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Analyzing a Combinatorial Pt:Ru Library for Differentiating Sugars in Solution Using Multivariate Data Analysis

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Workshop on Coupled Multielectrode Array Systems for Corrosion Monitoring and Electrochemical Studies

Technology Exchange Group 316X

Gaylord Opryland Resort and Convention Center

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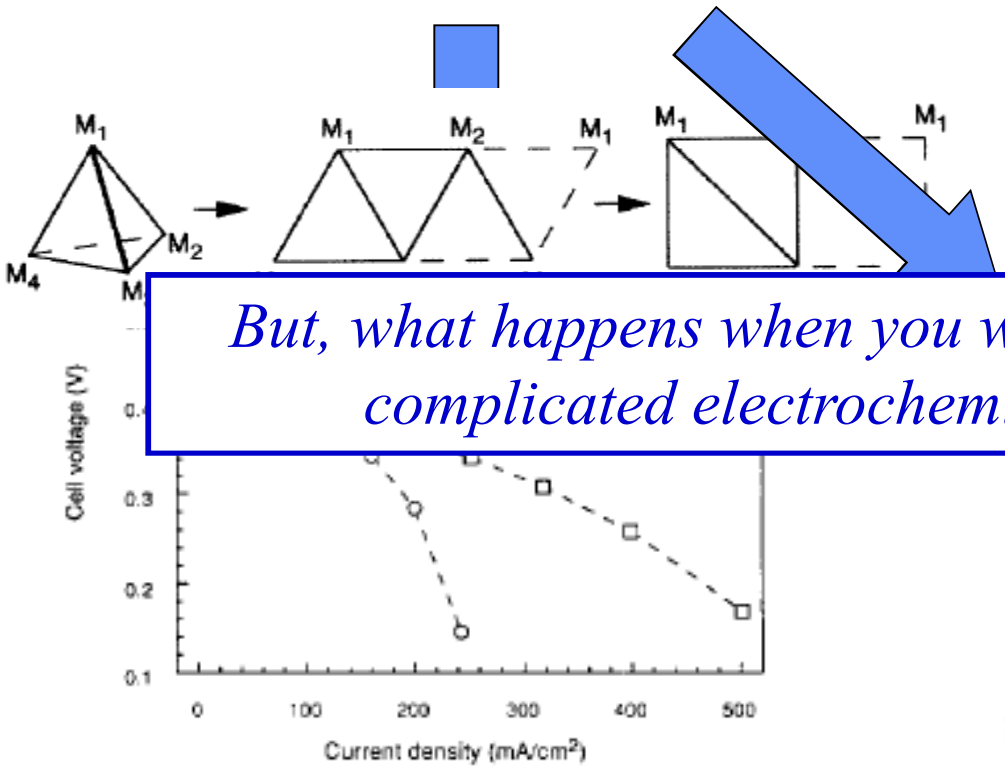
Combinatorial electrocatalyst synthesis differs from first principle type appoaches; the challenge is the screening method



But, what happens when you want to look at more complicated electrochemical data sets?

- Combinatorial synthesis first used in pharmaceutical industry (10^5 assays per day)
- Create large libraries of samples
- Challenge 1: creating library
  - roaches
  - rinters
- Challenge 2: sample screening
  - Electrochemical (usually very simple)
  - Optical / Spectroscopic

Chen et al, *JES*, **149** (8), 2002
Reddington et al, *Science*, pg. 1735-1737, 1998

