Innovative solutions for efficient lamps: mixture optimization using a DOE approach

Alessio Corazza (1), Maria Pia D'Ambrosio (2), Vincenzo Massaro (1)

SixSigmaIn Team

Enbis DEINDE 2011 Torino

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OUTLINE

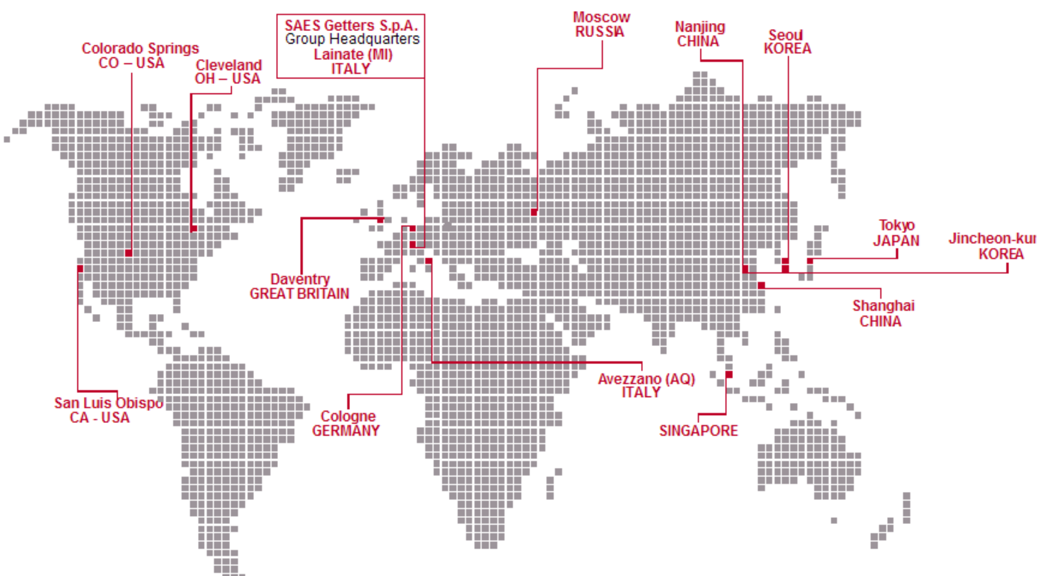
- Companies Profile: SAES Getters (1) and SixSigmaIn Team (2)
- Working principle of fluorescent lamps and mercury dosing
- Innovative Hg dispensers for lamps: Hg compounds and getters
- Mixture Optimization: Mixture-Process Design setting
- DOE evaluations: results and statistical model
- Conclusions

Company profile: SAES Getters

- SAES Getters is a multinational company, founded 70 years ago

- SAES Group is the world leader in a variety of scientific and industrial applications where stringent vacuum conditions or ultra-high pure gases are required (displays, lamps, electronic devices…)

- SAES Group is also focused on material science and special metallurgy (Shape Memory alloys, metal dispensing)



- Headquarters in Milan
- Production plants in Italy, USA, China, South Korea

Company profile: SixSigmaIn Team

The distinguishing feature of SixSigmaIn Team consists in the merging of competencies related to Statistical Problem Solving, Tools Development, Business Intelligence and Adult Learning. SixSigmaIn Team

- delivers advanced and customized DMAIC, DFSS, DoE, Tolerance and Reliability Analysis trainings with the best statistical tools and
- provides solutions (MTBridge Engine © automation) for an effective industrial application of statistical analysis.

