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Using the new functionalities of JMP Pro 11 to develop glass formulations for high-level nuclear waste conditioning:

mixture designs and predictive models

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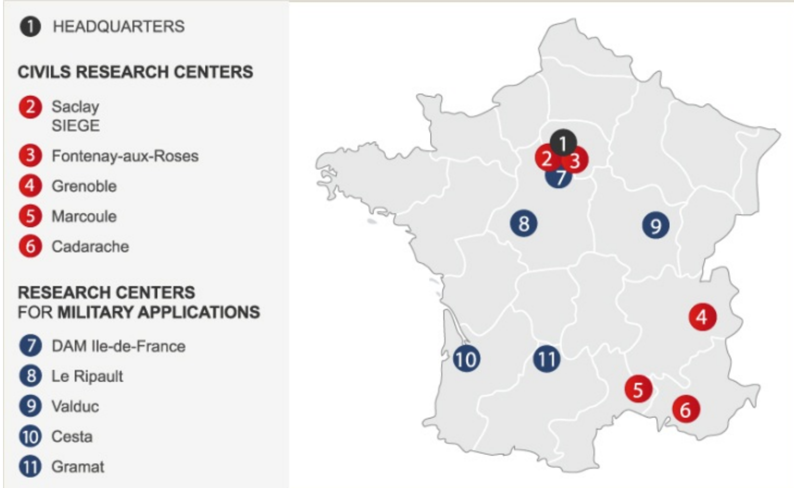
Outline

- Context
  - French Atomic Energy Commission (CEA)
  - High-level nuclear waste vitrification
  - Description of the data on nuclear glass composition and properties
- Mixture Designs
  - Background information
  - Methods to build Mixture DOEs
  - JMP Pro 11 and optimality criteria
- Interactive example using JMP Pro 11

Few words about CEA

- French government-funded technological research organization
- 16,000 researchers, engineers, technicians and staff
- 4.3 billion euros budget
- 10 research centers
- 754 priority patents filed in 2013



- Energy
  - Research on nuclear wastes
  - Nuclear systems for the future
  - New energy technologies
- Defense
  - Nuclear warheads and nuclear propulsion
  - The simulation program
- Technologies
  - Micro and nanotechnologies
  - Software technologies
  - Health technologies
- Fundamental research
  - Chemistry and radiation-matter interactions
  - Physical sciences
  - Climate and environment sciences
  - Controlled thermonuclear fusion
  - …

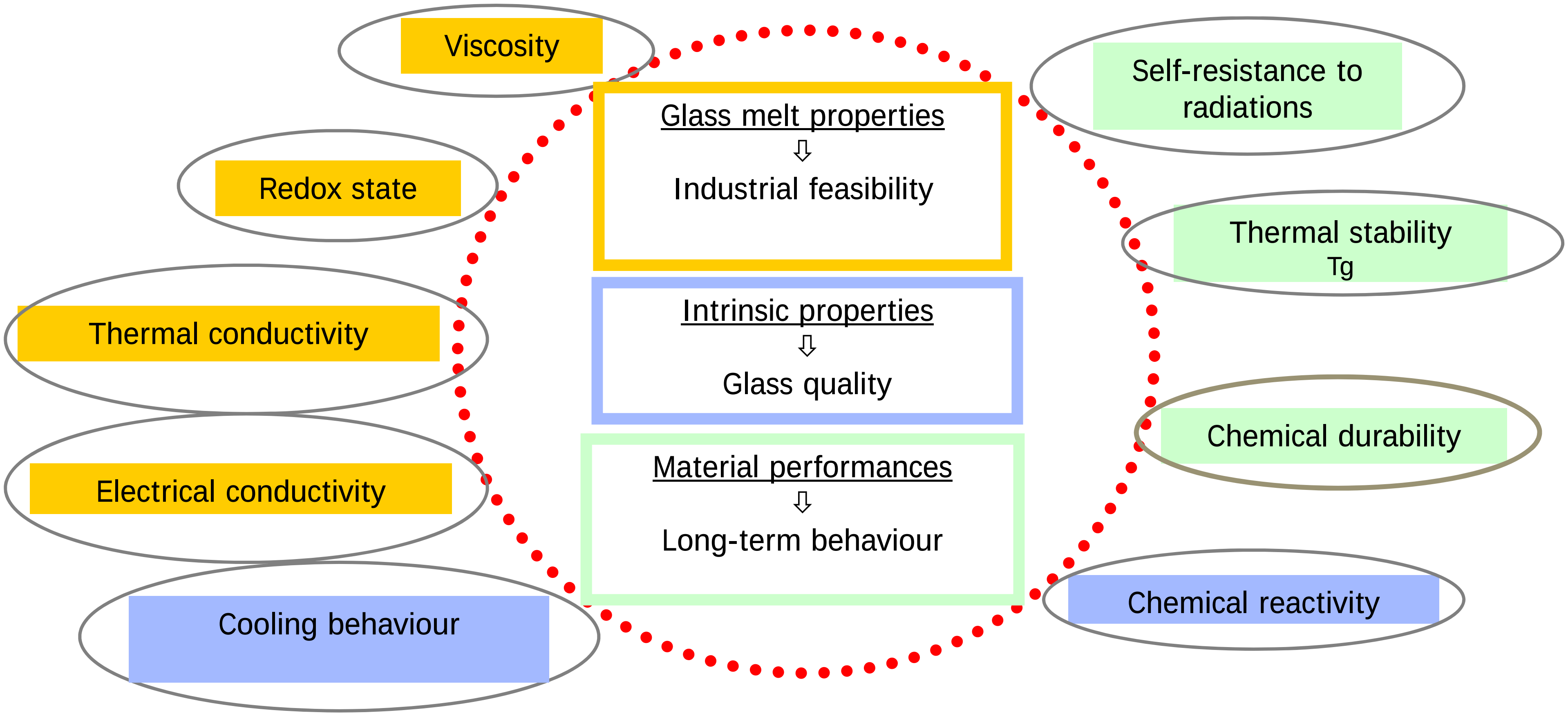
CONTEXT (1/3)