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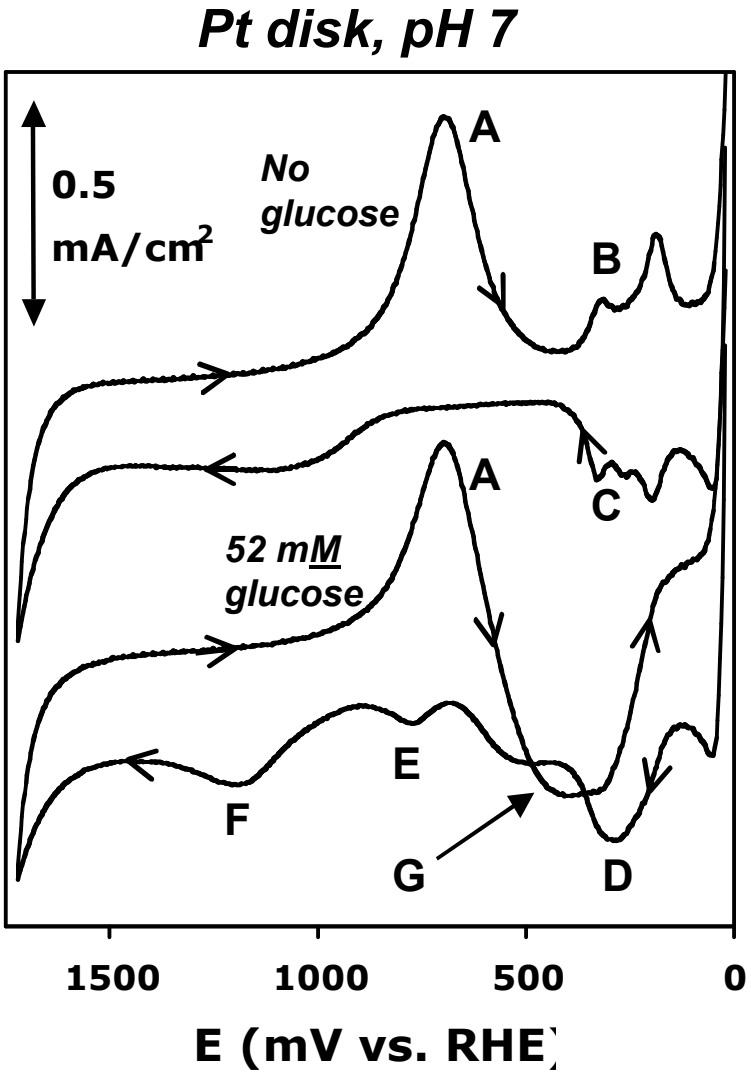
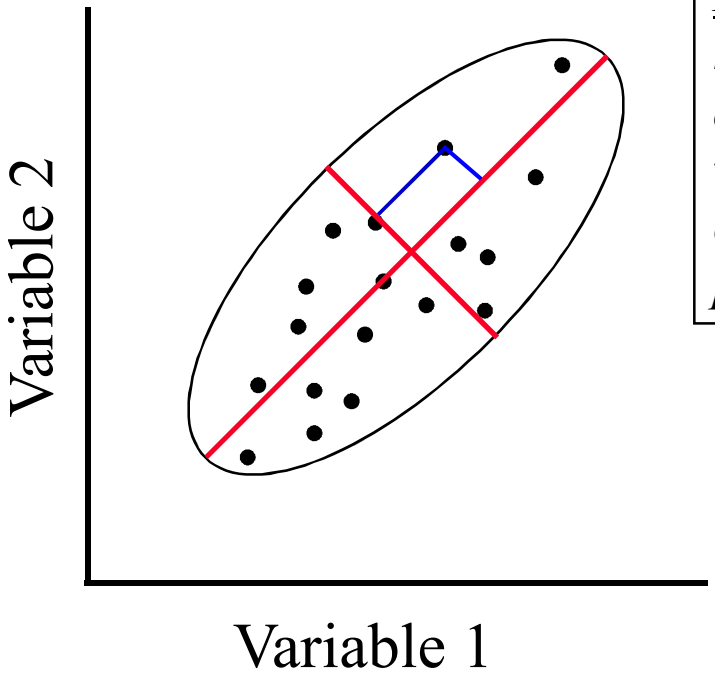
Complicated Electrochemistry: Glucose oxidation. Glucose electrochemistry is important for medical applications, sensing, for use as a fuel.



A	Pt surface oxide reduction
B	Deposition of adsorbed H
C	Oxidation of adsorbed H
D	$Pt\text{-}H + OH^- \rightarrow Pt + H_2O + e^-$
	$Pt + glucose + OH^- \rightarrow Pt\text{-}glucose_{ads} + H_2O + e^-$
E, F	$Pt\text{-}glucose_{ads} \rightarrow Pt\text{-}gluconolactone_{ads} + H^+ + e^-$
	$Pt + OH^- \rightarrow Pt(OH)_{ads} + e^-$
G	$Pt\text{-}gluconolactone_{ads} + Pt(OH)_{ads} \rightarrow gluconate + H^+ + 2Pt$

All regions are important; analysis of a library would quickly become unmanageable. How would you quantify all the important features?

Multivariate Data Analysis: A brief tutorial of Principal Component Analysis (PCA)



Definition: *PCA reduces the dimensionality of multivariate datasets (simplifying them) by transforming data into a new coordinate system such that the greatest variance lies on the first coordinate (first principal component), the second greatest variance on the second principal component, and so on.*

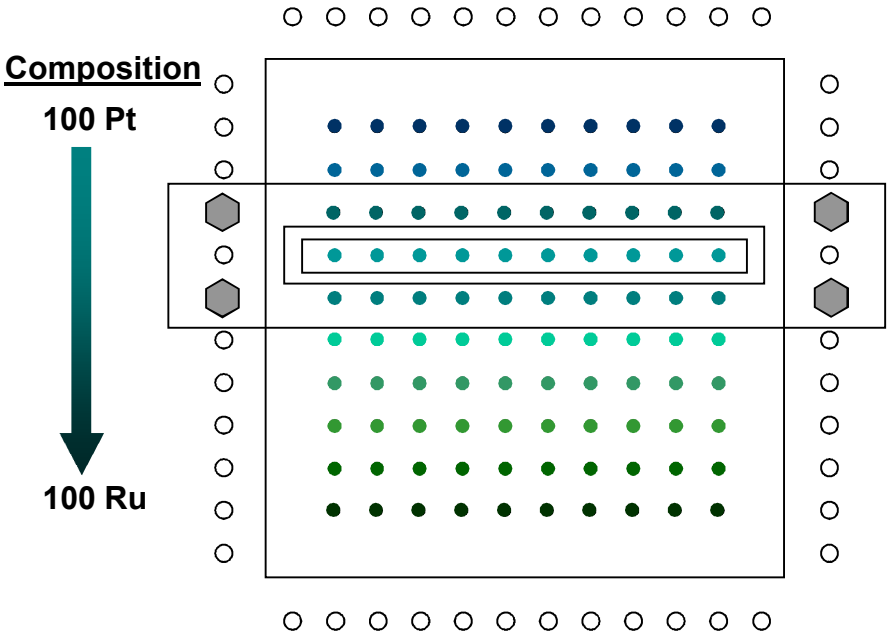
Vector with greatest variance (loading vector, p_1)
Integer value (principal component score, t_1)
Vector with 2nd most variance (loading vector, p2)
Integer value (principal component score, t_2)

