *</= 0.12%*

$$CE_{IIW} = C + \frac{Mn}{6} + \frac{(Cr + Mo + V)}{5} + \frac{(Ni + Cu)}{15}$$

Use when "Carbon Mass Fraction" is: *>/= 0.12%*

- Maximum on elements that affect the carbon equivalency (CE) are:
  - Mn, Cr , Mo , V , Ni , Cu (V, Si & B for CE*pcm*)
- XRF analyzer can put these formulas (less carbon) in the software and give you an *equivalency factor* (EQF) with all other elements and download them to an Excel spreadsheet.

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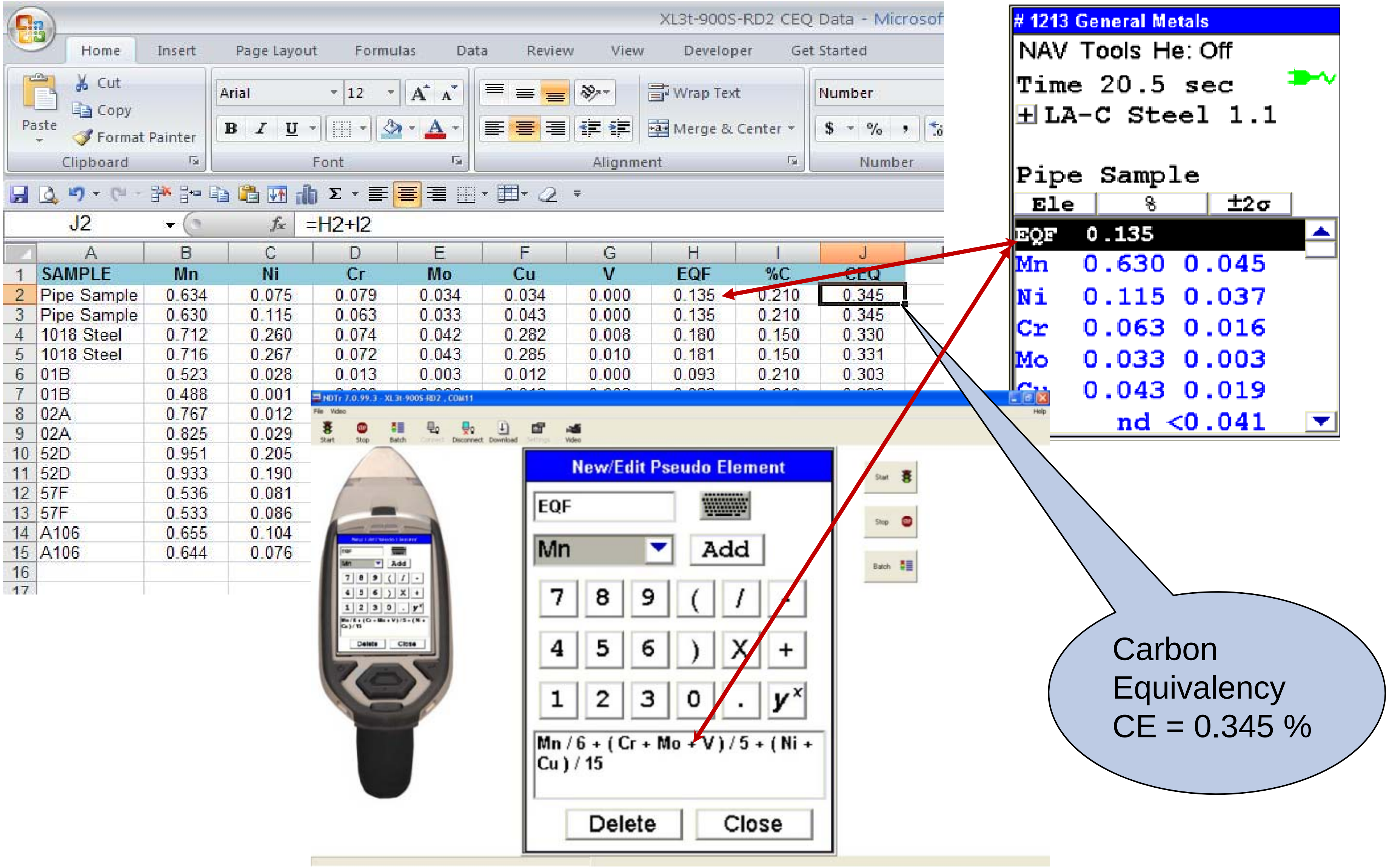
XRF Example of Equivalency Factor (EQF)