International Collaboration Network

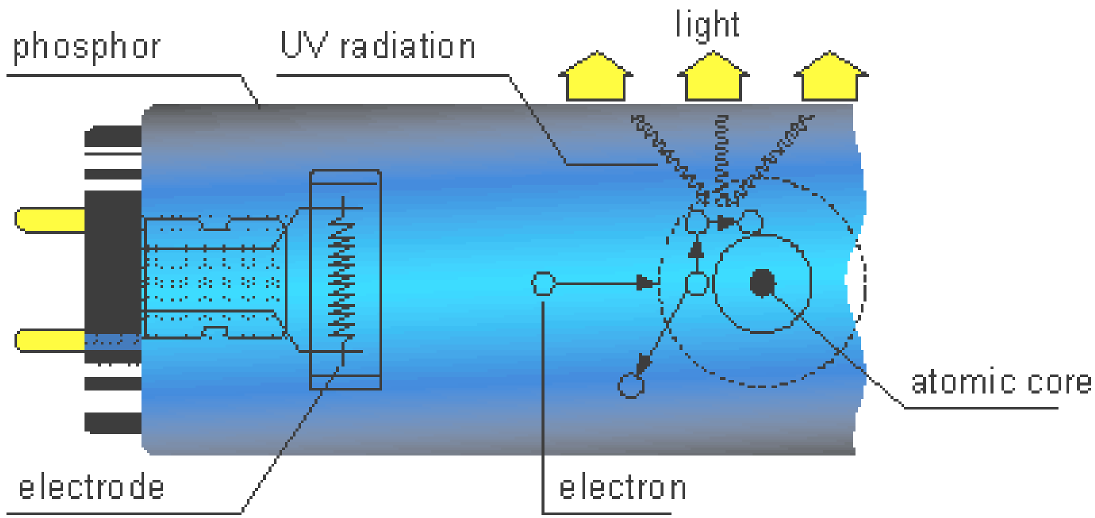
- Stat-Ease Inc • BMG Breakthrough Management Group Inc

SixSigmaIn Team's clients include the Italian locations of companies such as
• Siemens VDO / Continental Automotive Italy, • Osram, • Cabot , • Rolls Royce, • Philips,
• Reckitt-Benckiser, • Casappa Group, • Saes Getters, • Diasorin, • Agilent Technologies,
• GSK, • Solvay Pharma and others.

How works a Fluorescent Lamp

UV radiation is generated by mercury atoms during decay from excited state

→ UV light is transformed in visible light by the lamp phosphors coating



Lamp filling gas:

Ar or Ar/Kr or Ne (2-5 mbar) + Hg ($1*10^{-2}$ mbar during lamp operation)

$$Ar^* + Hg \rightarrow Ar + Hg^*$$

$$Hg^* \rightarrow Hg + UV$$

How mercury is dosed in lamp?

- Different Hg dosing technologies

  - Old technique of Liquid mercury dosing

  - Stable Hg compounds (TiHg)

Trends

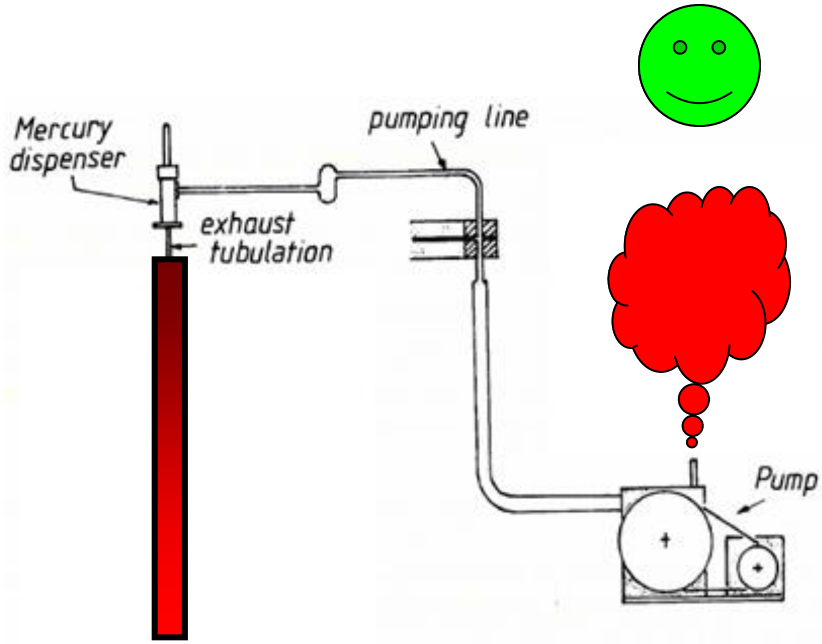
→ Reduction of Hg content in lamp: needs for improving Hg dosing precisions

→ Needs to simplify lamp manufacturing process

Old dosing technology: liquid Hg

Hg mechanical dosing is relatively cheap, but has several disadvantages:

- Risks of pollution and contamination of the working areas
- Lack of accuracy in the mercury dose: higher Hg amounts than those really necessary
- Need of frequent cleaning of the dosing and pumping equipment; need of calibrations of the dosers