$$\mathbf{X} = \mathbf{t}_1\mathbf{p}_1^T + \mathbf{t}_2\mathbf{p}_2^T$$

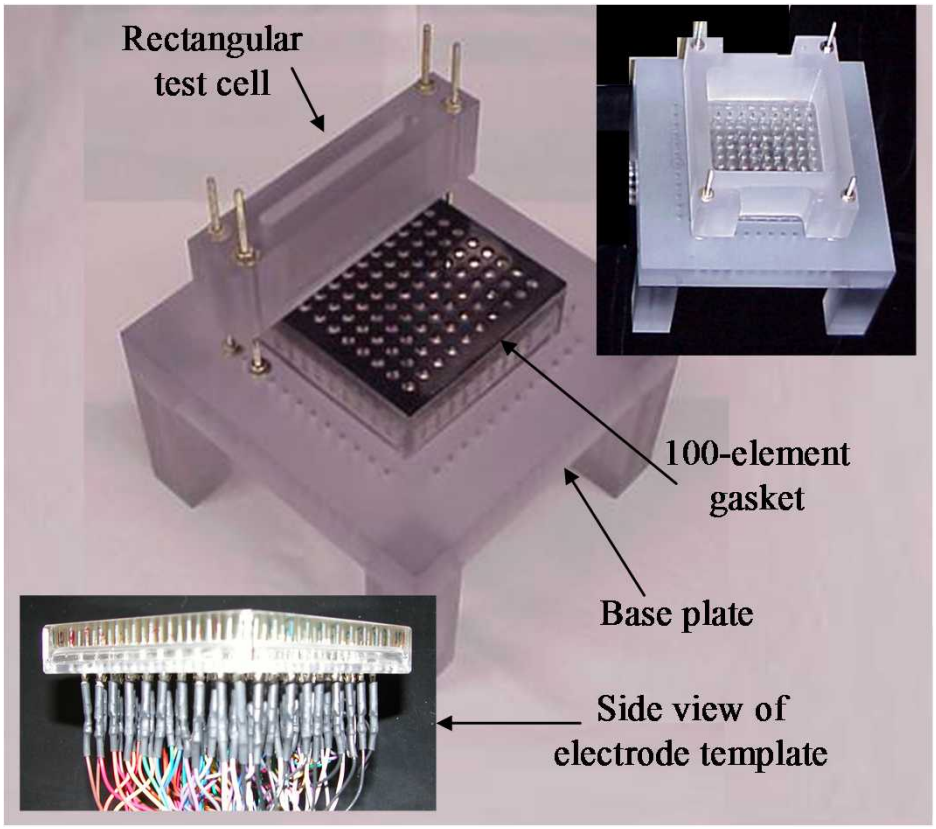
Now imagine not just two variables, but many thousands!

$$\mathbf{X} = \mathbf{T}_k\mathbf{P}_k^T + \mathbf{E}$$

Approach: Electrodeposit variants onto 10x10 array of Pt rods & test in sugar solutions



Pt rod diameter = 1mm



Electrodeposit Pt:Ru alloys in different rows, test all elements in parallel with 100 channel potentiostat

