

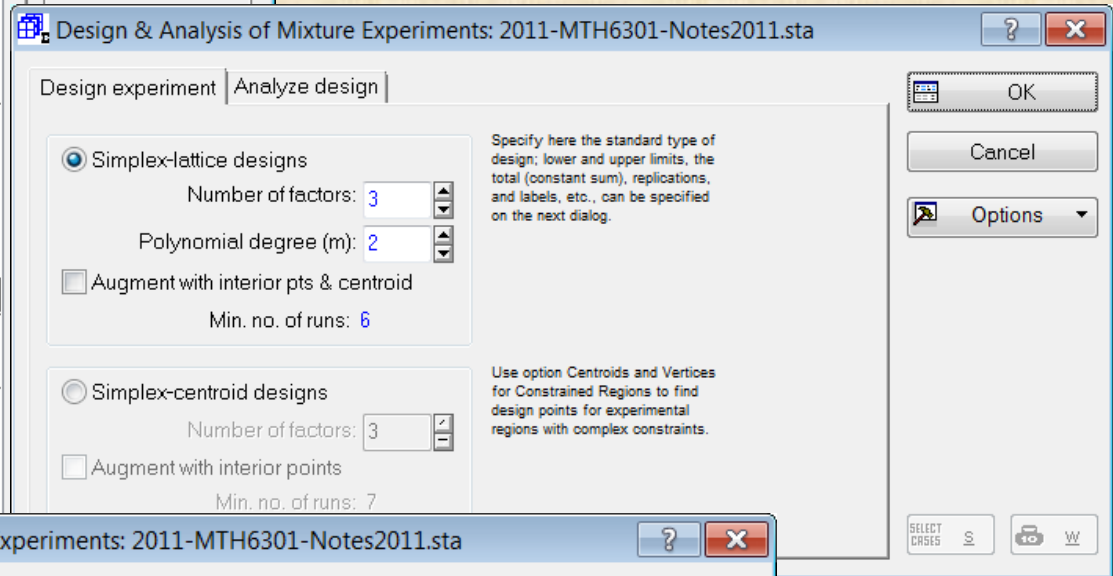
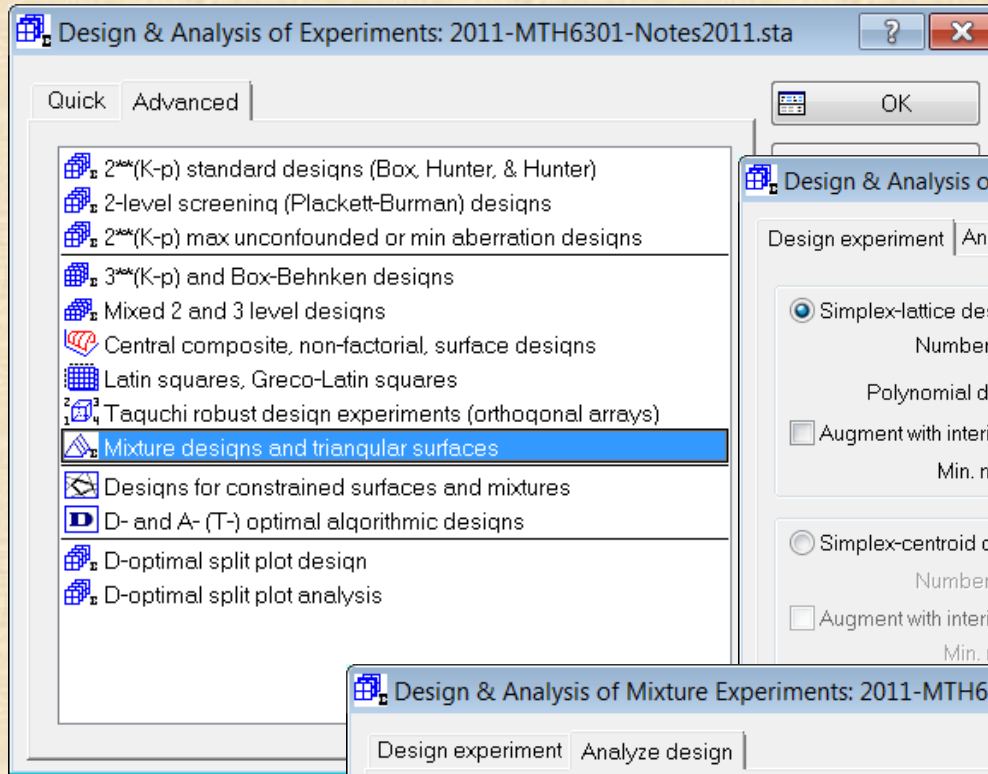
Chapitre 13