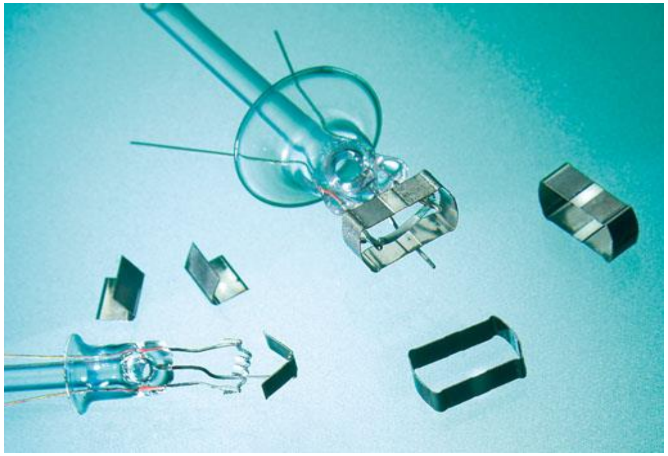


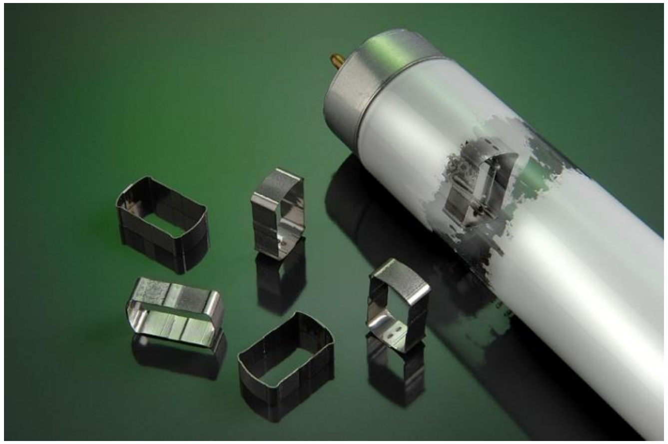
Materials for fluorescent lamps

Innovative dispensers are used to produce high quality fluorescent lamps:

- Hg based compounds for a safe and reliable Hg dosing, when the lamp is sealed

- Active materials and getters alloys to sorb gaseous impurities that have detrimental effects on the lamp performances



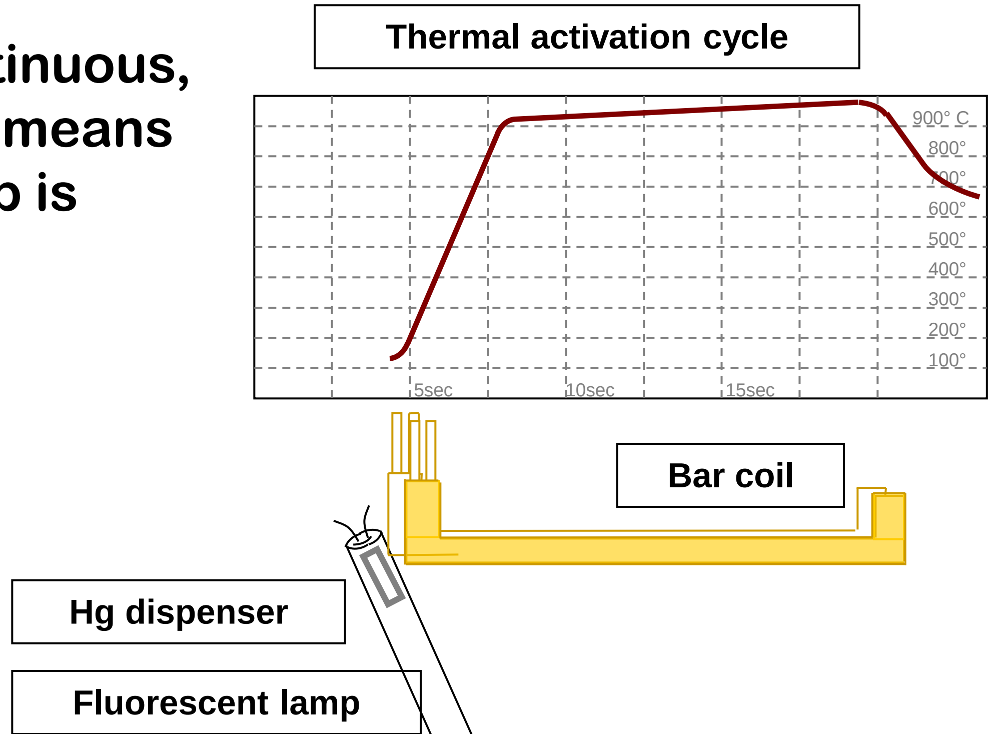


Activation of Hg dispensers

Thermal activation in continuous, on the production line, by means of a RF bar coil when lamp is sealed