	SAMPLE	Mn	Ni	Cr	Mo	Cu	V	EQF	%C	CEQ
2	Pipe Sample	0.634	0.075	0.079	0.034	0.034	0.000	0.135	0.210	0.345
3	Pipe Sample	0.630	0.115	0.063	0.033	0.043	0.000	0.135	0.210	0.345
4	1018 Steel	0.712	0.260	0.074	0.042	0.282	0.008	0.180	0.150	0.330
5	1018 Steel	0.716	0.267	0.072	0.043	0.285	0.010	0.181	0.150	0.331
6	01B	0.523	0.028	0.013	0.003	0.012	0.000	0.093	0.210	0.303
7	01B	0.488	0.001							
8	02A	0.767	0.012							
9	02A	0.825	0.029							
10	52D	0.951	0.205							
11	52D	0.933	0.190							
12	57F	0.536	0.081							
13	57F	0.533	0.086							
14	A106	0.655	0.104							
15	A106	0.644	0.076							

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Mercury contamination

Mercury in Oil & Gas Industry

Mercury in crude oil

- Naturally occurring element present in virtually all oil and gas worldwide
- Concentrations in reservoirs vary from low part per billion (ppb) to hundreds of ppb
- Hg Species in crude oil are typically elemental and/or inorganic compounds such as mercuric sulfide
- Hg Species from crude may accumulate in process equipment over time

Impact of Mercury

- Environmental and potential waste issues
- Health and safety issues: volatile sources, surface contamination, particulate contamination during hot work. Assets exposed to mercury must be decontaminated prior to further use.
- Safety issues: corrosion by metal amalgamation or possible liquid metal embrittlement (LME)

Mercury clean up. PSC worker using “special” mercury vacuum on flange.

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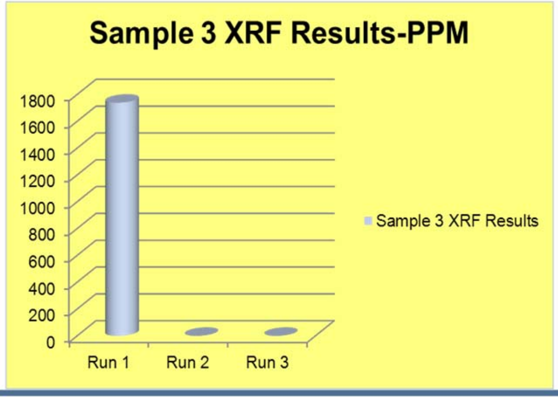
Mercury Contamination of a PIG

- **PIG** – **P**ipeline **I**nspection **G**auge
- Use XRF to analyze and monitor mercury contaminated parts of a PIG unit as they go through a cleaning and decontamination process
- PIG is placed into a closed tank and flushed with a decontamination solution to remove all surface contamination prior to the units disassembly.
- After disassembly all the parts are measured with XRF to verify mercury level.
- Mercury levels will decrease after each stage of the decontamination process.
- The ability to measure mercury contamination will assist customers in monitoring contamination of their systems



After Initial Clean

After Run 1

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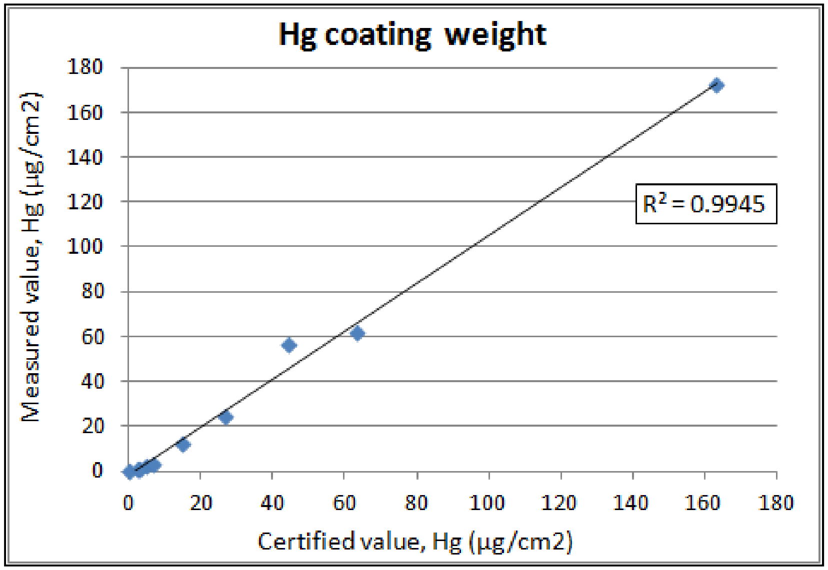
Niton XL3t mercury measurement