Plans pour mélanges

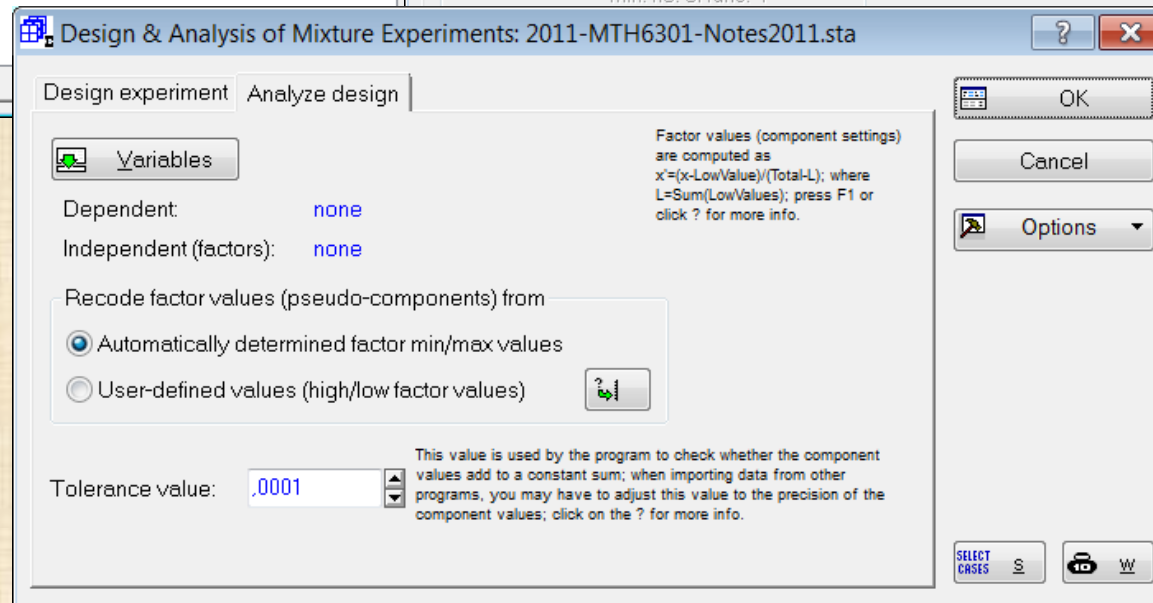
- plans pour mélanges
- **mélanges : modèles**
- exemple 13.1- tissus
- **mélanges avec contraintes**
- exemple 13.2 - peinture
- **exemple 13.3 - biotechnologie**