In order to simplify the process → need for reduction of activation Temperature and Time keeping a high Hg yield:

from 900°C for 30s
to
the Lowest possible T in range 650°-800°C for 10s



Currently: Hg yield >90% at 900°C
but < 38% at 800°C for 10s
< 15% at 650°C for 10s

Mixture Design of experiments to improve mercury yield at low temperatures

A specific study was carried out to identify the combination of mercury compounds and active materials suitable to maximize the Hg yield

- **Target: identify a three components mixture to maximize Hg yield at the lowest possible temperature**

- **Optimization of the three components combination using T as a process variable**

Mixture Experiments Involving Process Variables

In mixture experiments with process variables, the response depends not only on the proportions of the mixture components, but also on the effects of the process variables.

In this practical situation, where experiments with mixtures were carried out, it was necessary to consider running the experiments at different levels of one process variable, the activation temperature.

Experiments with mixture and process variables are often constructed as the cross product of a mixture and a factorial design.

Mixture Experiments Involving Process Variables

In this study case, the experimental trials were performed using 3 mixture components:

X_1

X_2

X_3,

being X_1 the mercury compound, X_2 and X_3 materials to promote the quick release of mercury in a sealed lamp, varying the process settings of the factor:

Temperature

along with the percentages of the mixture ingredients, where the studied response is the Hg yield.

Mixture Experiments Involving Process Variables

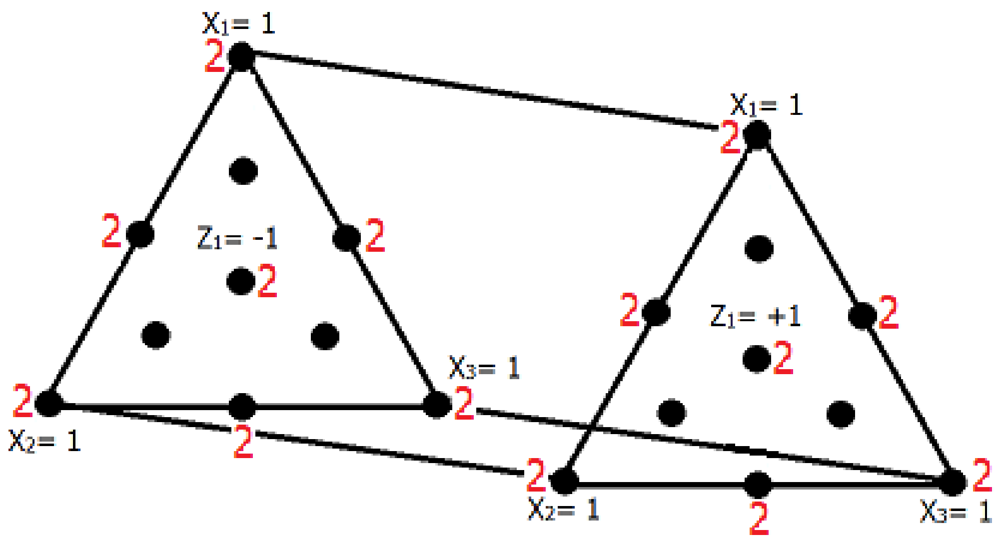
Purpose of the mixture-process design is to maximize the Hg yield at the lowest possible temperature.

The optimal formulation may become different depending on the operating conditions.

The methodology used to construct mixture designs involving process variables is composition of two smaller designs, one being a mixture designs for the mixture components only and the other being factorial design for the process variable.

With three mixture components having the proportions x_1 , x_2 and x_3, we included also one process variable, denoted by z_1 and the process variable was to be studied at two levels only.

Crossed design



The triangles represent the mixtures, which must be repeated at the two combinations of the process factor (Z_1).

The figure shows the location of the points in the mixture space and the number of replicates for the pure component blends, the binary blends and the centroid blend. The design includes one replicate of the axial check blends. There's a total of 34 runs.