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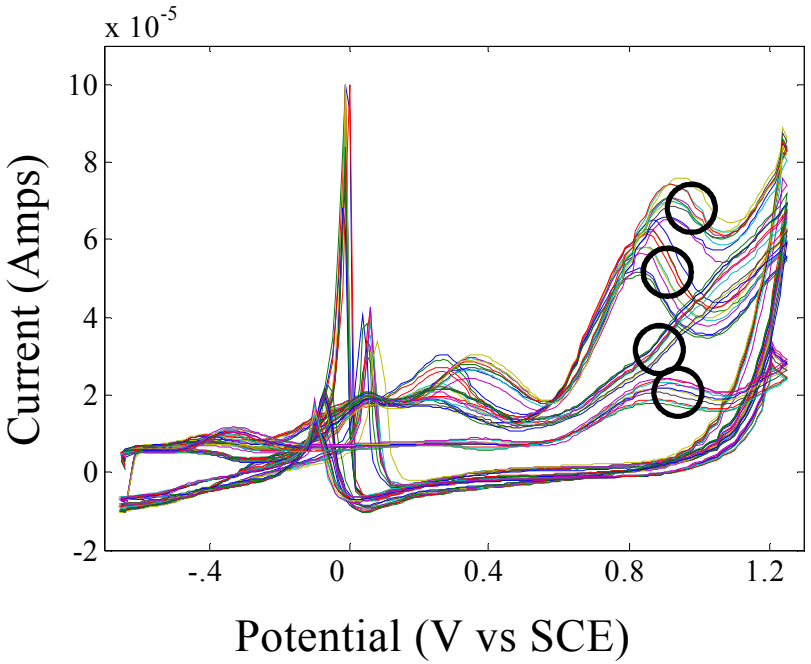
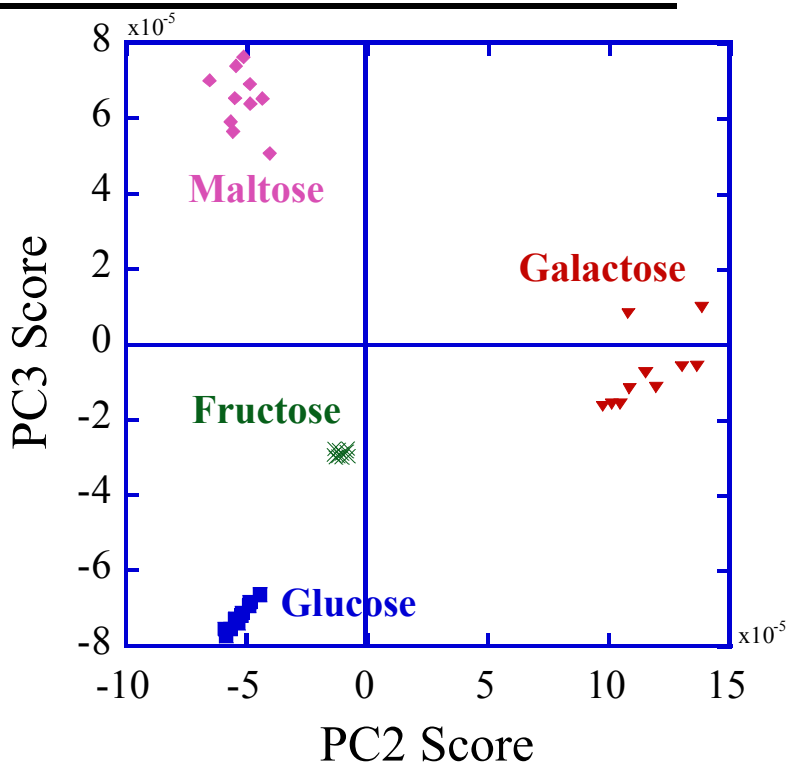
Apply PCA to one row of electrodes and perform cyclic voltammetry experiments in 1M solutions containing a single sugar



PCA



The ten duplicates group with one another and each sugar is in a different area of the scores plot – the data is classified (an "electrochemical tongue")

"Electrochemical Tongue" coined by: C. Krantz-Rulcker, M. Stenberg, F. Winquist, and I. Lundstrom, *Analytica Chimica Acta,* **426**, 217, (2001).

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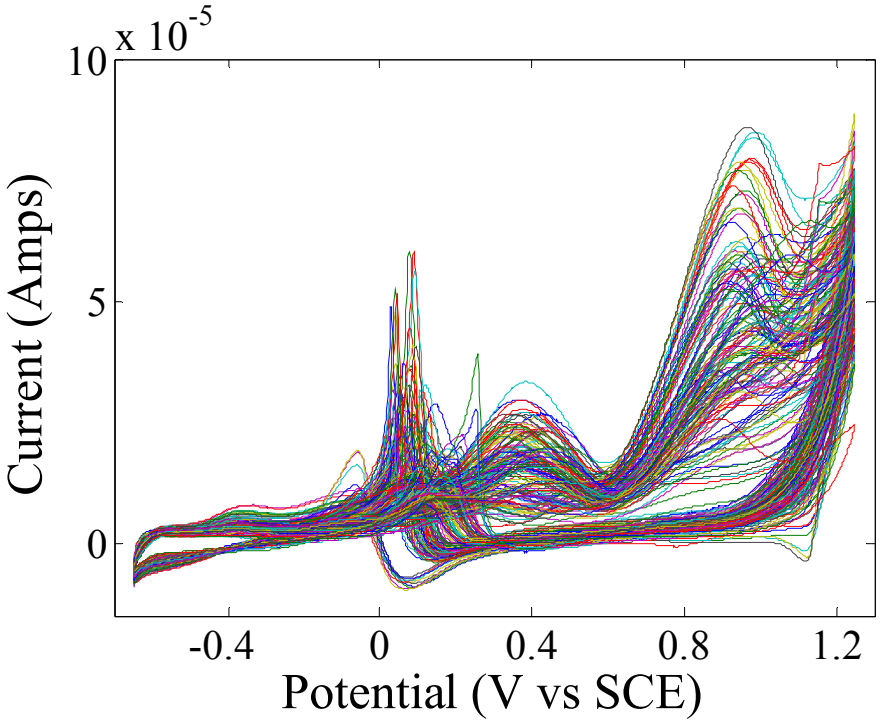
Acquire data from all 100 library members over mixed monosaccharide solutions; towards electrochemical sensing