Plans pour mélanges: conception et analyse avec STATISTICA

conception



analyse

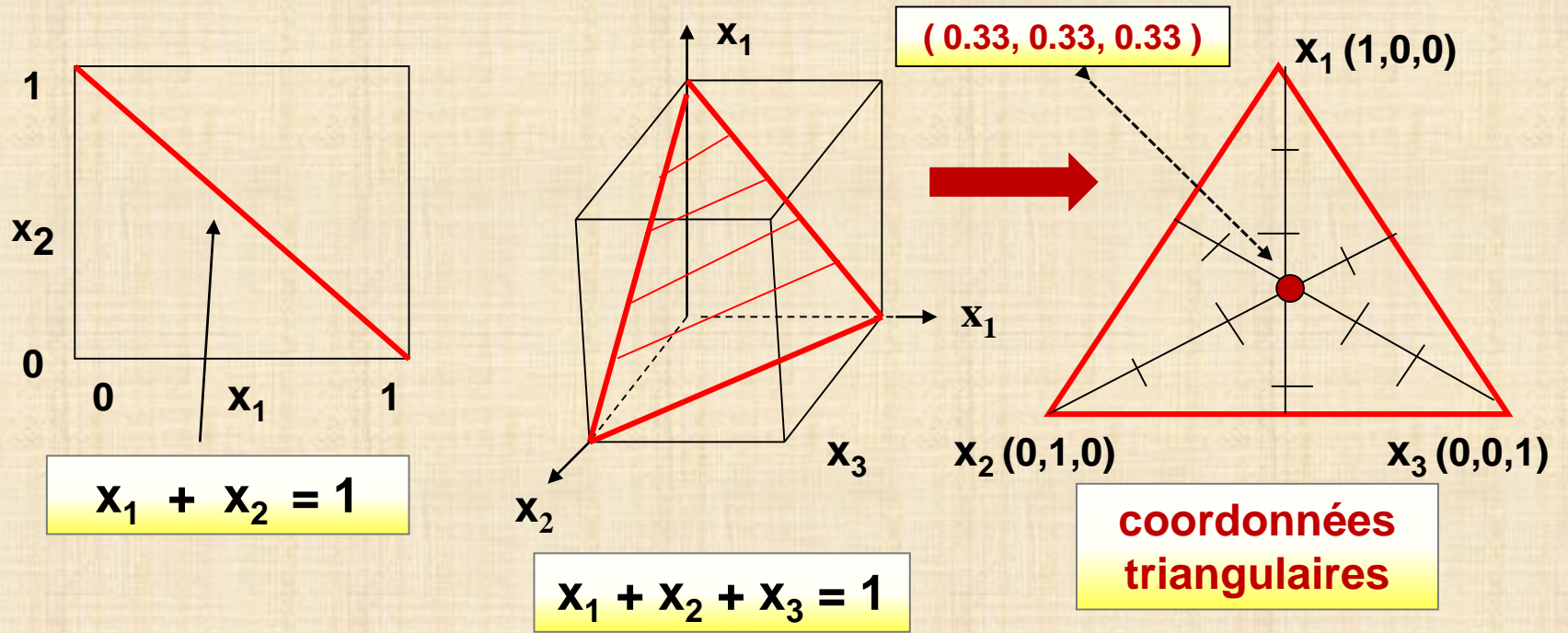


MÉLANGES

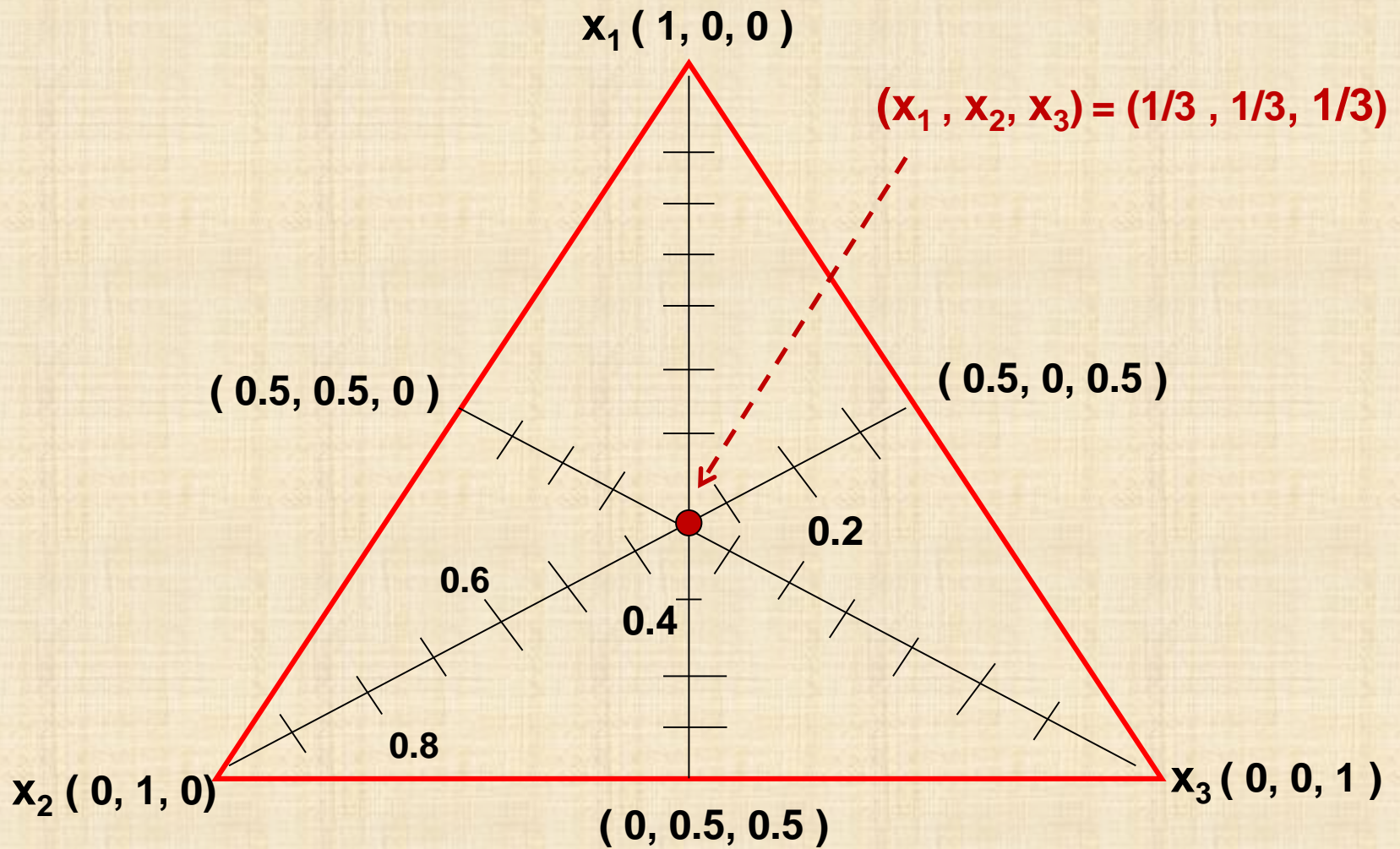
Domaines d'applications : alimentation, pharmaceutique, chimique, métallurgie, biotechnologie, ...