Mixture Experiments Involving Process Variables

We choose a simplex centroid design for fitting the special cube model in the mixture components

$$\eta_{SC} = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{123} x_1 x_2 x_3 + \varepsilon$$

and when combined with the main effect linear model in z_1

$$\eta_{PV} = \alpha_0 + \alpha_1 z_1 + \varepsilon$$

produces the 14 - term combined model

$$\eta\,(x, z) = \gamma^0{}_1 x_1 + \gamma^0{}_2 x_2 + \gamma^0{}_3 x_3 + \gamma^0{}_{12} x_1 x_2 + \gamma^0{}_{13} x_1 x_3 + \gamma^0{}_{23} x_2 x_3 + \gamma^0{}_{123} x_1 x_2 x_3$$
$$+ \gamma^1{}_1 x_1 z_1 + \gamma^1{}_2 x_2 z_1 + \gamma^1{}_3 x_3 z_1 + \gamma^1{}_{12} x_1 x_2 x_1 + \gamma^1{}_{13} x_1 x_3 z_1 + \gamma^1{}_{23} x_2 x_3 z_1$$
$$+ \gamma^1{}_{123} x_1 x_2 x_3 z_1 + \varepsilon$$

Mixture Experiments Involving Process Variables

In mixture experiments containing process variables, the traditional Scheffé-type model contains terms in the mixture components and crossproducts between the mixture components and the process variable.

The crossproduct coefficients estimate the effects of the process variables on the blending properties of the mixture components.

The component proportions x_i are restricted by either a lower bound and an upper bound, that is the component fraction is not allowed to vary from 0 to 100 and only a sub-region of the original simplex is of interest.

Mixture Experiments Involving Process Variables

The experiments were performed within the following blending limits:

$$40 < x_1 < 70$$

$$0 < x_2 < 30$$

$$0 < x_3 < 30$$

$$x_1 + x_2 + x_3 = 100$$

The concept of pseudo-component is used to define another simplex of new components (pseudo-components) present in the proportions x_i.

Statistical Methods and Software

The analysis and results of the experimental design were studied and interpreted by Design-Expert 8 Stat-Ease software package, to estimate the response of the dependent variable.

The response curves and contour plots are also generated.

The optimal composition at the lower temperature were calculated and analyzed using Analysis of Variance (ANOVA) and Response Optimization.

Results and Discussion

The regression model with all terms had several individual coefficients that were not significantly different from zero, so various terms were removed by backwards elimination until the model with 10 terms shown below was produced.

The fitted predictive model is (in terms of U-Pseudo Components and Coded Factors):

Logit(Hg Yield) = Ln[(Hg Yield + 0.00)/(100.00 - Hg Yield)]

$$= 0.42X_1 - 1.8X_2 + 0.36X_3 + 0.13X_1X_2 + 0.27X_1Z - 0.50X_2X_3 + 2.37X_2Z + 0.12X_3Z - 3.37X_1X_2Z - 3.59X_2X_3Z$$

and:

R^2 = 96.81%

Adj R^2 = 95.61%

Pred R^2 = 93.59%

Adeq Precision= 36.451

Results and Discussion

The analysis of variance showed the overall equation to be highly significant (p-value in ANOVA <0.0001) and not significant lack-of-fit.

The data from these experiments was analyzed giving the right importance to the validity of assumptions.

Residual plots (the plots of observed vs. predicted values) were also examined for outliers.

A variance-stabilizing transformation on the response, by a mathematical function such as logit function was applied to the original data, because the “funnel effect”, or inhomogeneity of variance, was observed in the residual plots.

Results and Discussion

In fact, a situation which often generates heteroscedasticity is when the range of Y is intrinsically finite. For example, if Y is a percentage yield, it must lie between 0% and 100%. A transformation can be used to map the finite range of Y onto a doubly-infinite range. The most commonly used transformation of this kind is the logit.

After transformation, the Diagnostics and Influence graphs of residuals showed:

- **indication of being normally distributed;**
- **random structure in residual plots (homogeneity of variance).**
- **no strong evidence of influential observation in the data.**

Results and Discussion

The fitted predictive model was used to generate response surface graphs, which make interpretation much easier than looking at all the coefficients.

The easier way to understand the results is to create contour plots of the Hg% versus the composition of the three components (X_1, X_2, and X_3) at the two process factor levels – Temperature (Z_1) .