Vitrification of High-Level Waste (HLW)

- Beginning of the 60's: **glass material** is chosen for high-level nuclear waste conditioning (Canada, France, USA, Germany, Russia)
- Because glass is hard to dissolve and is chemically stable, radionucleides can be confined in a **glass matrix** for long periods of time
- Liquid waste is calcinated and mixed with **crushed glass (frit)** in a furnace
- **Molten glass** is then poured into stainless steel canisters where it solidifies into a stable form

CONTEXT (2/3)

Glass property data



Example of a glass composition domain

Factors

wt% of oxide	SiO_2	B_2O_3	Na_2O	Al_2O_3	CaO	ZnO	NiO+CoO	Fe_2O_3	MoO_3	ZrO_2	FP	Platinoids
min	41.9	11.9	8.1	3.6	3.5	2.0	0.05	0.05	0.8	1.2	1.7	0.7
max	51.7	16.5	12.3	6.6	4.8	3.5	1.1	4.5	3.0	3.7	13	3.1

Constraints

wt% of oxide	$(SiO_2+B_2O_3+Al_2O_3)$	(ZrO_2+MoO_3+FP)	MoO_3 / (0.4875 FP)	Platinoids / (0.4875 FP)
min	60.00	8.50	0.206	0.227
max	100.00	19.20	3.620	3.741

MIXTURE DESIGNS

MIXTURE DESIGNS

Theoretical Principle of Additivity

M.B. Volf, "Mathematical Approach to Glass", Elsevier Science Publishing company, 1988

- If glass were a mere mixture of the individual oxides, as seemingly indicated by the classical laboratory analysis, the **additive equation** would be generally valid:

$$G = \sum g(G)_i \, x_i$$

G is the property of the glass
$g(G)_i$ is the additive factor for oxide i and property G
x_i is the amount of oxide i

- But glass is not a mixture of oxides. Errors in additive calculation could be due to the degree of cross-linking, anomalies in the cross-linked structure, phase separation, interaction between ions,…
- However, on investigating a suitably narrow composition range, where the more complex interactions can be neglected, **one can express the effect of the individual components on a certain property by the additive equation.**

Basics on mixture designs (1/2)

J.A. Cornell, *Experiments with mixtures – Designs, Models, and the analysis of mixture data*, Third edition, Wiley, Ed. New-York, 2002
P. Goos, B. Jones, "Optimal Design of Experiments – A case study approach", John Wiley and Sons, 2011

- In a mixture experiment, the proportions of the components x_i must satisfy the constraints:

$$0 \leq x_i \leq 1 \quad \text{and} \quad \sum_{i=1}^{q} x_i = 1$$

- In **constrained mixture experiments**, there are additional constraints consisting of lower and/or upper bounds on the q components:

