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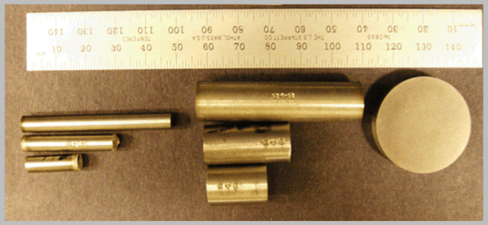

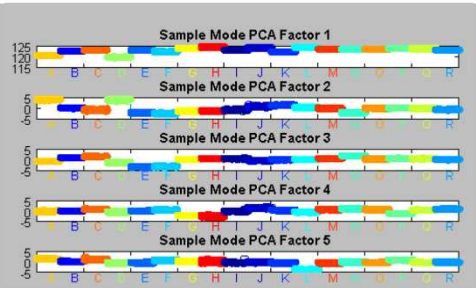

Materials Assurance through Orthogonal Materials Measurements

Curtis D. Mowry, Mark H. Van Benthem, Donald F. Susan, Mark A. Rodriguez, James J. M. Griego, Pin Yang, David Enos and Katherine Simonson

Sandia National Laboratories
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Abstract

Concern over counterfeiting or adulteration of products and materials is growing. Methods of assurance based solely on a material or product passing a performance requirement may fail to find an undesirable material change, whether unintentional or nefarious. Typical methods of assurance based on material composition may be undesirable because they require destructive testing or have low probability of detecting small material changes. We approach this problem from a different perspective: measure an orthogonal set of materials properties using multiple, simple, and non-destructive methods to build a material "signature", then utilize statistical models to test whether the material is what the provider purports it to be. Our method allows a range of applications from raw materials to finished parts. We will present results of this materials assurance scheme using over a dozen steels with varying composition. Discussion will include methods of data collection, data processing, and the ability to differentiate these steels non-destructively.

Definitions

- Materials
  - Context in this talk – stainless steels
  - “Raw” – vendor- or manufacturer-supplied (aka “as received”)
  - “Finished part” – value-added (machined, assembled, or cast)
- Assurance
  - “a positive declaration intended to give confidence”
  - “promise or pledge; guarantee, surety”
- Orthogonal
  - Pertaining to or involving right angles or perpendiculars
  - Statistically uncorrelated (i.e. zero covariance)

Motivation

- Why do we need materials assurance?
  - System performance (predictable & safe) and confidence
  - Errors, counterfeit, adulteration – people and products at risk
- It “passed” the specification – it must be good!
  - Specifications can often be broad, miss alterations
  - Criteria not always primary failure mode
  - Error, contamination, adulteration, or fraud may not be detected
- Why not make the specification more precise?
  - Cost (of manufacture and for verification testing)
  - Supplier pushback
- Just do more testing!
  - Cost, who validates, who performs, etc.

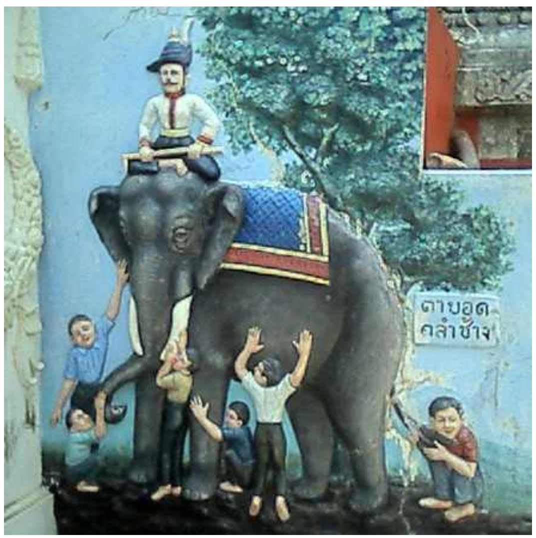
Consequences – "Specification" testing did not find problems or fraud

- 1. Specification test: nitrogen content or total protein
  - Dog food – passed // melamine used to spike N // deaths & hospitalization
  - Infant formula – passed // melamine used to spike N // deaths?
- 2. Specification test: nutritional, GMP
  - Infant supplements – passed // algae or mold undetected // illnesses
- 3. Specification test: NO_x emissions (while CO_2 testing)
  - Diesel vehicles – passed // software fraud // altered performance

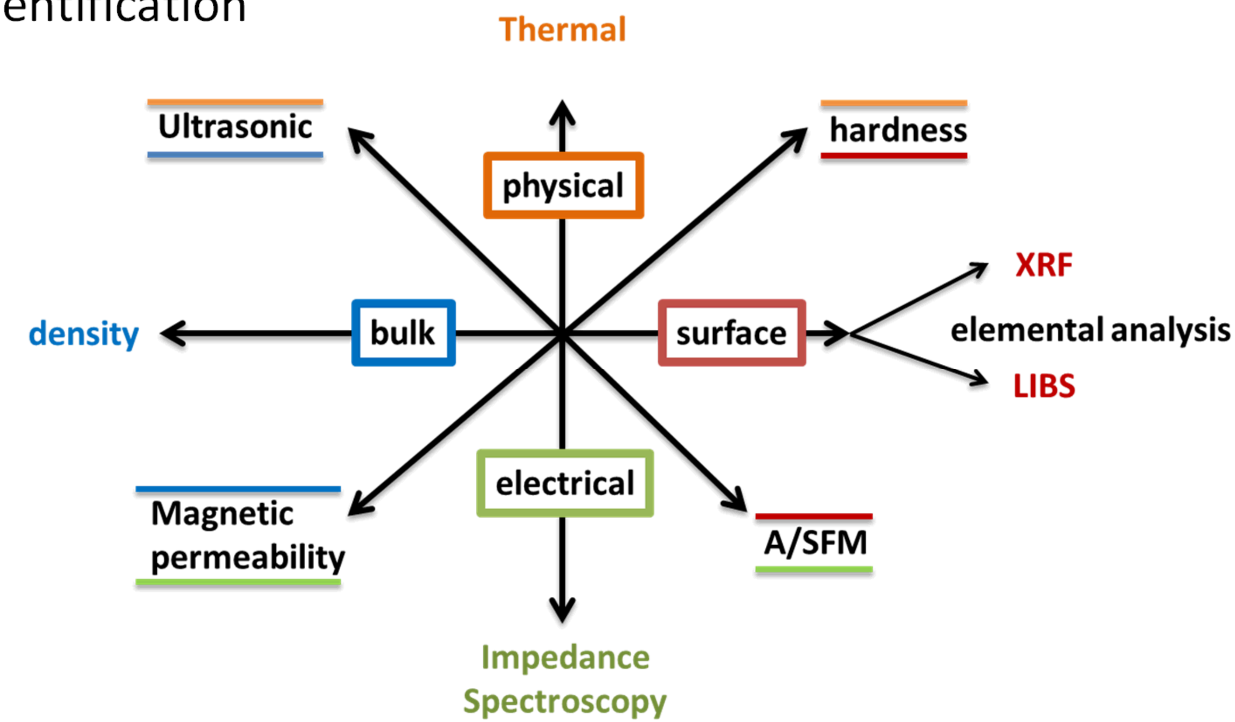
If you are looking "here" (total N) then you might be spoofed "there" (protein).