mélange (« mixture ») : les facteurs X_j sont les proportions de p composants (ingrédients)

simplexe $X_1 + X_2 + \dots + X_p = 1$ $0 \leq X_j \leq 1$
les facteurs X_j ne sont pas linéairement indépendants : contraintes



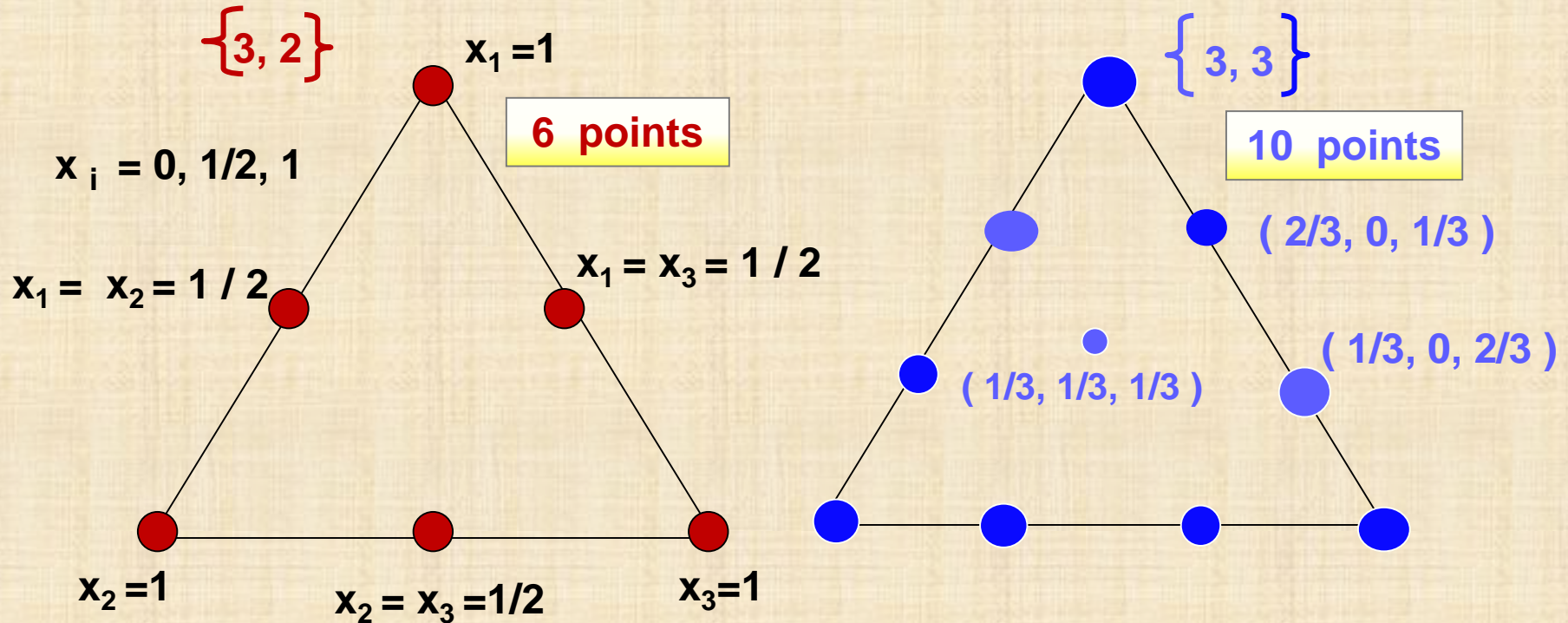