$$RMSECV = \sqrt{\frac{\sum_{i=1}^{m}(\hat{y}_i - y_i)^2}{m}}$$

- 3-factor, 5-level design of experiments resulted in 15 training solutions
- Training solutions contain between 10mM and 1M glucose, fructose, and galactose
- Partial least squares (PLS) regression model built for each sugar
  - $RMSECV_{glucose}$ = 152mM
  - $RMSECV_{galactose}$ = 184mM
  - $RMSECV_{fructose}$ = 133mM
  - 70 – 99% of variance captured in 4 or 5 principal components (model dependent) reducing data sets from 1000's of variables
- 12 test solutions were tested, and their concentrations predicted using the PCR model

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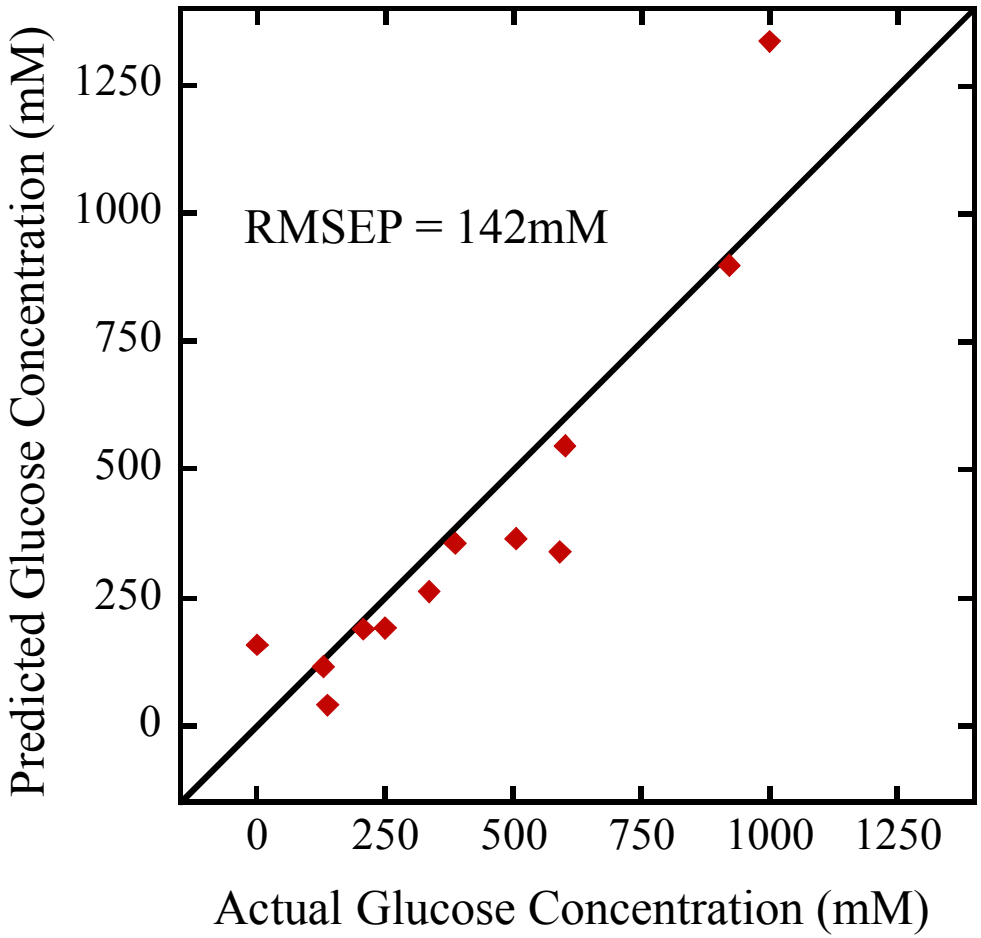
Glucose was well predicted aside from one statistical outlier