Concept – can we "fingerprint" by a rapid, cheap, nondestructive group of tests?

- **Ideal** measurements provide
  - Orthogonal property space (uncorrelated properties)
  - Confidence in identification



Buddhist/Hindu Fable



Goal – gain increased confidence of identity.

https://en.wikipedia.org/wiki/File:Blind.JPG – public domain photo

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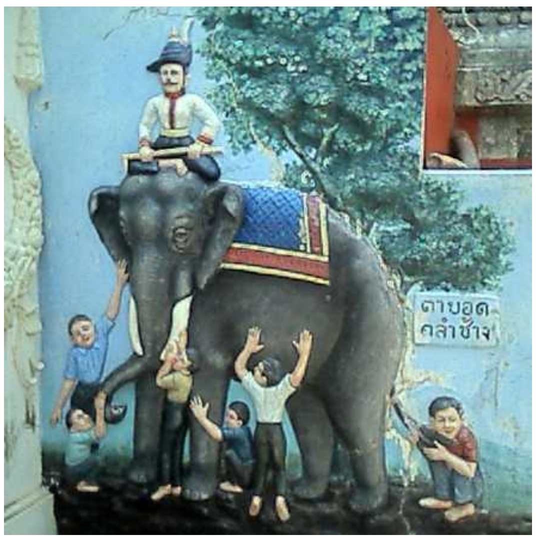

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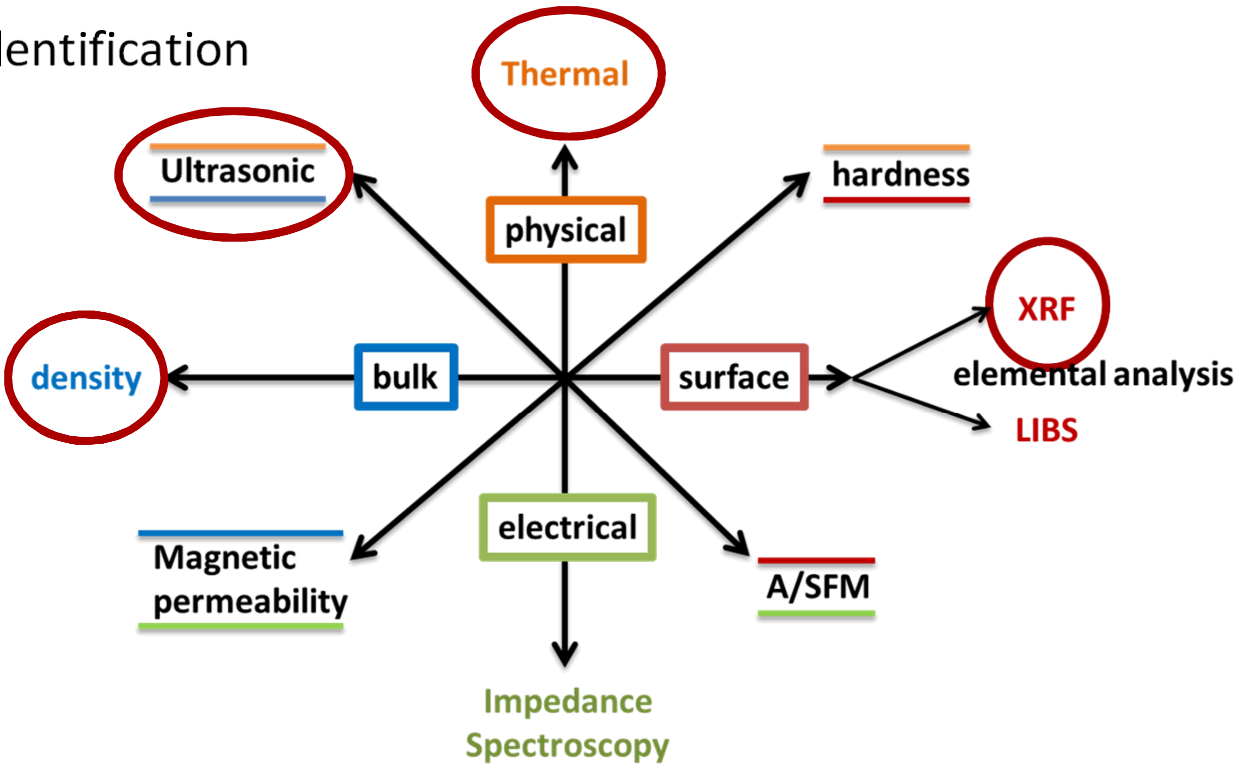

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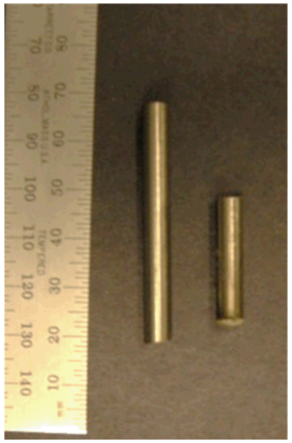
Steel samples with diversity of physical and chemical properties.

- All with certifications of chemical composition.

Sample ID	Type	Description
A	SRM	Cr 13 - Mo 0.9 modified AISI 410
B	SRM	Cr 18 - Ni 9 modified AISI 321
C	SRM	Cr 24 - Ni 13 modified AISI 309
D	SRM	Cr 9 - Mo 0.3 modified AISI 403
E	SRM	Cr 16.1 – Ni 9.9
F	SRM	Cr 18.5 – Ni 9.5
G	CarTech	316 Cr 17.6 – Ni 12.6
H	CarTech	316L Cr 17.5 – Ni 13.1
I	CarTech	866 type 303-Se Cr 17.8 – Ni 8.7
J	CarTech	type 347 #538 Cr 17.8 – Ni 9.9
K	BAS	Cr 15.2 – Ni 6.2
L	BAS	Cr 12.3 – Ni 12.6
M	BAS	Cr 18.3 – Ni 9.6
N	BAS	Cr 25.6 – Ni 20.7
O	BAS	Cr 18.0 – Ni 9.0
P	BAS	Cr 17.6 – Ni 8.7
Q	BAS	Cr 18.1 – Ni 9.0
R	BAS	Cr 18.7 – Ni 8.8