coordonnées triangulaires



plans SIMPLEX - LATTICE

notation : $\{p, m\}$ p composants

$$x_i = 0, 1/m, 2/m, \dots, 1 \quad i = 1, 2, \dots, p \quad m = 2, 3, \dots$$

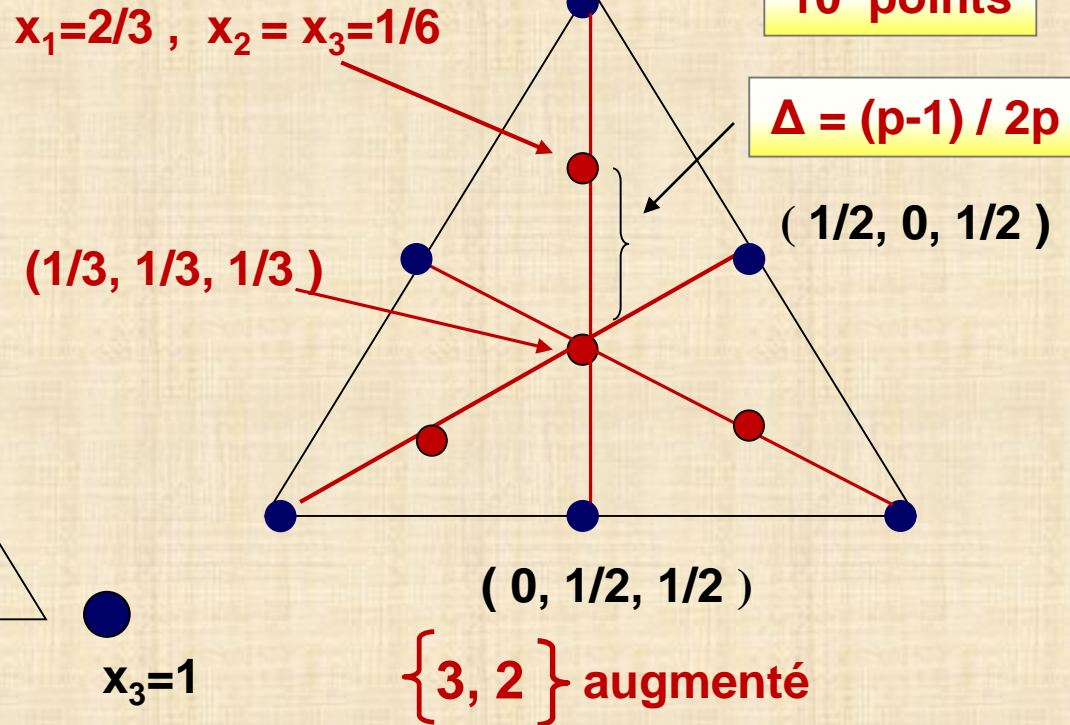
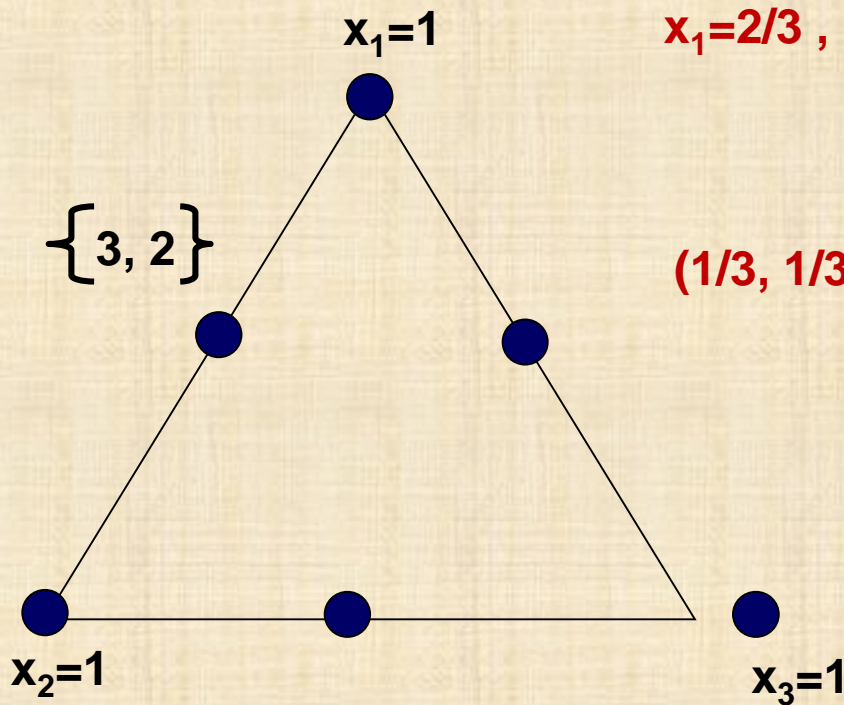