- The handheld XRF technique offers a quick, and cost effective way of screening mercury surface contamination
- The mercury analysis is available as an option for XL3t instruments:
- General Metals mode:
  - Reports mercury as % weight or ppm
  - For quick pass/fail screening
- Coatings mode:
  - Report mercury as coating weight (µg/cm2).
  - Determines the precise amount of mercury
- Niton XL3t 980 GOLDD+ mercury detection limits is less than 1 µg/cm2 (30s)
- The most common alloys such as iron, nickel or copper do not form alloys with mercury, mercury is always surface contamination, which makes the coating weight analysis the best way to quantify amount of mercury.



Niton XL3t 980 GOLDD+ accuracy and repeatability using coatings mode analysis.

	Hg (µg/cm2)
1	2.82
2	2.47
3	2.74
4	2.15
5	2.23
6	2.62
7	2.83
8	2.53
9	2.01
10	2.19
Avg.	**2.46**
Std. Dev.	**0.30**
Given	**2.70**

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PMI for Refractory Anchor, Brick & Fiber

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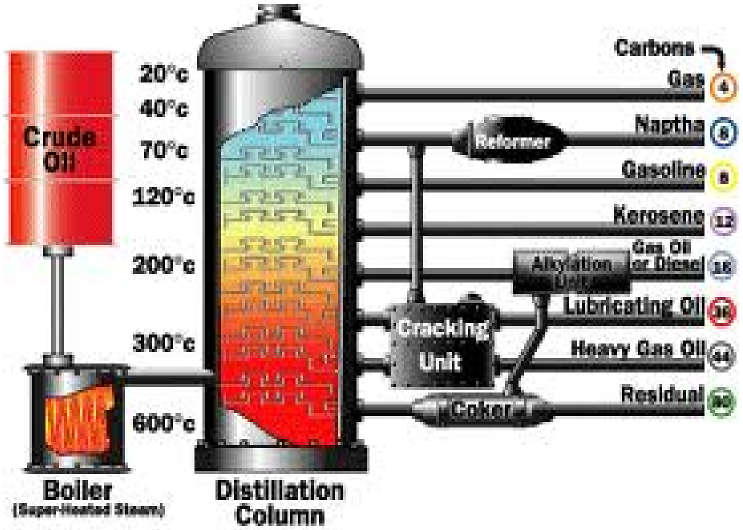
PMI for Refractory Applications in Petro-Chemical and Refinery Processes

- FCC Units
- Crude Units
- Sulfur Units
- Acid Production units
- Cokers
- Reactors
- Regenerators
- Heaters
- Boilers
- Etc…..