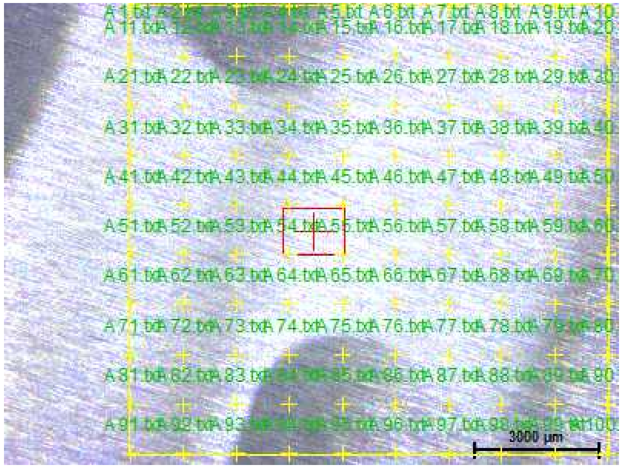
Test 1: XRF elemental analysis

- XRF (x-ray fluorescence)
  - Elemental analysis (>0.1% wt.)
  - Surface technique (~1um depth)
  - Fast, non-destructive

Bruker M4 Tornado m-XRF

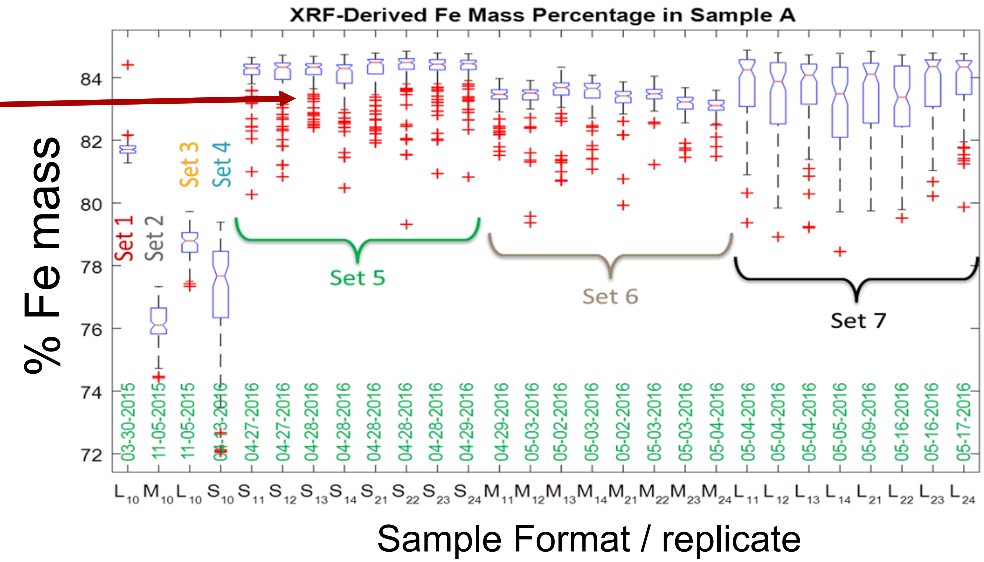
100 point measurements

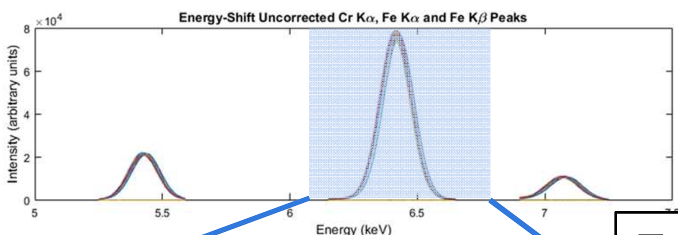
Rh X-ray source focused to 25um
each spot was measured for 30s
X-ray energy 50kV and 200uA
Chamber under vacuum at 19 mBar

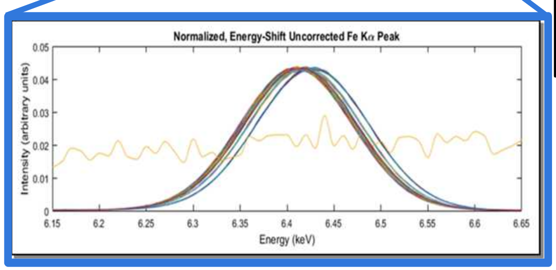


Instrument-reported XRF tabular data shows unexpected variance (“A”- 410 SS).

- Replicates of form factors showing unexpected variance.
- Instrument reports composition value based on internal calibration.
- Detector drift







Zoom of Fe Kα peak shows shift

Set 5

Set 6

Set 7

Shift of the energy axis is due to detector drift – instrument reports varying elemental content (sums to 100%).

Solution: processing full spectra removes drift yielding consistent replicates (“A”- 410 SS).

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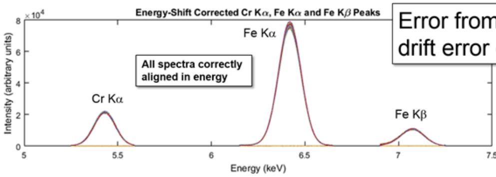
Spectral Shift Correction

- We employed the Cr Kα, Fe Kα, and Fe Kβ emission lines to derive a linear shift function and forced the Fe Kα peak at 6.404 keV to be intercept of the energy-axis correction function.
- We adjusted all spectra energy axes with this correction function.

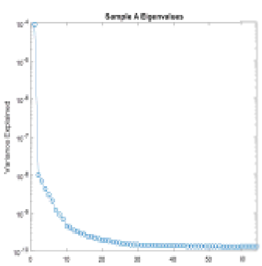


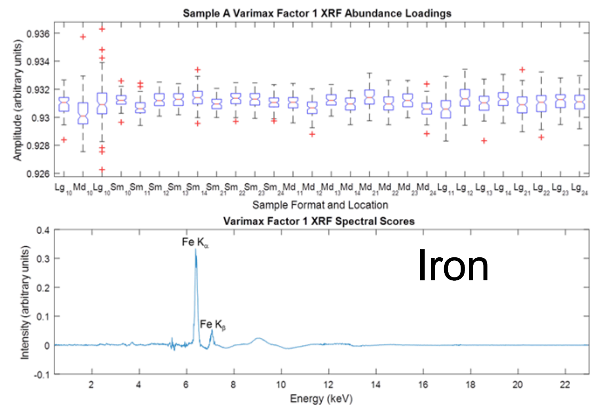
Error from detector drift error corrected!