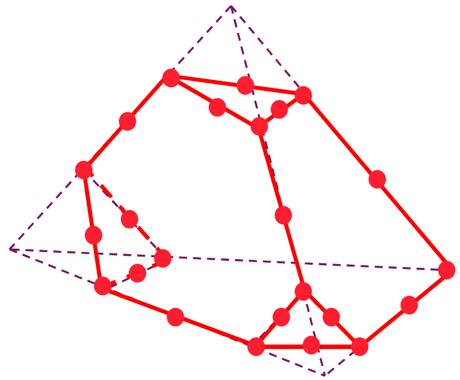
$$L_i \leq x_i \leq U_i \,, \quad i = 1, 2, \ldots, q$$

and/or on linear combinations of components:

$$C_k \leq \sum_{i=1}^{q} A_{ki} x_i \leq D_k \,, \quad k = 1, 2, \ldots, K$$

Basics on mixture designs (2/2)

- Adding constraints defines a (q -1)-dimensional irregular polyhedral experimental region
- Traditional approach to building optimal mixture designs is to generate **a set of candidate points** from which design points are optimally selected
- Candidate set may include vertices, other boundary points and interior points of the experimental region



The former distance-based design method (90's → 2011)

- Former method used by our R&D teams for nuclear glass formulation was based on a distance-based design approach
- Distance-based selection chooses points, among the set of candidate points, in a way that achieves maximum spread throughout the design region (point exchange algorithm)
- As the numbers of components and constraints increase, the number of candidate points appropriate to cover the experimental region grows rapidly
- Consequently, the demand for computing resources to generate and store the candidate points will also increase
- In the case of 13-component nuclear glass + individual and relational constraints

⇒ 12D-polyhedron with ~ 25,000 vertices and 150,000 edges

MIXTURE DESIGNS

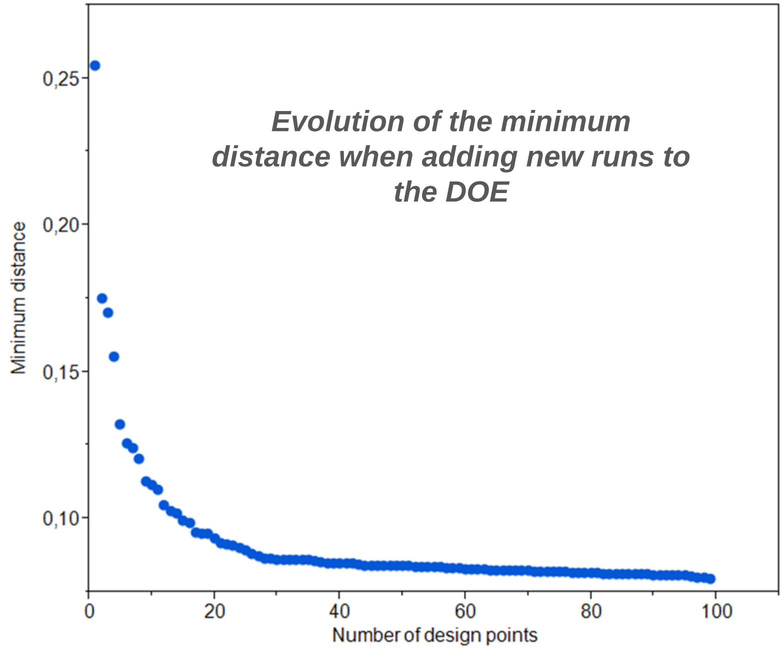
The former distance-based design method (90's → 2011)

- Since if was not possible to use commercial software packages because of this limitation, an internal software had to be developed
- The code we have developed enables to create and store the full set of candidates, and calculate the best design based on Euclidian distance criteria

The former distance-based design method (90's → 2011)

- Algorithms published in literature (McLean-1966, Snee-1979, Piepel-1988) such as XVERT, CONVRT, CONSIM, CONAEV,… were implemented to our internal software for calculating candidate points
- **Distance criteria algorithms** were embedded to build mixture DOE's:

Criteria
Minimum distance between the design points
Maximum distance between the design points
Average distance between the design points