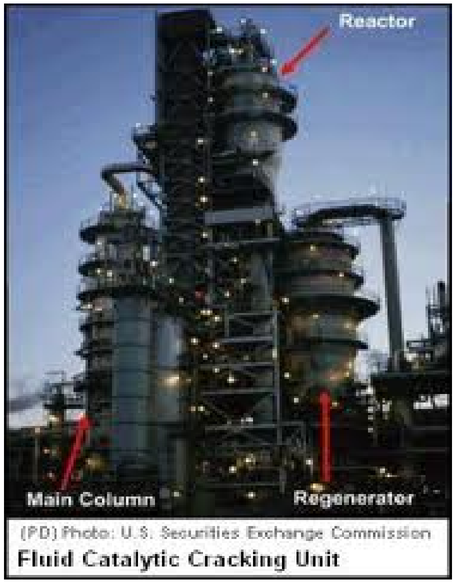


Table 5 - Plug header and return bend materials

Material	ASTM specifications		
	Forged	Wrought	Cast
Carbon steel	A105 A 1B1, class 60 or 70	A 234, WP8	A 216, WCB
C-1/2Mo		234, WP1	A 217, WC1
1 *1/4Cr-1/2Mo*		234, WP11	A 217, WC6
21/4Cr-1Mo		234, WP22	A217, WC9
3Cr-1Mo		-	-
5Cr-1/2Mo		234, WP5	A217, C5
9Cr-1Mo		234, WP9	A 217, C12
9Cr-1Mo-V		234, WP91	A217, C12A
18Cr-8NJ Type 304		03, WP304	A 351, CF8
18Cr-8Ni Type 304H		3, WP304H	A 351, CF8
18Cr-8Ni Type 304l		03, WP304l	A 351, CF8
16Cr-12Ni-2Mo Type 316		03, WP316	A351, CF8M
16Cr:12Ni-2Mo Type 316H		3, WP316H	A351, CF8M
16Cr-12NI-2Mo Type 316l		03, WP316l	A351, CF3M
18Cr-10NI-3Mo Type 317		03, WP317	-
18Cr-10Ni-3Mo Type 317l		03, WP317l	-
1 BCr-10Ni-Ti Type 321		03, WP321	-
18Cr-10Ni-Ti Type 321H		3, WP321 H	-
18Cr-10Ni-Nb Type 347		03. WP347	A351. CF8C
18Cr-10NI-Nb Type 347H		3, WP347H	A351,CFBC
Nickel alloy BOOH/800HTS		8366	A 351, CT-15C
25Cr-20Ni	A 182, F310	A403, F310	A 351, CK-20 A 351, HK40

a Minimum grain size shall be ASTM #5 or coarser.

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Table 10 - Maximum design temperatures for tube-support materials

Material	ASTM Specification		Maximum Design Temperature	
	Casting	Plate	°C	(OF)
Carbon steel	A216 GrWCB	A283GrC	425	(800)
21/4Cr-1Mo	A217 GrWC 9	A 387 Gr 22, Class 1	650	(1 200)
5Cr-1/2Mo	A217 GrC5	A 387 Gr 5, Class 1	650	(1 200)
19Cr-9Ni	A 297 Gr HF	A 240, Type 304H	815	(1 500)
25Cr-12Ni	-	A 240, Type 309H	870	(1600)
25Cr-12NI	A 447 Type II	-	980	(1 800)
25Cr-20NI	-	A 240, Type 310H	870	(1 600)
25Cr-20Ni	A351 Gr HK40	-	1090	(2000)
50Cr-50NI-Nb	A 560 Gr 50Cr-50Ni	-	980	(1 800)
For exposed radiant and shield-section tube supports, the material shall be 25Cr-12Ni or higher alloy.				