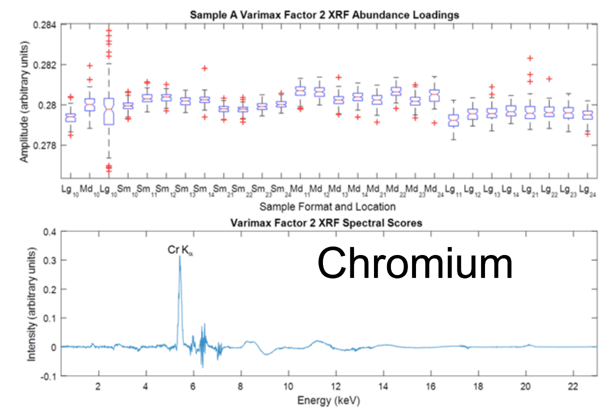
Corrected data ported to Principal Component Analysis routine in Matlab

Principal Component Analysis (PCA)

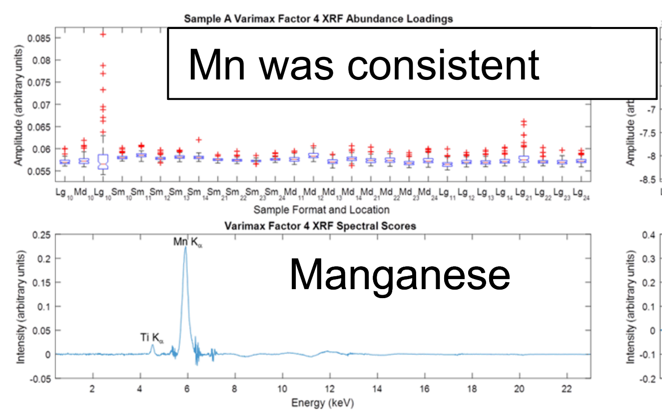
- Poisson-scale data, D
  - Compute mean in energy domain and create scaling matrix, H
    - $\bar{d}_m = \frac{1}{n}\mathbf{D}\mathbf{1}_n$, $\mathbf{H} = diag\left(\bar{d}_m^{-\frac{1}{2}}\right)$
  - Compute mean in observation domain and create scaling matrix, K
    - $\bar{d}_n = \frac{1}{m}\mathbf{1}_m\mathbf{D}$, $\mathbf{K} = diag\left(\bar{d}_n^{-\frac{1}{2}}\right)$
  - Scale the data
    - $\tilde{\mathbf{D}} = \mathbf{HDK}$
- Perform PCA and un-scale factors
  - $\tilde{\mathbf{T}}\tilde{\mathbf{P}}^{\mathrm{T}} = \tilde{\mathbf{D}}$
  - $\mathbf{T} = \mathbf{H}^{-1}\tilde{\mathbf{T}}$, $\mathbf{P} = \mathbf{K}^{-1}\tilde{\mathbf{P}}$
- Varimax Rotation of 9 PCA Factors
  - Rotate for spectral simplicity
  - Improves isolation of emission lines

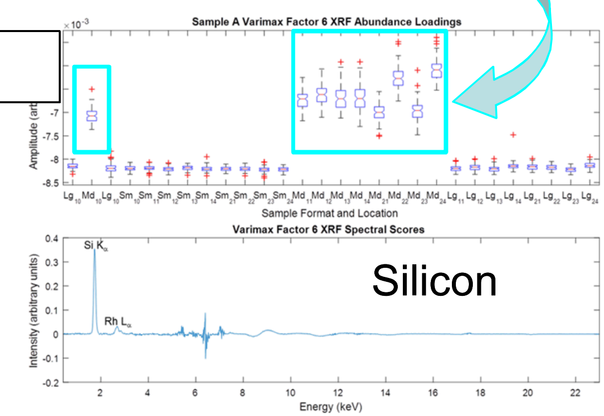






An interesting surprise! Md samples <u>clearly show higher Si content</u> even at low levels of concentration

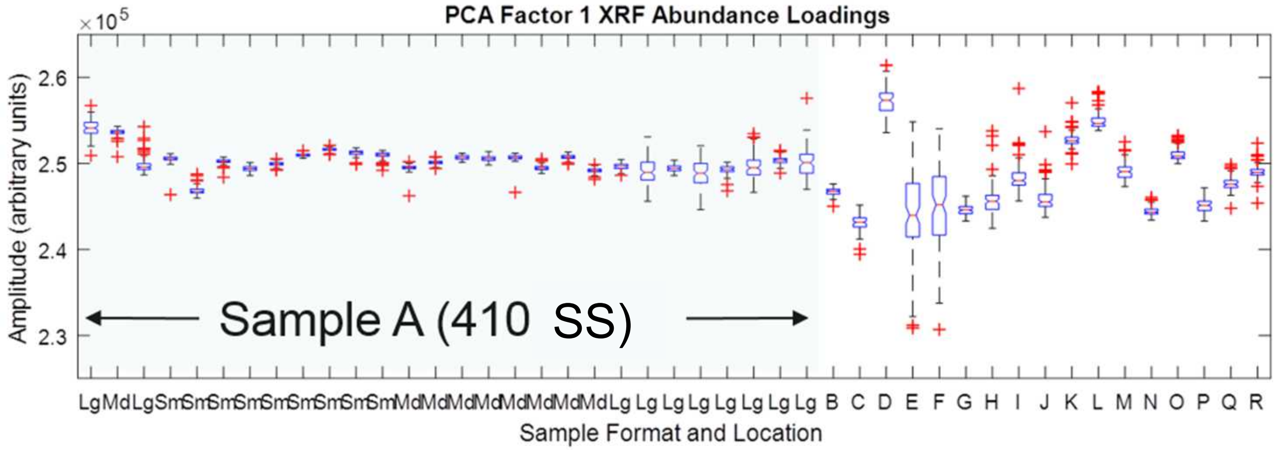




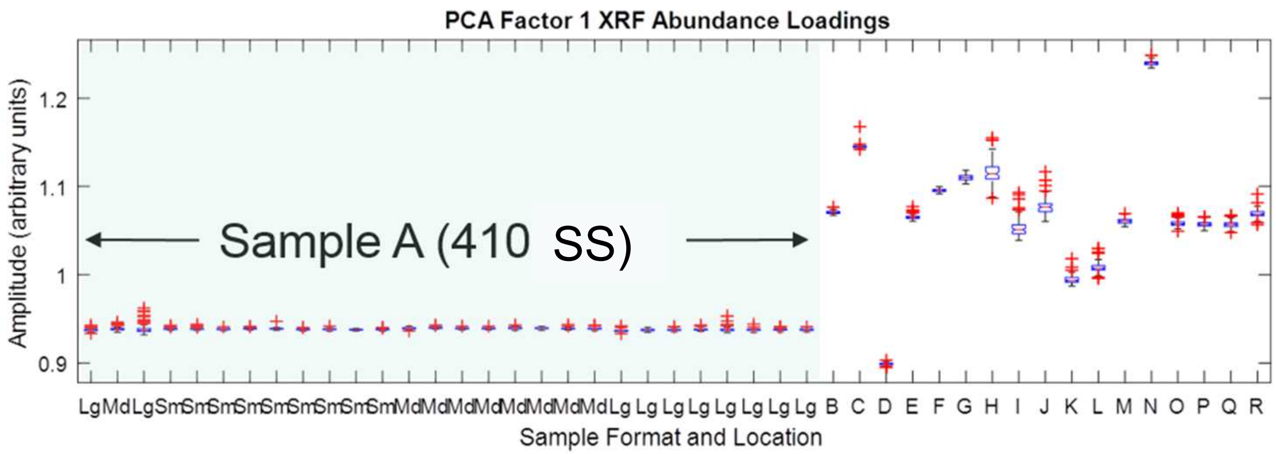
Using full XRF spectra resulted in uniform Fe, Cr composition.