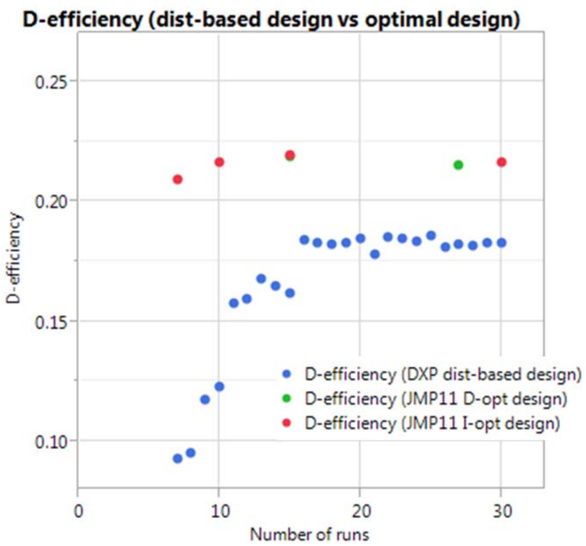


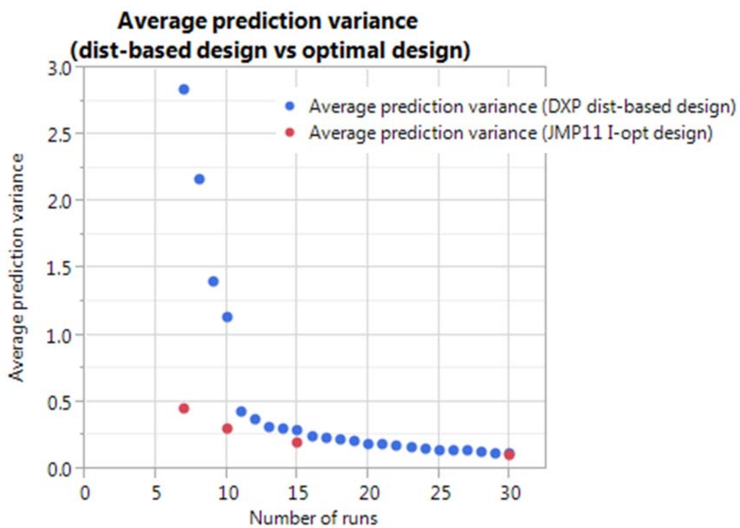
MIXTURE DESIGNS

- Distance-based mixture DOEs have been carried out over the past 15 years at CEA (property-composition models)
- In parallel, robust coordinate-exchange algorithms have been implemented in JMP
  - With respect to the **regression coefficients**

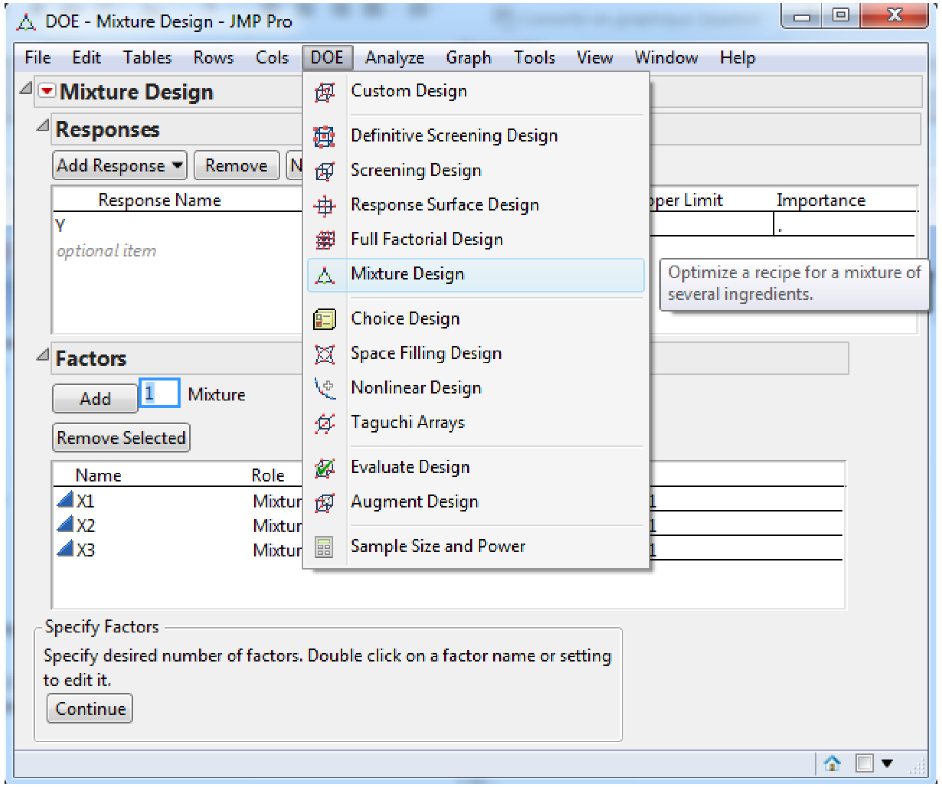
    D-optimal designs : maximize det[X'X])
  - With respect to the **prediction variance of the response**