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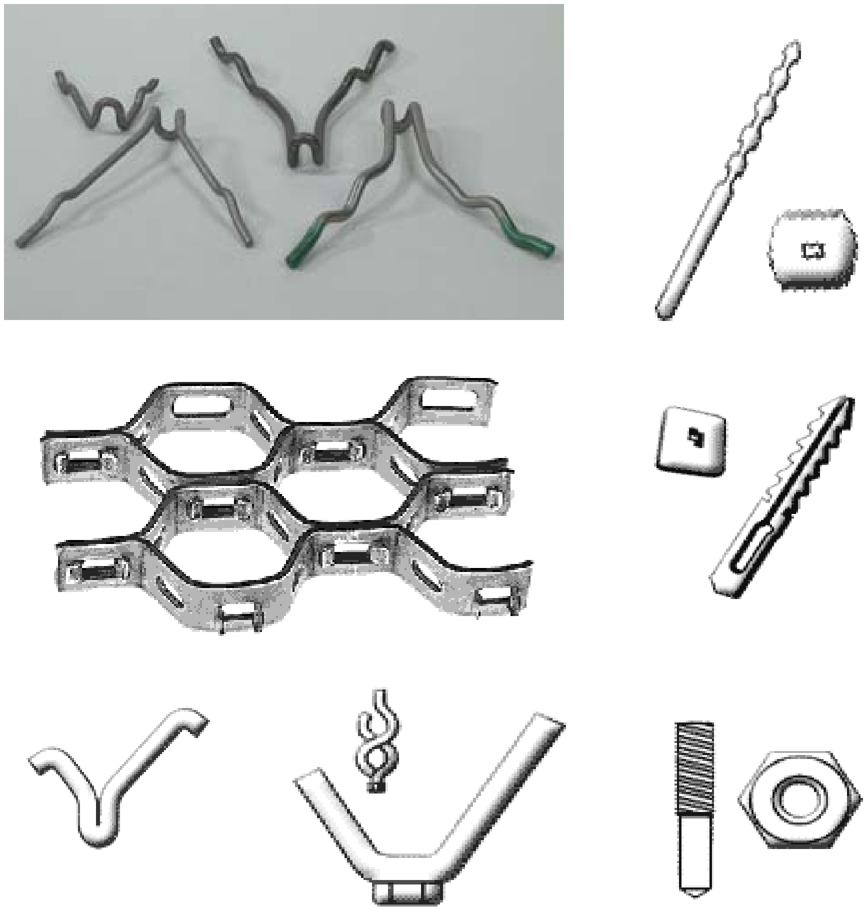
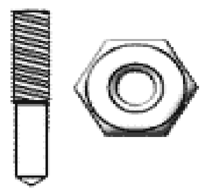
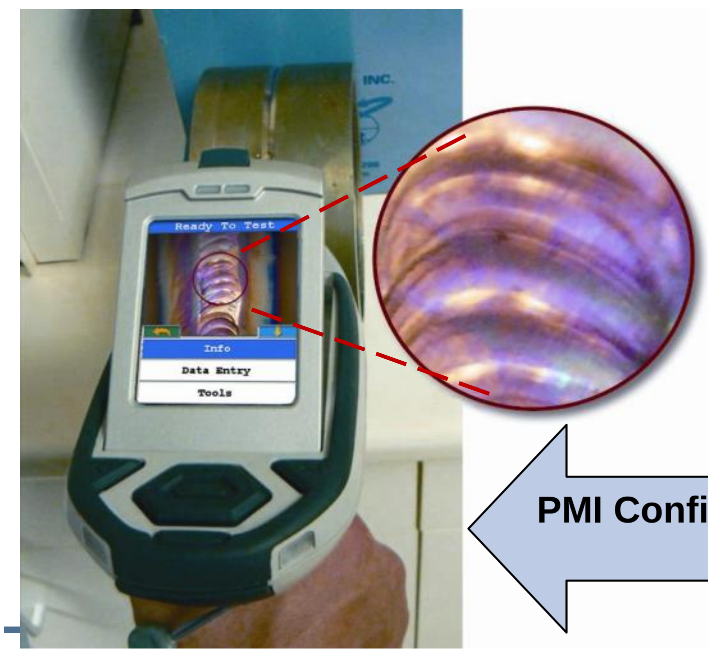
Refractory Anchors



- Refractory metal is available in hex steel grid, special grid and expanded metal. All material is available in stainless steel and grades T304, T316, T310, T330 as well as all of the standard grades.
- Other refractory insulation and refractory lining products include wire mesh, expanded metal mesh and hex steel grid. Contact us today for a quote.
- Refractory anchors and related materials are used for anchoring and assembling refractory ceramic fibre linings or for reinforcing monolithic linings of castables, plastics or ramming mixes

Table 11 - Maximum temperatures for anchor tips



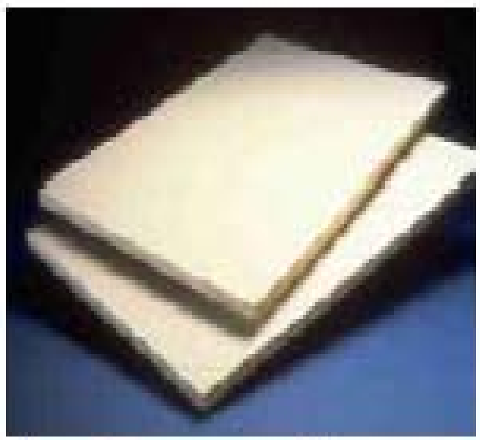


Anchor material	Maximum anchor temperature	
	'C	(OF)
Carbon steel	455	850
TP 304 stainless steel	760	1400
TP 316 stainless steel	760	1400
TP 309 stainless steel	815	1500
TP 310 stainless steel	927	1700
TP 330 stainless steel	1038	1900
Alloy 601 (UNS N06601)	1093	2000
Ceramic studs and washers	> 1093	> 2000

PMI Confirms the Correct Material is Installed for the Correct Temperature.