$$N = (p + m - 1)! / m! (p - 1)! \quad \text{points}$$

majorité des points situés sur la frontière

plans SIMPLEX – LATTICE augmenté avec des points axiaux

axe composant i : droite point de base $x_i = 0$ et $x_j = 1/(p-1)$ $j \neq i$
 au sommet opposé $x_i = 1$ et $x_j = 0$ $j \neq i$



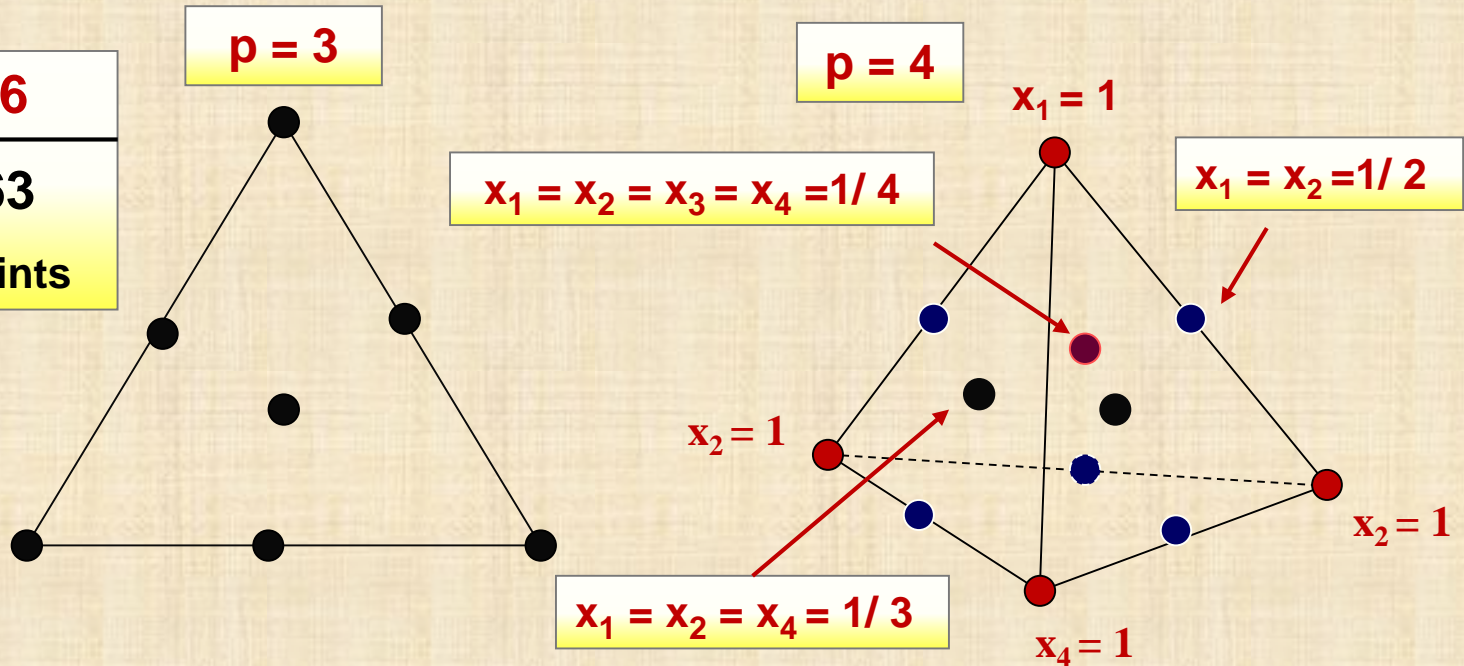
préférable au plan $\{3, 3\}$ pour
détecter manque d'ajustement