PCA of corrected XRF spectra gives better consistency and differentiation.

Using just XRF spectra to assess alloy differentiation.



Without correction of XRF composition: large variation of replicates.



WITH correction of XRF composition: consistent composition and smaller variance for all steels.

Tests 2-6: Density, Sound Velocity (SV), Heat Capacity (Cp), Coefficient of Thermal Expansion (CTE)

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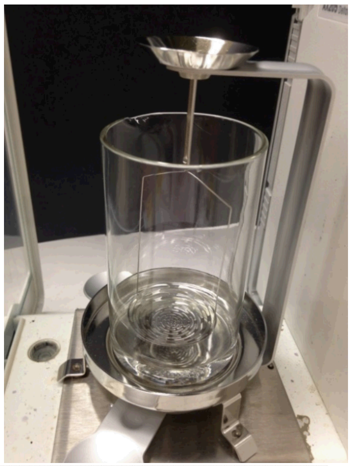
Density



Archimedes Balance

- **Mettler-Toledo AE160 balance**
- **MS-DNY-43 density kit**

$$\rho = \frac{A}{A\text{-}B}(\rho_0 - \rho_L) + \rho_L$$

Sound Velocity

- **2.25 MHz, 5 MHz Panametric - NDT single element longitudinal and shear wave transducers.**
- **Olympus Panametrics –NDT model 5800 computer controlled Pulse/Receiver**