    I-optimal designs : minimize $\int_R f'(x)(\boldsymbol{X}'\boldsymbol{X})^{-1} f(x)dx$





- Interactive example: construction of a 7-component **optimal mixture design** for nuclear glass formulation

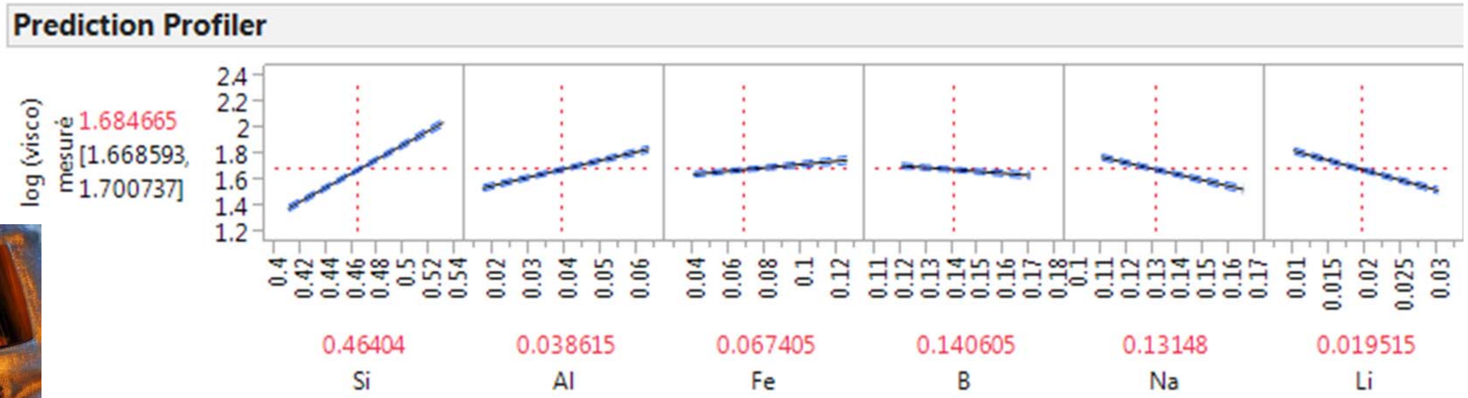


EXAMPLES OF APPLICATION PERSPECTIVES

CONCLUSION - PERSPECTIVES

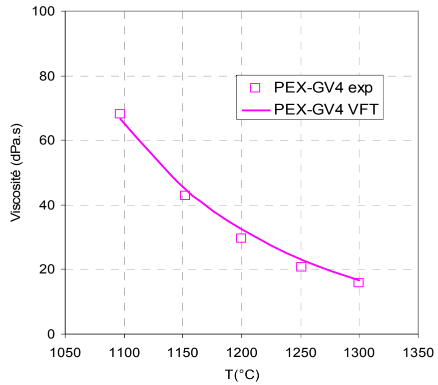
JMP applications in the R&D of nuclear glass formulation

- ❑ Robust property-composition predictive models
  - ➢ Mixture DOE, Stepwise and Prediction Profiler platforms in JMP Pro 11



$$Ln(\eta) = \sum_{i=1}^{q} A_i x_i + \frac{\sum_{i=1}^{q} B_i x_i}{T - \sum_{i=1}^{q} T_i x_i}$$

VFT model (effect of composition and temperature on viscosity)



CONCLUSION - PERSPECTIVES

JMP applications in the R&D of nuclear glass formulation (continued)

- **Big data analysis**
  - Graph builder, PCA and Clustering platforms in JMP Pro 11