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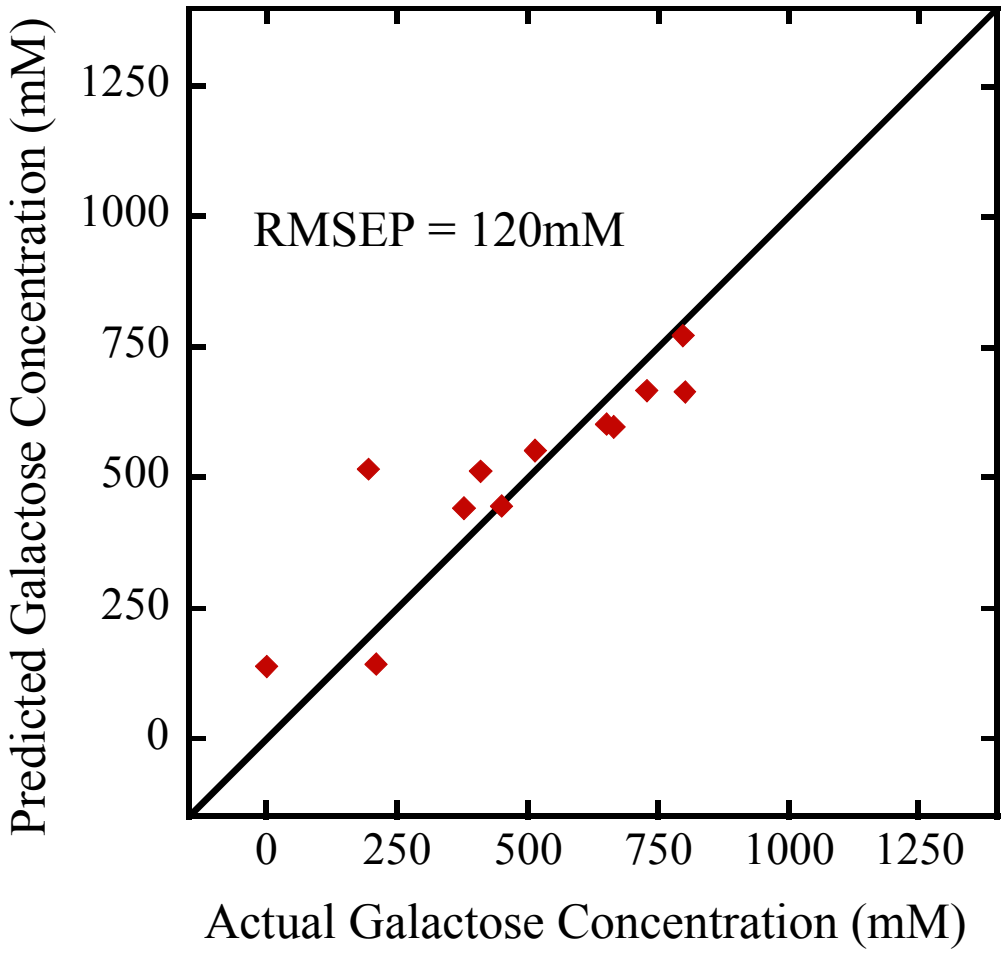
Galactose was also well predicted



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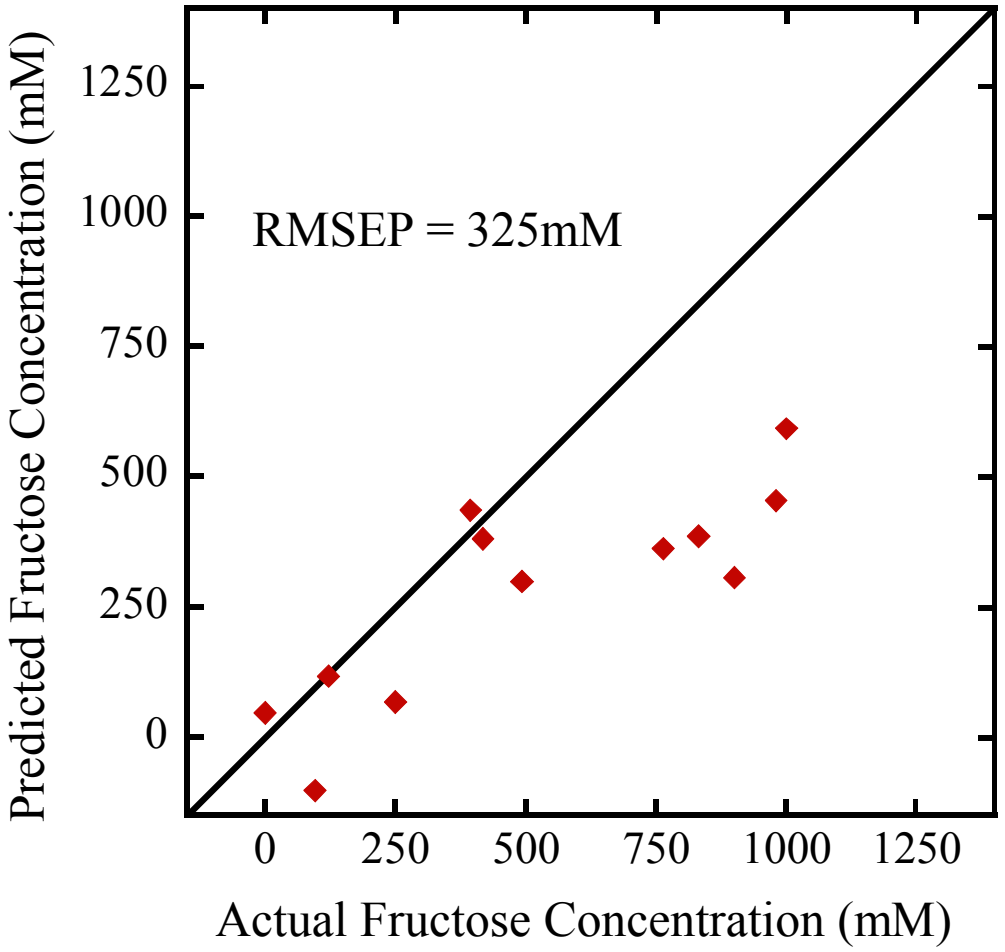
The fructose model failed at higher concentrations, possibly due to electrode saturation