This is shown in Figure 3 and the lines show iso-response values

Results and Discussion

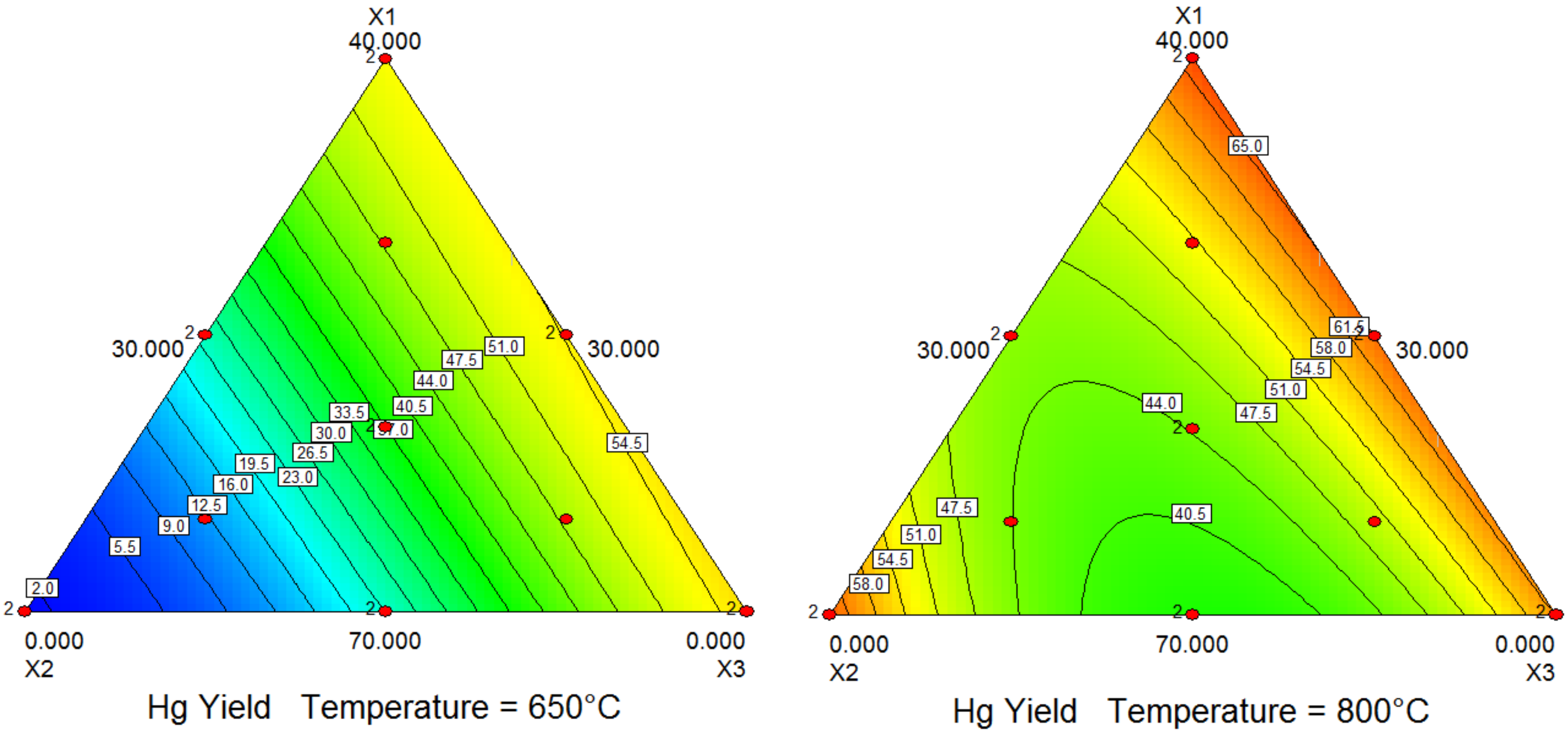


Fig. 3: Contour Plots at 650°C and 800°C

Results and Discussion

The pattern of the contours changes as the Temperature varies. At 650°C, the contour lines are almost parallel to the X_1X_3 subsimplex.

This means that once a level of X_2 is selected, one can vary the relative amount of X_1 and X_3 with virtually no effect on the Hg Yield.

This suggested that the effects of X_1 and X_3 are similar to one another.

At 800°C, the contour lines most closely reflect the fit of the Scheffé quadratic model.