Heat Capacity

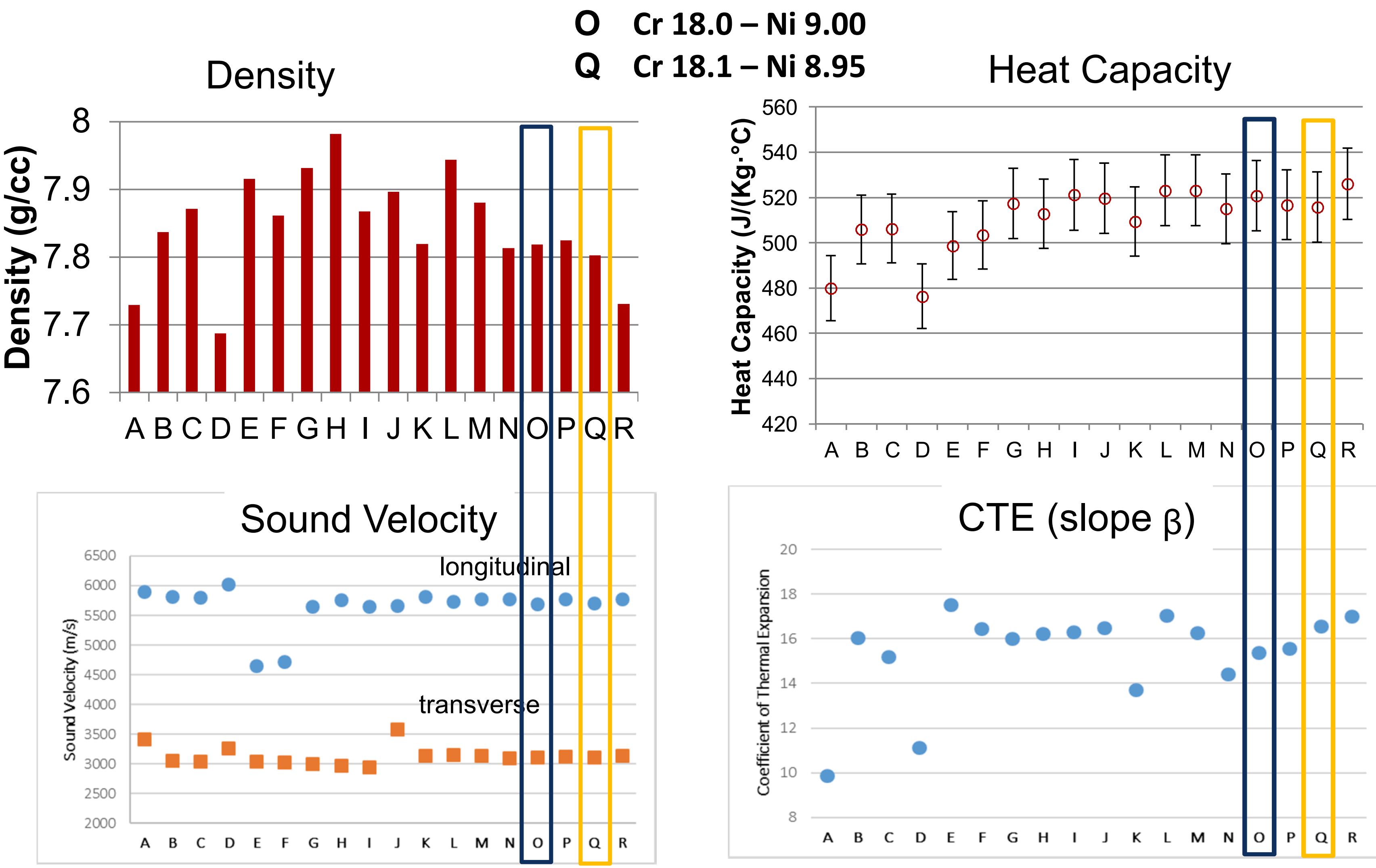
- **Netzsch LFA 467**

CTE

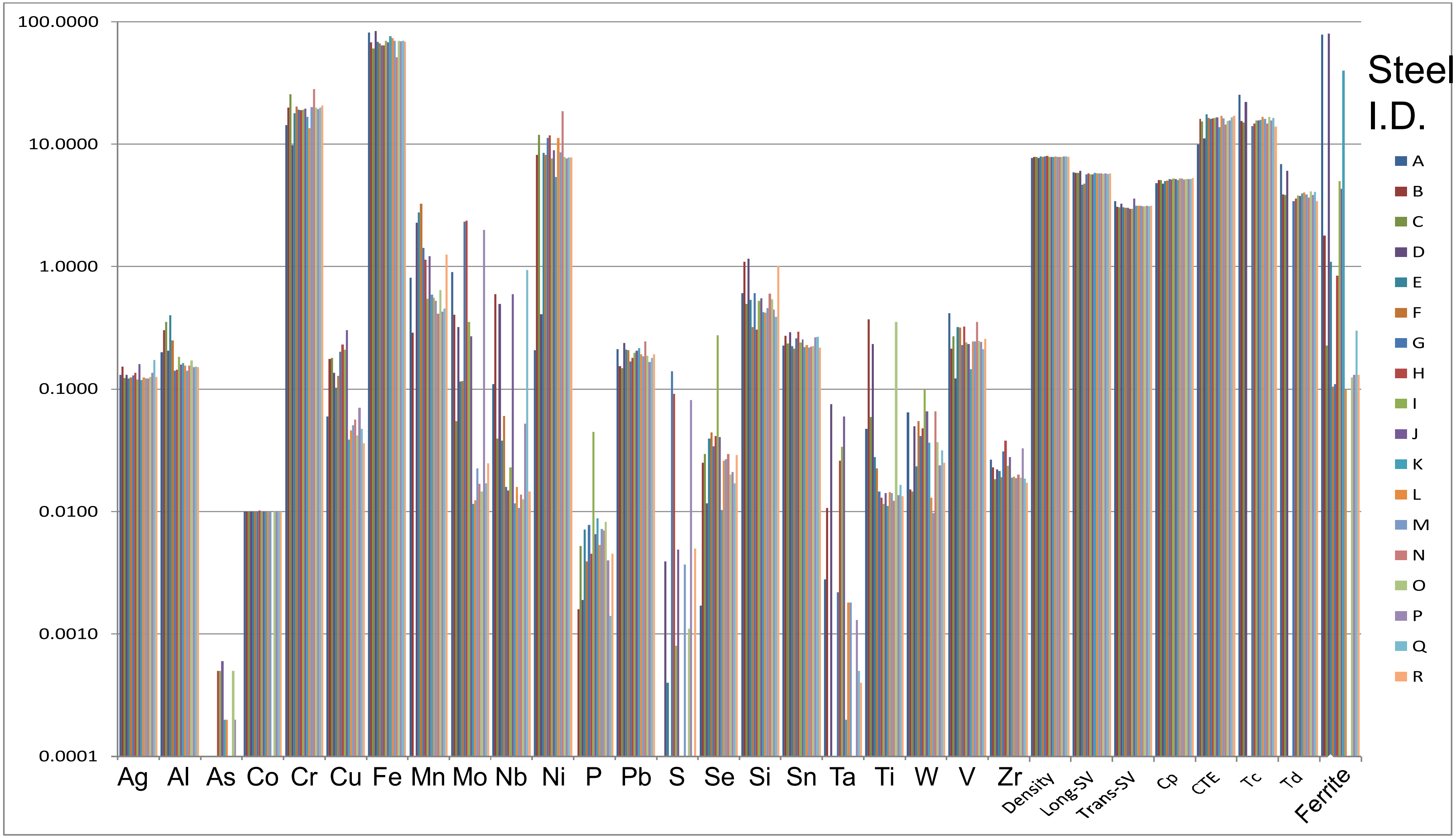
- **Thermomechanical Analyzer (TMA)**
- **Volumetric measurement – change of physical dimension as a function of temperature.**
- **Model: TA TMA Q400 (with cold stage)**
- **Temperature Range: -50 to 125°C**
- **Heating rate: 3°C/min.**

ρ= density, A: weight in air, B: weight in liquid, ρ_0 & ρ_L density of liquid and air

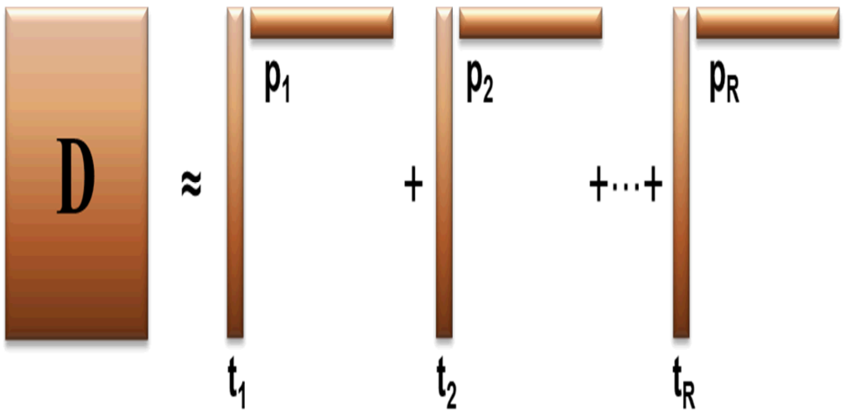
Results: Density, SV, Cp, CTE – building a fingerprint.



Full data set with elemental composition



Factor analysis of combined data set uses PCA followed by MCR



- Principal Component Analysis (PCA)
  - Given a matrix containing data, D, as a first step in many analyses we want principal components

$$D \cong TP^T$$

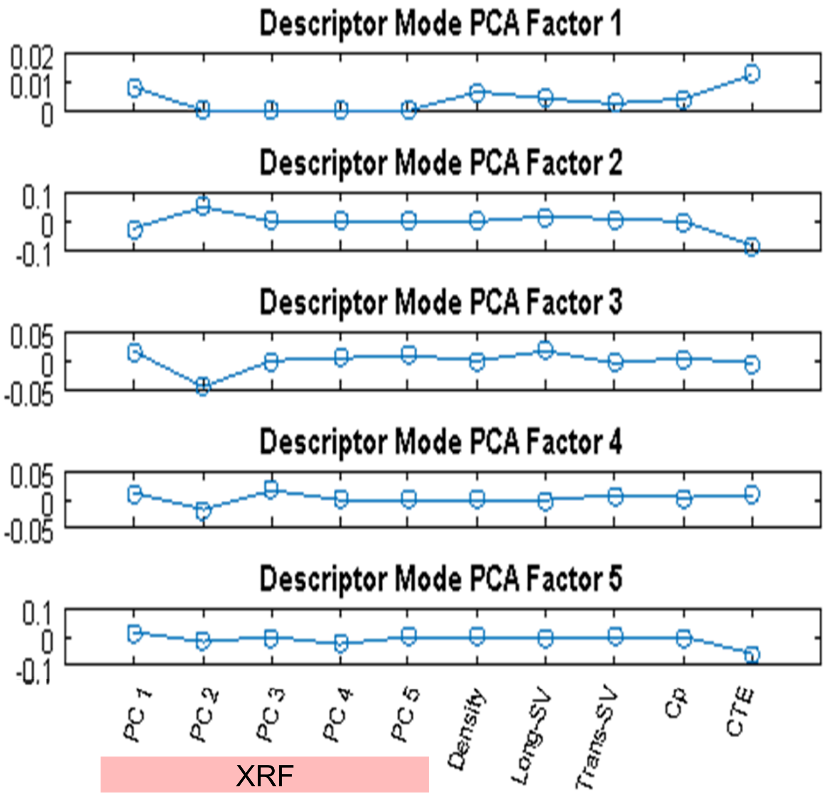
  - Such that T and P are an orthogonal basis sets, that is a reduced dimensional representation of D, with ordered maximized variance.
    - T is orthogonal (scores); P is orthonormal (loadings).
- Multivariate Curve Resolution (MCR)
  - Impose constraints on solution space
  - Nonnegative matrix factorization

Replicate values for density, sound velocities (SV) (×0.01), heat capacity (Cp), and coefficient of thermal expansion (CTE) (×0.1) were simulated using means and standard deviations from random normal distribution.