50+ columns

Properties and composition data

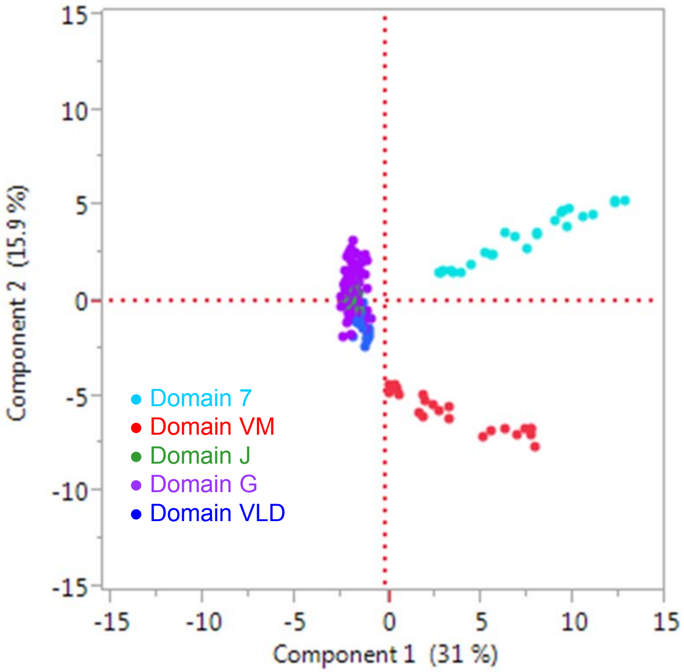
5 000+ rows

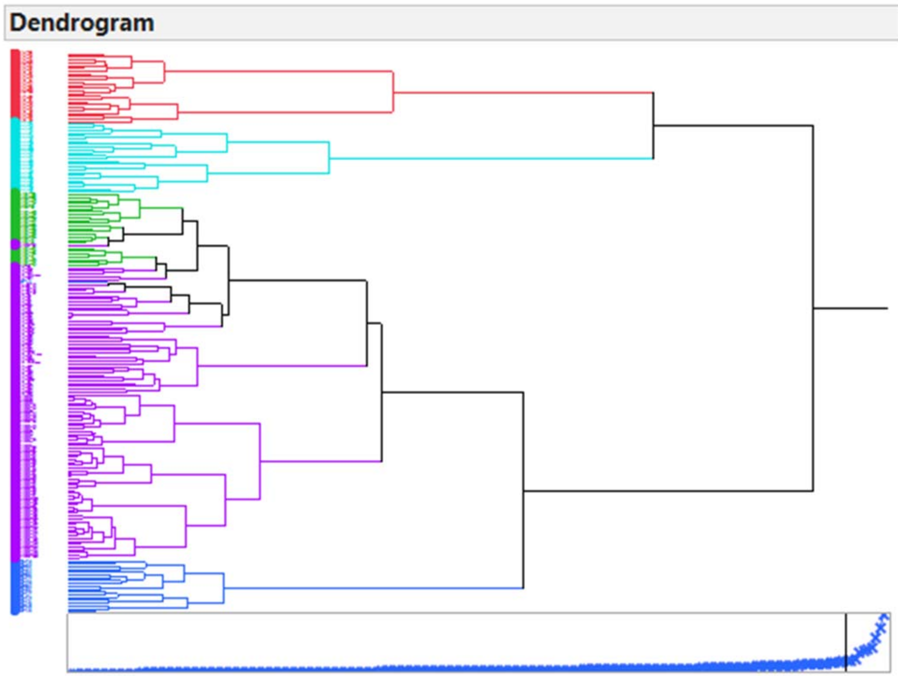
Glass samples

Spinels	Mo phases	P phases	P2O5	MoO3	RuO2 / …							Fe2O3	NiO	Cr2O3	SO3
yes	no	no	0	0	0.00							0.0425	0.003	0.0018	
no	no	no	0.0078	0.0155								0	0.003	0	0.00
no	no	no	0.009	0.018	0.00							0.0229	0.003	0.001	0.00
no	no	no	0.005	0.01	0.00							0.0216	0.003	0.0009	0.00
no	no	no	0.0066	0.0131	0.00							0.0185	0.003	0.0008	0.00
no	no	no	0	0	0.00							0.0075	0.003	0.0003	
no	no	no	0	0	[illegible]							0.0205	0.003	0.0009	
no	yes	no	0.0081	0.0163	0.0023	0.4499	0.135	0.15	0.1252	0.031	0.022	0.0305	0.003	0.0013	0.00
no	no	no	0.0071	0.0141	0.0025	0.4499	0.165	0.11	0.0982	0.031	0.022	0.0331	0.003	0.0014	0.00
no	no	no	0	0	0.0013	0.5199	0.165	0.11	0.0501	0.031	0.022	0.0169	0.003	0.0007	
no	no	no	0	0	0.0024	0.4498	0.135	0.15	0.0925	0.031	0.022	0.0312	0.003	0.0013	
				[illegible]	0.001	0.4899	0.165	0.15	0.04	0.031	0.022	0.0135	0.003	0.0006	0.00
				0	0.0025	0.4767	0.12	0.1333	0.13	0.031	0.022	0.0332	0.003	0.0014	
				[illegible]	0.0007	0.5199	0.12	0.1291	0.0872	0.031	0.022	0.0089	0.003	0.0004	0.00
				[illegible]	0	0.49	0.165	0.11	0.0714	0.031	0.022	0	0.003	0	0.00
				[illegible]	0.0028	0.5008	0.12	0.1333	0.1092	0.031	0.022	0.0369	0.003	0.0015	0.00
				[illegible]	0.0032	0.4799	0.12	0.11	0.13	0.031	0.022	0.0425	0.003	0.0018	0.00
				0	0.0017	0.4899	0.165	0.15	0.0678	0.031	0.022	0.0229	0.003	0.001	
				0	0.0023	0.45	0.15	0.11	0.1256	0.031	0.022	0.0307	0.003	0.0013	
no	no	no	0.0068	0.0135	0.0007	0.4899	0.165	0.15	0.0876	0.031	0.022	0.0092	0.003	0.0004	0.00
no	no	no	0.0046	0.0091	0.0009	0.4723	0.1305	0.145	0.0929	0.031	0.022	0.0122	0.003	0.0005	0.00
no	no	no	0.003	0.006	0.0011	0.51	0.13	0.1444	0.0807	0.031	0.022	0.0142	0.003	0.0006	0.00
no	no	no	0.0023	0.0045	0.0021	0.4899	0.1435	0.13	0.0821	0.031	0.022	0.0277	0.003	0.0012	0.00
no	no	no	0.0046	0.0093	0.0027	0.4549	0.1337	0.1371	0.1154	0.031	0.022	0.0352	0.003	0.0015	0.00
no	no	no	0.0068	0.0136	0.0023	0.4808	0.131	0.1305	0.1023	0.031	0.022	0.03	0.003	0.0013	0.00