Warmer colors indicate higher values for Hg Yield, which can be maximized by going to a blend located, at 800°C, in the area on the right edge and on the left corner of the plot and, at 650°C, in the area on the right edge.

Results and Discussion

A 3D version of the contour plots at these conditions is shown in Figure 4.

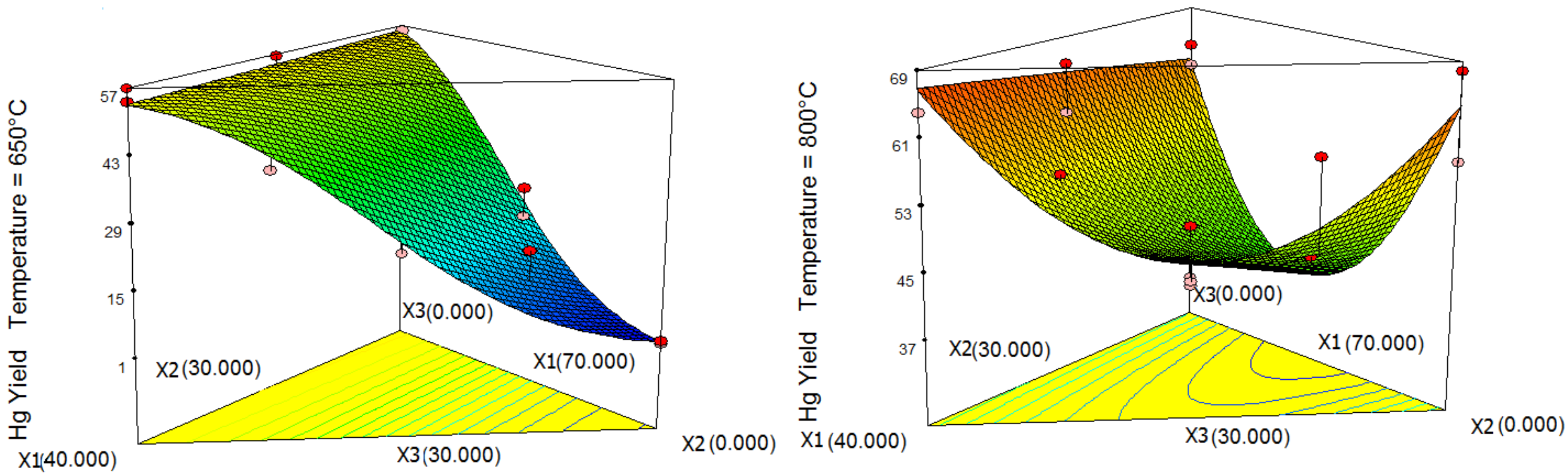


Fig. 4: The three-dimensional surface plots at 650°C and 800°C

Results and Discussion

An important reason for fitting this model to data was to find the best combination of the input variables, component proportions in a mixture setting, involving the Temperature, where we could come as close as possible to a goal.

With the **Numerical Optimization**, we wanted to search the design space, using the model we created in the analysis, to find input settings that meet the following goals:

Maximize X_1;

In range X_2;

In range X_3;

Minimize Temperature;

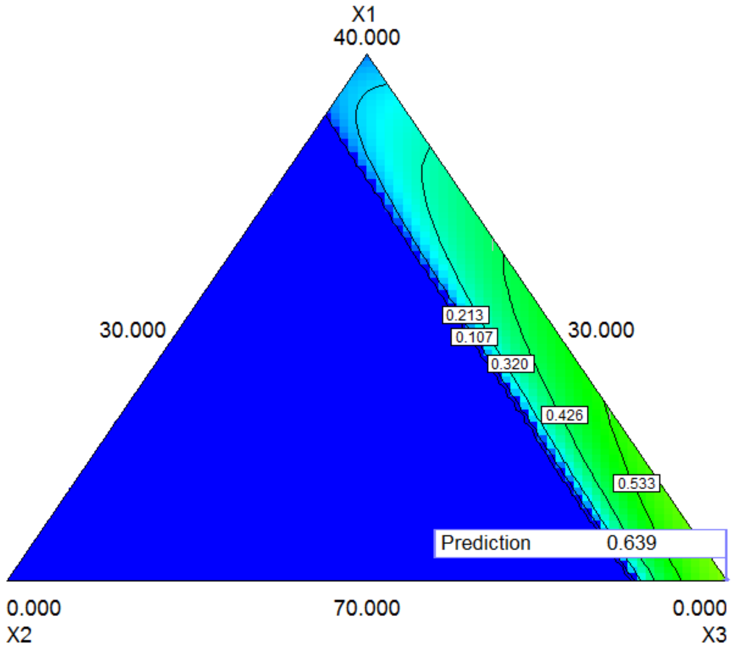
Maximize %Hg.