Refractory Brick PMI Inspection Possibilities



- How do you confirm on “Turn-a-rounds” and Maintenance the correct Refractory Material is properly replace ?
- Thermo Niton XRF can verify all refractory materials
  - Refractory anchors, tips, support materials
  - Refractory fibre
  - Refractory board
  - Refractory bricks

Other Features

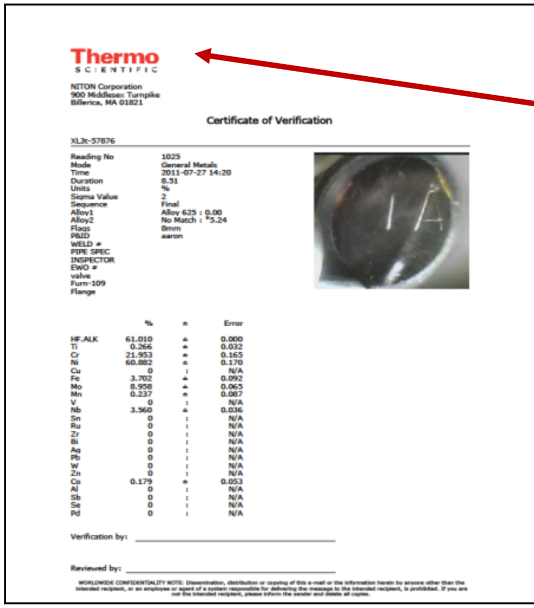
Other refinery applications

- Coating thickness
- Polymer analysis
- Gasket analysis
- Scaling and corrosion residue, deposits

Accessories

- Wireless Printer
- Barcode reader
- Portable Test Stand
- HotFoot
- Hotwork Standoff

Recording & Reporting PMI Test Results: API RP 578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NITON Corporation
900 Middlesex Turnpike
Billerica, MA 01821

Certificate of Verification

XL3t-57876

Reading No	1025
Mode	General Metals
Time	2011-07-27 14:20
Duration	8.51
Units	%
Sigma Value	2
Sequence	Final
Alloy1	Alloy 625 : 0.00
Alloy2	No Match : *5.24
Flags	8mm
P&ID	aaron
WELD #	
PIPE SPEC	
INSPECTOR	
EWO #	
valve	
Furn-109	
Flange	

	%	±	Error
HF.ALK	61.010	±	0.000
Ti	0.266	±	0.032
Cr	21.953	±	0.165
Ni	60.882	±	0.170
Cu	0	:	N/A
Fe	3.702	±	0.092
Mo	8.958	±	0.065
Mn	0.237	±	0.087
V	0	:	N/A
Nb	3.560	±	0.036
Sn	0	:	N/A
Ru	0	:	N/A
Zr	0	:	N/A
Bi	0	:	N/A
Ag	0	:	N/A
Pb	0	:	N/A
W	0	:	N/A
Zn	0	:	N/A
Co	0.179	±	0.053
Al	0	:	N/A
Sb	0	:	N/A
Se	0	:	N/A
Pd	0	:	N/A

Verification by: ______________________

Reviewed by: ______________________

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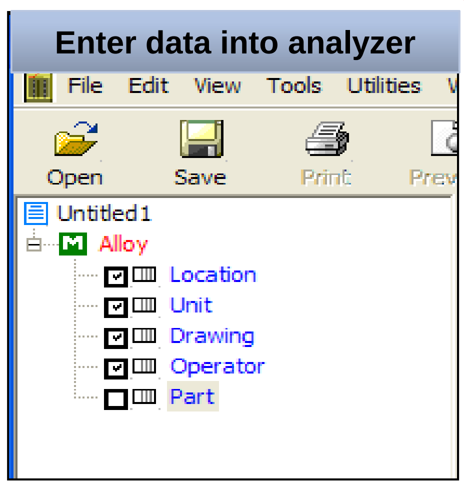
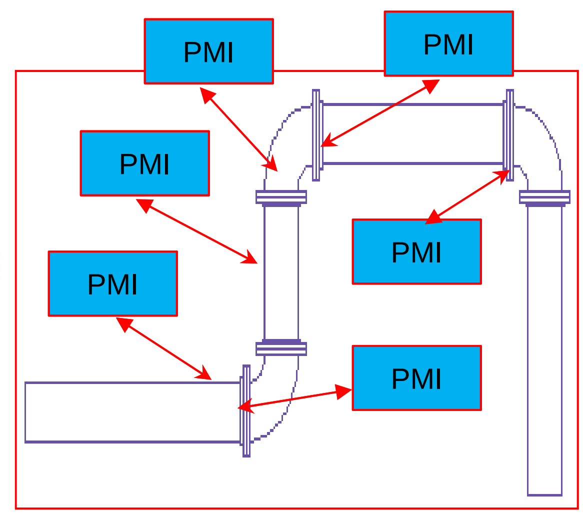
Traceability to field components; the **information listed in "PMI Test Records"** should be reported in such a manner that they are traceable to the point of installation.