no	no	no	0.002666	0	0.0002666	0.585	0.08	0.2	0.02	0.02	0.01	0.02	0.002133	0.000133	0.00
yes	no	no	0	0.0115	0.006	0.4	0.165	0.07	0.0875	0.05	0.04	0.08	0.005	0.003	0.00
no	no	no	0.01	0.016	0.006	0.413	0.08	0.2	0.02	0.05	0.04	0.08	0.005	0.003	0.00
no	no	no	0	0.022	0	0.485466	0.165	0.2	0.02	0.046533	0.01	0.02	0.002	0	0.00
no	no	no	0.01	0.016	0.006	0.585	0.08	0.072	0.035	0.05	0.04	0.02	0.005	0.003	0.00

JMP applications in the R&D of nuclear glass formulation (continued)

- **Big data analysis**
  - Graph builder, PCA and Clustering platforms in JMP Pro 11





CONCLUSION - PERSPECTIVES

Perspectives

- JSL to customize the Mixture Design platform
  - D-efficiency & Avg Pred Variance vs number of runs
- Connect JMP to our glass database and investigate new statistical methods for glass data analysis
  - Abstract submitted for Discovery Summit Europe, Brussels, March 2015

MIXTURE DESIGNS - REFERENCES

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F. Louvet, L. Delplanque, *Les plans d'expériences, une approche pragmatique et illustrée*, Témoignage de l'Association Expérimentique, 1996-2005

Henry Scheffé (1907-1977)

Fellow of the Institute of Mathematical Statistics in 1944, the American Statistical Association in 1952 and the International Statistical Institute in 1964. He achieved high office in these organizations, being elected as president of the International Statistical Institute and vice president of the American Statistical Association.

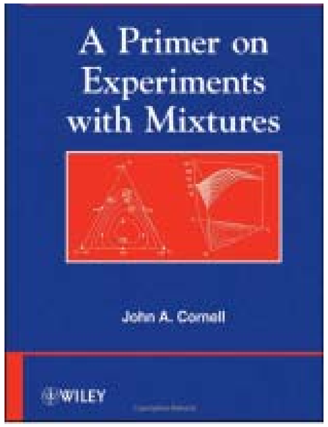
$$\hat{y} = \sum_{i=1} \hat{\beta}_i x_i + \sum_{i<j}\sum \hat{\beta}_{ij} x_i x_j$$

Scheffé H., « *Experiments with Mixtures* », Journal of the Royal Statistical Society, B, 20, 344-360, 1958

John A. Cornell

Professor, Department of Statistics, University of Florida
Fellow, American Statistical Association, 1984. American Society for Quality Control, 1989.
Elected to membership in the International Statistical Institute, 1984.
Editor, *Journal of Quality Technology,* ASQC, 1989-91.