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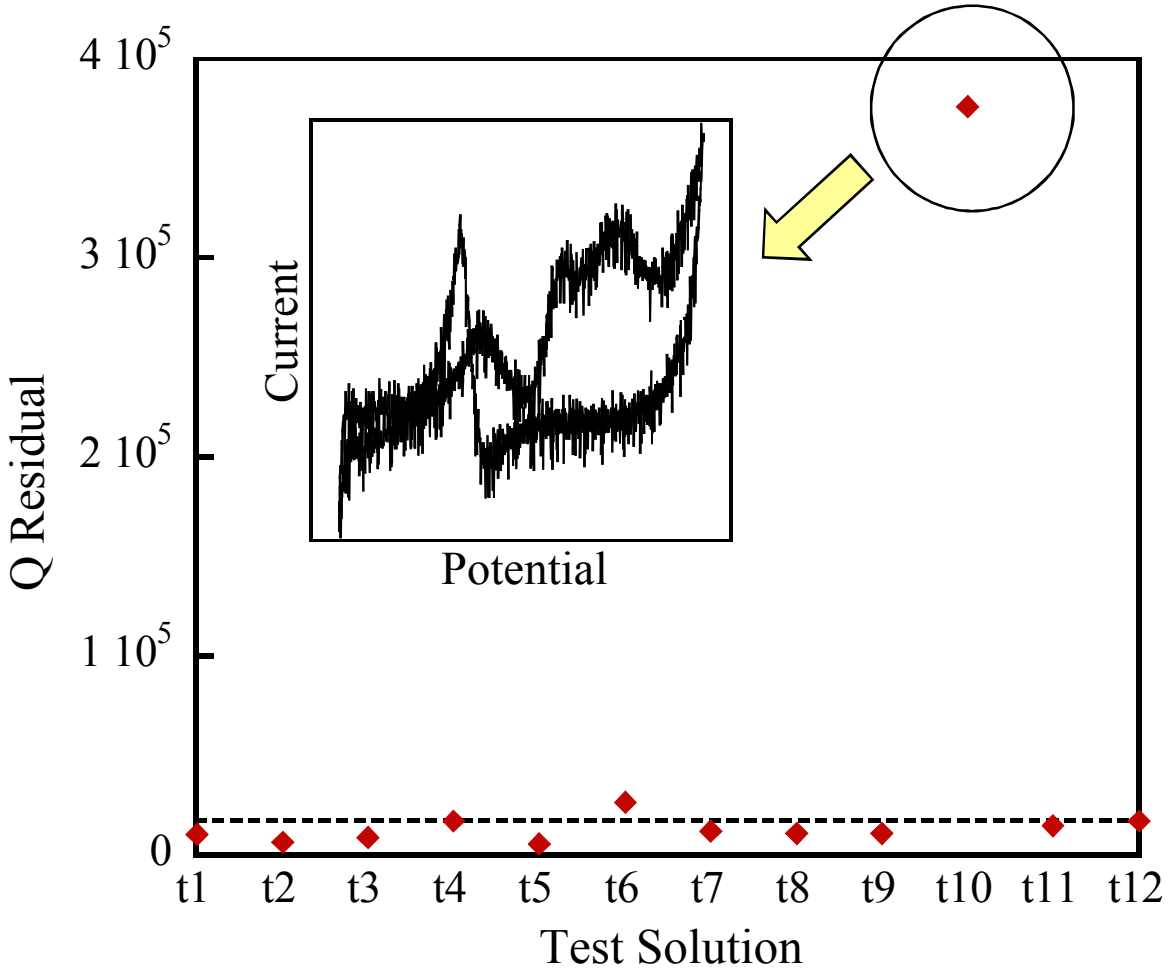
Additional statistics (Q-residual) can identify outliers and aid investigation as to their cause



- Test solution number 10 was identified as a statistical outlier.
- Examination of the raw data revealed unusually low signal – noise ratio.

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Conclusions and Acknowledgements

Conclusions

• Experiments do not have to be "dumbed down" because the data is impossible to analyze.
• PCA of electrochemical data sets allow classification
• PCR models were built over a large concentration range with relatively few training samples yet had encouraging results.
• We believe the differentiation is greater because of the compositionally diverse array; in future work we aim to prove this.