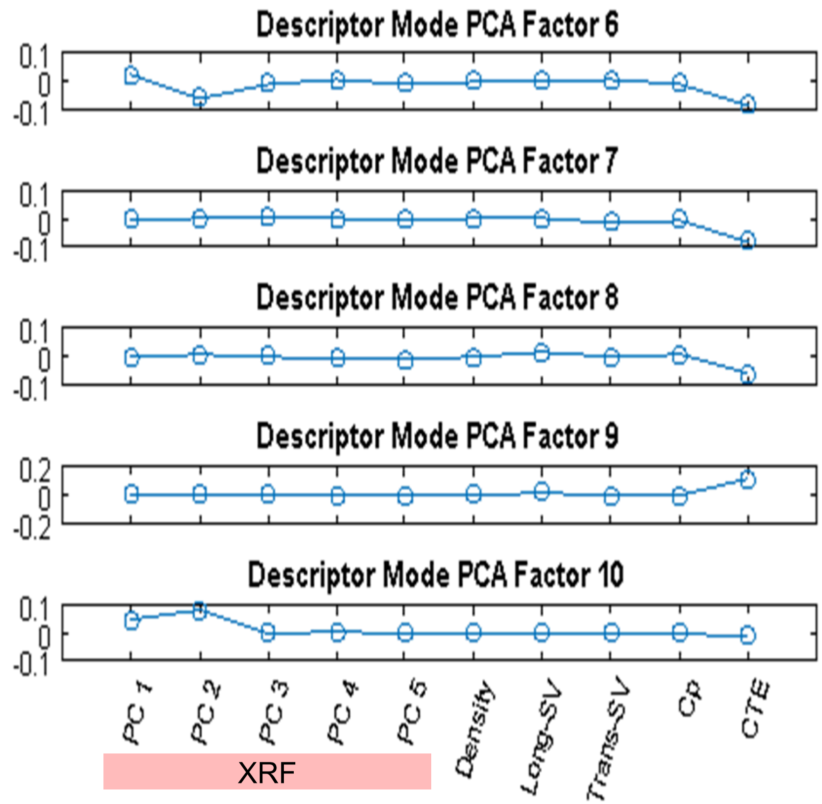
Data used in the present one-class classification scheme omits As, Co, S, and Ta elemental data due to limited incidence in steel samples. Due to missing values for thermal diffusivity (Td) and thermal conductivity (Tc) and ferrite content, these are also omitted.

1. M. R. Keenan, [Multivariate Analysis of Spectral Images Composed of Count Data] John Wiley & Sons, Ltd, Chichester, West Sussex, England(2007).

Combined data analysis: matrix factor results to maximize differentiation



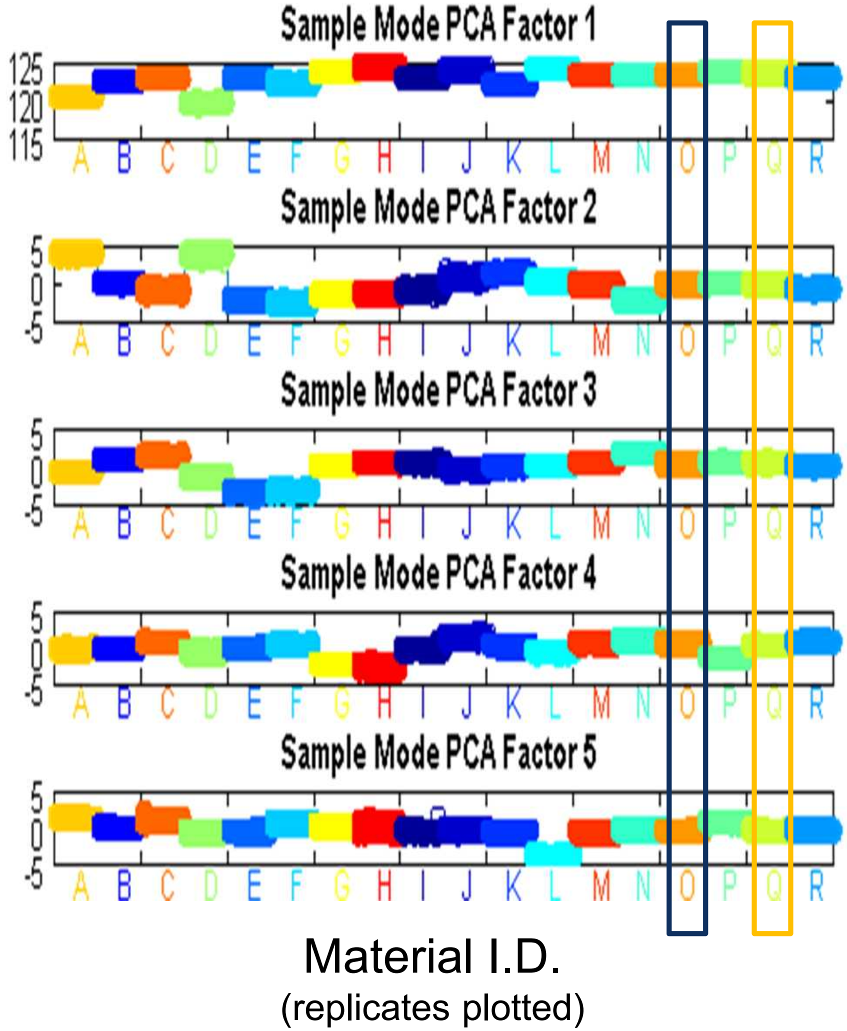
Components (based on tests)