W.J. Youden Prize Awarded by the Chemical Division of ASQC for the most outstanding expository paper that appeared in Technometrics in 1973. Title of paper: "Experiments with Mixtures: A. Review", 1974.
Shewell Award: Co-winner for presentation and paper titled, "Designs, Models, and the Analysis of Mixture Data," 25th Annual Fall Technical Conference, Gatlinburg, TN, 1981.
Golden Quill Awards from ASQC for authoring, "How to Run Mixture Experiments for Product Quality" and "How to Apply Response Surface Methodology," 1991.
Testimonial award from ASQC in recognition of Leadership and Distinguished Service as Editor, *Journal of Quality Technology,* 1994, and as Editor, "*How To Series",* 1995.
Brumbaugh Award Co-winner awarded by ASQC for paper judged to have made the greatest contribution to the development of industrial applications of quality control, 1995.
The Shewhart Medal awarded by the American Society for Quality "For definitive work in the area of mixture component experimentation, for extensive presentations on experimental designs to industrial practitioners, and outstanding editorial contributions in the area of quality control", 2001.



Greg Piepel

PNNL Lab Fellow
Fellow of the American Statistical Association
On September 11, 2008, the Board of Directors of the American Society for Quality (ASQ) elected Piepel a Fellow of the Society for his "outstanding contributions to the experimental design and analysis of mixture experiments, for important applications of statistics and quality to nuclear waste immobilization, and for service to the profession."

Mixture Experiment Approaches: Examples, Discussion, and Recommendations

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JOHN A. CORNELL
University of Florida, Gainesville, FL 32611

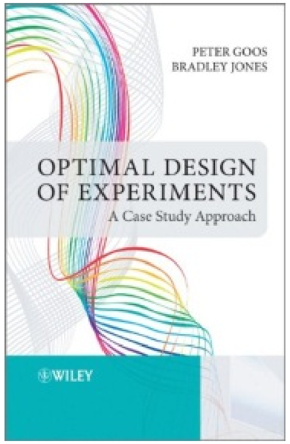
Journal of Quality Technology
Vol. 26, No. 3, July 1994

Programs for Generating Extreme Vertices and Centroids of Linearly Constrained Experimental Regions

GREGORY F. PIEPEL
Pacific Northwest Laboratory, Richland, WA 99352

Journal of Quality Technology
Vol. 20, No. 2, April 1988

Bradley Jones



Principal Research Fellow, JMP

- **Fellow** American Statistical Association (2008)
- **Youden Prize** American Statistical Association (2012) Best expository paper in Technometrics
- **Statistics in Chemistry Award** American Statistical Association (2012) For an application of definitive screening designs to improve the performance of a catalyzed reaction to sequester green house gasses.
- **The Brumbaugh Award** American Society for Quality (2009 and 2012) for the "Split-plot Designs: What, Why and How" paper and for the "A Class of Three-Level Designs for Definitive Screening in the Presence of Second-Order Effects" paper that made the single largest contribution to the development of industrial application of quality control
- **Lloyd S. Nelson Award** American Society for Quality (2009 and 2011) for the paper having the greatest impact to practitioners.
- **Technometrics Ziegel Prize** American Statistical Association and American Society for Quality (2013) for the best book reviewed in Technometrics the previous year. The book was "Optimal Design of Experiments: A Case Study Approach"
- **The Shewell Award** American Society for Quality (2013) for the best paper presented at the ASQ Fall Technical Conference in the previous year.

Construction of a 21-Component Layered Mixture Experiment Design Using a New Mixture Coordinate-Exchange Algorithm

Piepel, G.F., Cooley, S.K., and **Jones, B.** (2005), "Construction of a 21-Component Layered Mixture Experiment Design Using a New Mixture Coordinate-Exchange Algorithm", *Quality Engineering*, 17 579-594.

Thank you for your attention

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JMP® 11

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SEPTEMBER 15 - 18, 2014

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