Acknowledgements

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Sandia National Laboratories'
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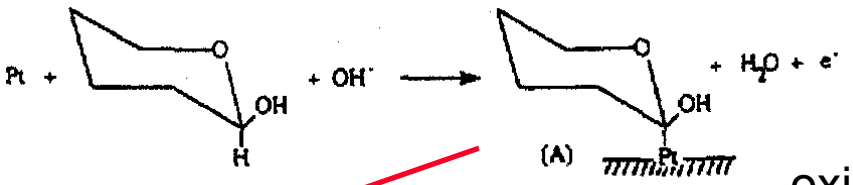
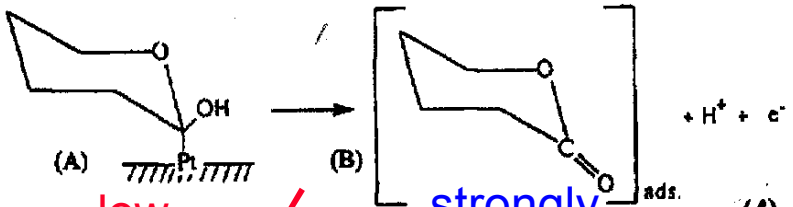
Initial Mechanism for Glucose Oxidation on Pt at Basic pH

chemisorption and oxidation of β-D-glucose on Pt

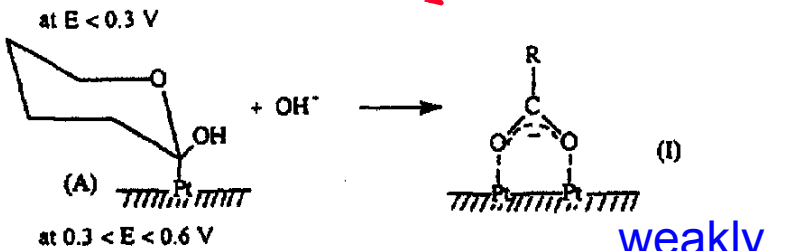


oxidation of intermediate to glucono-δ-lactone



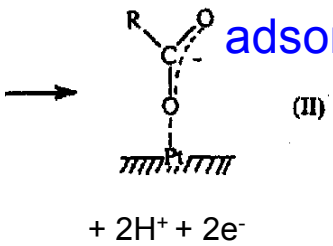
low probability

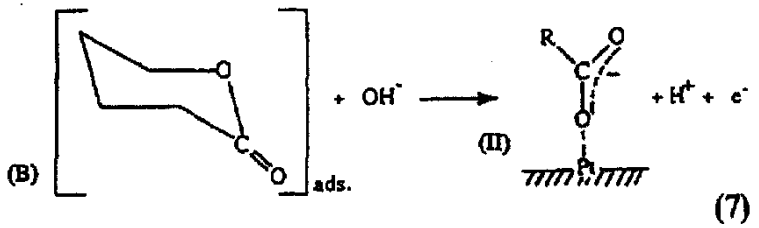
strongly adsorbed



weakly adsorbed

oxidation of intermediate to gluconate anion





oxidation of glucono-δ-lactone to gluconate anion

B. Beden et al., Electrochim. Acta 41(5), 1996, 701-709

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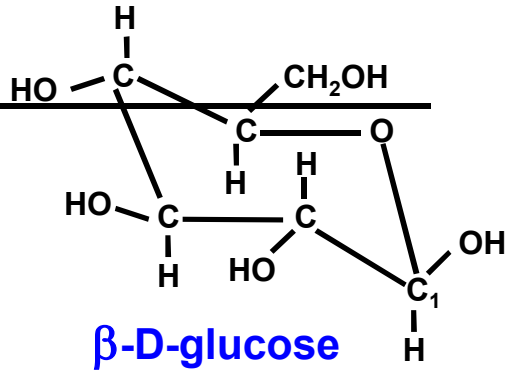
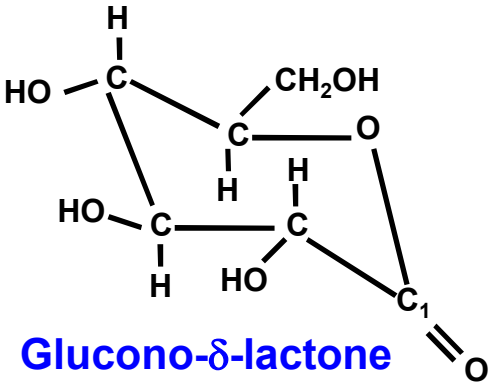
Glucose Electrochemistry
Previous Work

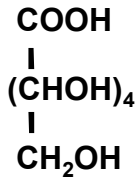
- β-glucose: proton on anomeric carbon is axial (down)
  - Preferred orientation for glucose oxidation
- Mutarotation produces equilibrium mixture (~ 37/63 α/β)
- Glucose electrochemistry extensively studied as function of pH, temperature, working electrode, *etc.*
  - Lamy, Kokoh, Leger, Beden, Largeaud, *et al.*
  - Ernst, Heitbaum, & Hamann
  - Yeager, *et al.*
  - Adzic, *et al.*
  - Becerik, Kadirgan, *et al.*
  - Many others
- Voltammetry, electrolysis, *in situ* FTIR, liquid chromatography used to study mechanism
  - ***Example*** - Pt, pH 7.3, triple-potential-step oxidation for optimal gluconic acid formation:
    - 9% conversion of glucose to ~ 65% gluconic acid with notable residuals of glucuronic, glyoxylic, oxalic, and tartaric acids (among many other products)



β-D-glucose



Glucono-δ-lactone



Gluconic acid

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