Results and Discussion

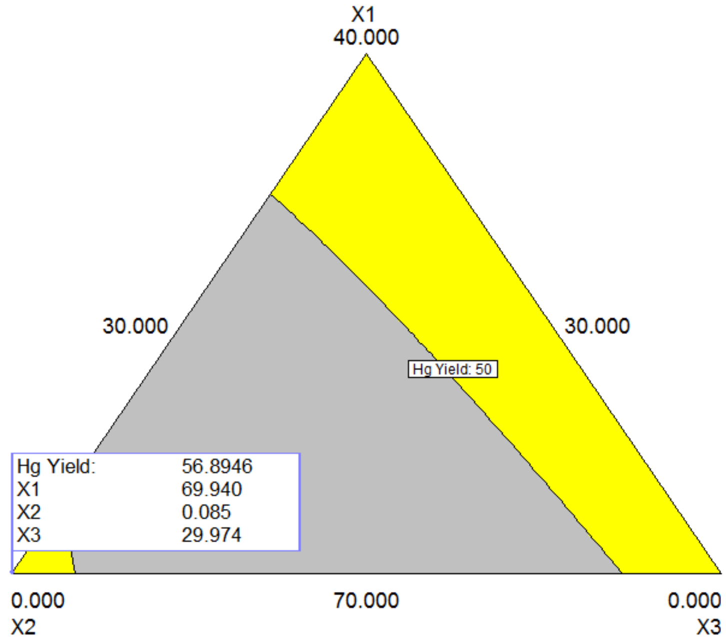
N°	X_1	X_2	X_3	T°	Hg Yield	Desirability
1	70	30	0	654	55.98	0.639
2	70	30	0	659	56.19	0.639
3	70	30	0	662	56.33	0.638
4	70	30	0	666	56.46	0.638
5	70	30	0	669	56.59	0.637
6	70	30	0	680	57.04	0.632
7	70	30	0	747	59.69	0.538
8	70	0	30	791	57.09	0.268

Results and Discussion

The Graphical optimization displays the area of feasible response values in the input space. Regions that do not fit the optimization criteria are shaded.



Desirability



Overlay Plot

It is evident from the graphs in Figure 3 and in Figure 4 that, in terms of absolute values, the highest Hg yields are obtained at 800°C, but in any case the solutions found at 650°C are the most interesting ones because the minimization of the process temperature is the preferred selection criterium.

Conclusion

A study is in progress to identify the best combinations of mercury compounds and promoters in order to improve mercury dispensers for fluorescent lamps.

A mixture DOE optimization was performed on the combination of two promising promoters with the Ti-Hg mercury alloy in order to maximize the mercury release at the lowest possible temperatures in the range 650°- 800°C.

By applying the design of experiment, we were able to achieve the objective of determining the most influence inputs which have significant effect on the Hg Yield, identifying the appropriate conditions for each significant input to achieve good Yield.

A mixture-process design was conducted with 34 runs and the results were analyzed with the contour and response surface plots.

Conclusion

Based on these results, the appropriate setting conditions for 3 components have been determined at the lower temperature to get high value of Hg Yield.

Through numerical optimization, using the model created in the analysis, it was possible to find in the design space the components ratios to obtain the relatively good yield of 56% at the temperature of 650°C. Results are remarkable taking into consideration that they are obtained with an activation time of only 10 seconds. However, even if improvements are really significant, the achieved Hg yield is not yet satisfactory and R&D work will continue.

Further Study

The research activity is now going on, using this study as an input information for further investigation. Experiments are now focused on a new 3 components mixture where the component X3, having low effect on the response at low temperatures, has been replaced by a most promising promoter.

In the new mixture-process design, it will be better evaluated the effect of the temperature, the process variable, also at the center value of the factor range.

Acknowledgments

The authors wish to thank Dr. F. Anzani for his valuable suggestions and discussions and Mr. G. Colombo for performing the experimental work.

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