The best way to tie the **"Report Documentation"** to the field **P&ID or ISO drawings**, is to mark the drawings (electronically or manually) and enter this (drawing number) in the XRF/OES analyzer.

It is strongly suggested that **you keep both paper and electronic files** on this documentation.





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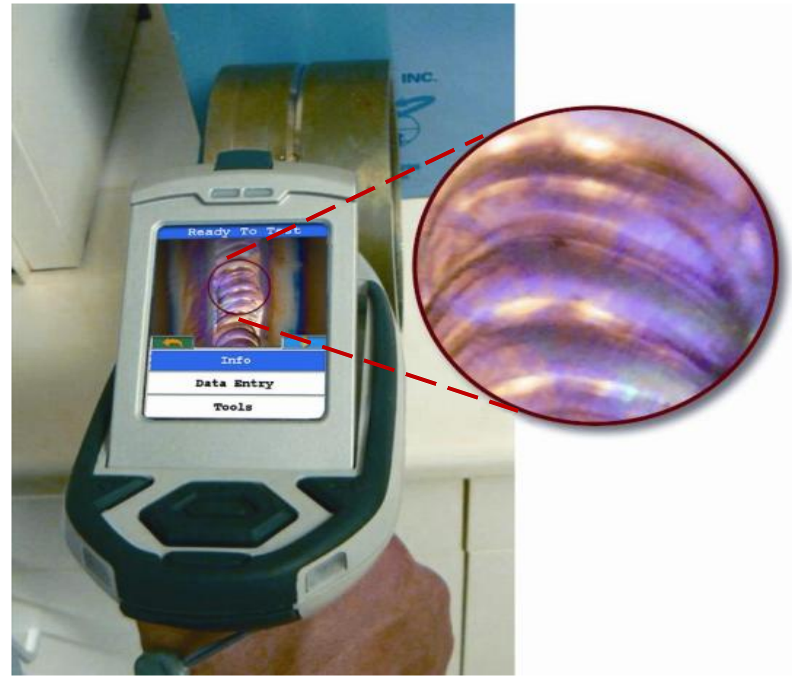
Camera and Small Spot Features

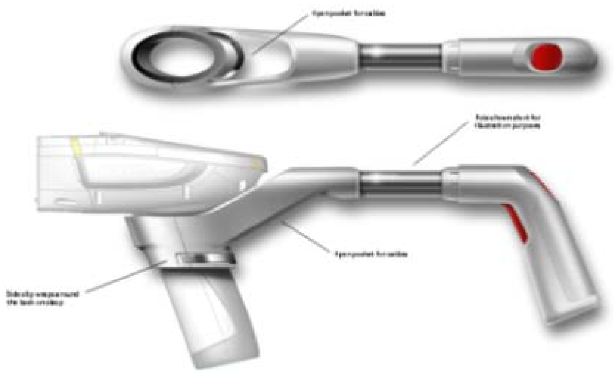
- The integrated color CCD camera & small spot, built into the nose of the analyzer
- Allow the user to
  - View a live picture of the analysis area,
  - Save the image along with the elemental analysis results and spectra.
- Here we are viewing a welded object through the lens of the Thermo Scientific Niton XL3t analyzer camera.



Contribution of filler material:	Contribution of Member A	Contribution of Member B
.70 x .70 = 49% Ni	.15 x .67 = 10% Ni	.15 x .08 = 1.2% Ni
.70 x .15 = 10.5% Cr	.15 x .32 = 4.8% Cu	.15 x .18 = 2.7% Cr
.70 x .08 = 5.6% Fe		.15 x .74 = 11.1% Fe

The final weld bead chemistry should be:
60.2% Ni (49% + 10% + 1.2%); 13.2% Cr (10.5% + 2.7%); 16.7% Fe (5.6% + 11.1%); and 4.8% Cu.

Field Use for Hot Pipes and Difficult Access



Extension Pole

- Variable pole length
- Dual Electronic Triggers
- Clip on Tri-Pod adapter for hands-free analysis of samples on ground or table

Niton XL3t *without* hot work standoff: <u>150ºC (max)</u>

Niton XL3t *with* hot work standoff: <u>500ºC (max)</u>

Niton XL3t with HotFoot™ hot surface adapter: <u>450º C</u> (max)