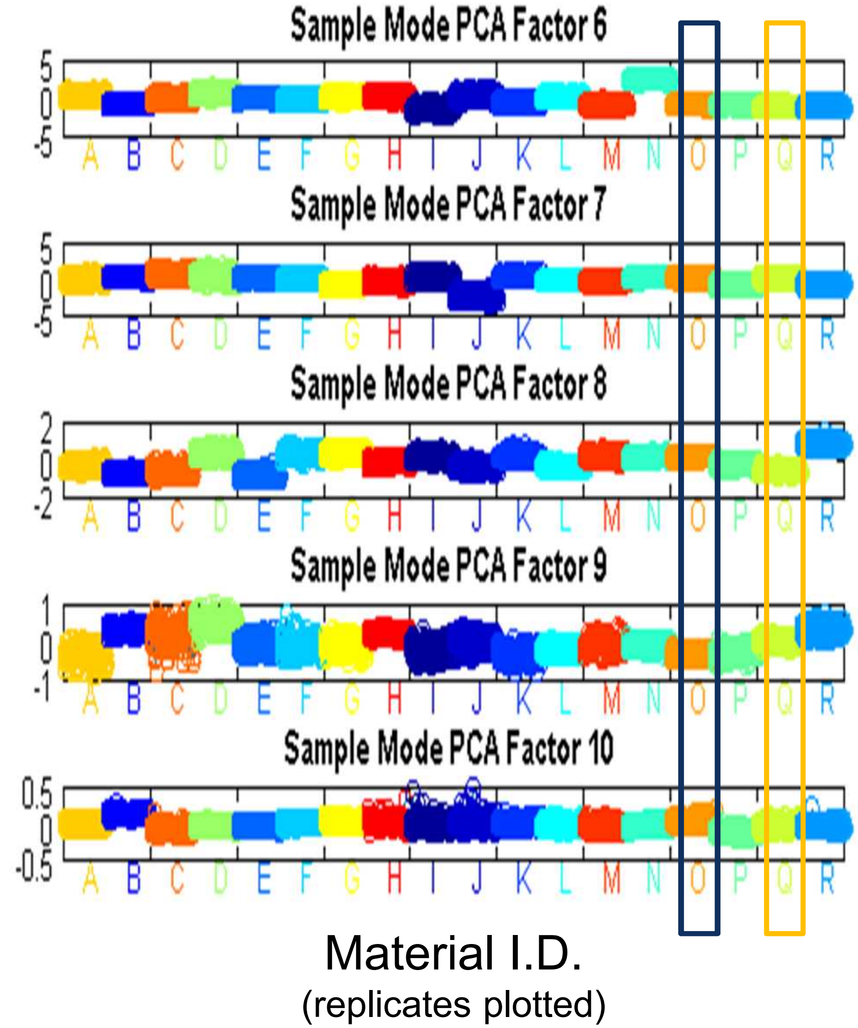


Components (based on tests)

Plots show relative contribution of each test to each PCA factor.

Combined Data Analysis: a look at sample replicates





Target prediction rates using descriptors and cross-validation – can we classify?

Target Prediction Rates for Steels (% True Positives) – "fingerprint is robust"

Steel Sample ID																	
A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
95	92	96	94	96	96	96	93	96	95	95	94	97	93	93	94	94	95

Non-target Prediction Rates (% False Positives) – "possibility of being spoofed"

Steel Sample ID																	
A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

	Steel Sample ID																	
Factors used in feature fusion	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**	**K**	**L**	**M**	**N**	**O**	**P**	**Q**	**R**
	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	2	3	2	2	2	2	2	2	2	2	2	2	2	2	2	3	2	2
	3	4	3	3	3	3	3	4	3	3	3	3	3	3	3	4	4	4
	4	5	4	4	4	4	4	8	4	4	4	4	4	4	4	5	6	7
	5	10	5	6	6	5	5	9	6	7	6	5	7	6	9	7	8	8

Summary and Conclusion

- Summary
  - Goal: to achieve a classification method based on a series of simple, non-destructive tests
  - We used 6 simple measurements (XRF, density, acoustic (2 modes), Cp, and CTE) to define a material “fingerprint” on 19 stainless steels
    - All non-destructive; 2 tests are currently size independent
    - 4 tests require alternate instrumentation for size independence
    - Determined and eliminated XRF limitation to reduce variance
- Conclusion
  - Through the use of PCA, we developed a one-class classifier which is able to identify materials within the population to greater than 93% success probability, with no false positives.

Future Work and Acknowledgements

- Future Work
  - Measuring more alloys with smaller compositional differences
  - Measurements of hardened or surface treated
  - Include more tests
- Acknowledgements

<u>Measurements</u>

Micah Ohlhausen, Adam Pimentel	Density
Daniel Stefan	Sound Velocity
Peter Duran	CTE, Ferritescope

- The Sandia National Laboratories Laboratory Directed Research and Development (LDRD) program provided funding for this project.
- Sandia is a multiprogram laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Composition as per certificates of analysis provided with standards.

	Fe	Cr	Ni	Mn	Si	Cu	V	Mo	Sn	Co	C	B	Nb	P	S	Ti	Pb	As	Ta	Ag	Se
A	83.2	13.31	0.28	0.77	0.52	0.065		0.92			0.06-0.1		0.11	0.02-0.03	0.01-0.02						
B	68.8	18.35	9.11	0.53	1.19	0.19		0.43			0.06-0.1		0.6	0.02-0.03	0.01-0.02						
C	61.8	23.72	13.26	0.23	0.37	0.19		0.059			0.06-0.1		0.03	0.02-0.03	0.01-0.02						
D	85.3	9.09	0.52	2.13	1.25	0.16		0.33			0.06-0.1		0.49	0.02-0.03	0.01-0.02						
E	70.5	16.1	9.9	2.88		0.11	0.032	0.12	0.0035	0.13		0.0005	0.032			0.002	0.0017				
F	68.1	18.5	9.4	3.38		0.14	0.064	0.12	0.006	0.12		0.0012	0.056			0.003	0.0025				
G	64.42	17.60	12.61	1.67	0.69	0.25	0.051	2.45	0.006	0.14	0.061			0.029	0.023		0.001			5E-04	
H	64.53	17.45	13.12	1.34	0.3	0.25	0.07	2.44		0.43	0.018			0.028	0.022						
I	71.00	17.75	8.68	0.75	0.59	0.23		0.37		0.17	0.050			0.14	0.008						0.26
J	68.77	17.8	9.9	1.40	0.63	0.35	0.07	0.28		0.13	0.043		0.61	0.017	0.002						
K	77.45	15.2	6.16	0.64	0.44						0.082			0.013	0.017		0.0007	.011			
L	73.77	12.35	12.55	0.74	0.46						0.092			0.010	0.018		0.0005	.007			
M	70.65	18.30	9.65	0.77	0.51						0.088			0.015	0.017						
N	51.96	25.75	20.70	0.77	0.64					0.054	0.100			0.016	0.010		0.0005	.003			
O	71.02	18.00	9.00	0.9	0.59	0.03	0.04			0.022	0.073			0.011	0.016	0.30					
P	70.12	17.60	8.70	0.66	0.5			2.21	0.006		0.074		0.05	0.050	0.021		0.0014	.01	<0.001		
Q	70.71	18.05	8.95	0.68	0.45						0.069		1.06	0.015	0.019				0.0018		
R	69.61	18.7	8.85	1.47	1.14					0.034	0.152			0.016	0.026						

Red values calculated by difference.