Plans SIMPLEX - CENTROID

$N = 2^p - 1$ points formés de

- p points sommet : $(1, 0, 0, \dots, 0)$ $(0, 1, 0, 0, \dots, 0)$ $(0, 0, \dots, 1)$
- $p(p-1)/2$ points segment: $(\frac{1}{2}, \frac{1}{2}, 0, 0, \dots, 0)$ $(\frac{1}{2}, 0, \frac{1}{2}, 0, \dots, 0)$... $(0, 0, \dots, \frac{1}{2}, \frac{1}{2})$
- $p(p-1)(p-2)/6$ points centroïde: $(\frac{1}{3}, \frac{1}{3}, \frac{1}{3}, 0, \dots, 0)$... $(0, 0, \dots, \frac{1}{3}, \frac{1}{3}, \frac{1}{3})$
-
- 1 point centroïde global: $(\frac{1}{p}, \frac{1}{p}, \dots, \frac{1}{p})$

p	3	4	5	6
N	7	15	31	63
N: nombre de points				



Modèles pour mélanges

Linéaire $Y = \beta_0^* + \beta_1^* x_1 + \beta_2^* x_2 + \dots + \beta_p^* x_p$ modèle usuel

devient $= \sum_{j=1}^{j=p} \beta_j x_j + \varepsilon$ avec $\beta_j = \beta_0^* + \beta_j^*$ car $\sum x_j = 1$

modèle de régression passant par l'origine : $\beta_0 = 0$

Quadratique $Y = \sum \beta_j x_j + \sum_{i < j} \sum \beta_{ij} x_i x_j + \varepsilon$

Cubique

$$Y = \sum \beta_j x_j + \sum_{i < j} \sum \beta_{ij} x_i x_j + \sum_{i < j < k} \sum \beta_{ijk} x_i x_j x_k + \sum_{i < j} \sum \delta_{ijk} x_i x_j (x_i - x_j) + \varepsilon$$

Cubique spécial

$$Y = \sum \beta_j x_j + \sum_{i < j} \sum \beta_{ij} x_i x_j + \sum_{i < j < k} \sum \beta_{ijk} x_i x_j x_k + \varepsilon$$

Exemple – 13.1- tissu

mélange 3 composants : x1 = polyethlene x2 = polystyrene x3 = polypropylene

Y = élongation tissu force appliquée

plan simplex-lattice (3,2) répété n = 2 pour point = 1, 2, 3, 4, 5 et n = 3 pour point = 6

i	point	rep	x1	x2	x3	Y
1	1	1	1.0	0.0	0.0	11.0
2	1	2	1.0	0.0	0.0	12.4
3	2	1	0.5	0.5	0.0	15.0
4	2	2	0.5	0.5	0.0	14.8
5	2	3	0.5	0.5	0.0	16.1
6	3	1	0.0	1.0	0.0	8.8
7	3	2	0.0	1.0	0.0	10.0
8	4	1	0.0	0.5	0.5	10.0
9	4	2	0.0	0.5	0.5	9.7
10	4	3	0.0	0.5	0.5	11.8
11	5	1	0.0	0.0	1.0	16.8
12	5	2	0.0	0.0	1.0	16.0
13	6	1	0.5	0.0	0.5	17.7
14	6	2	0.5	0.0	0.5	16.4
15	6	3	0.5	0.0	0.5	16.6

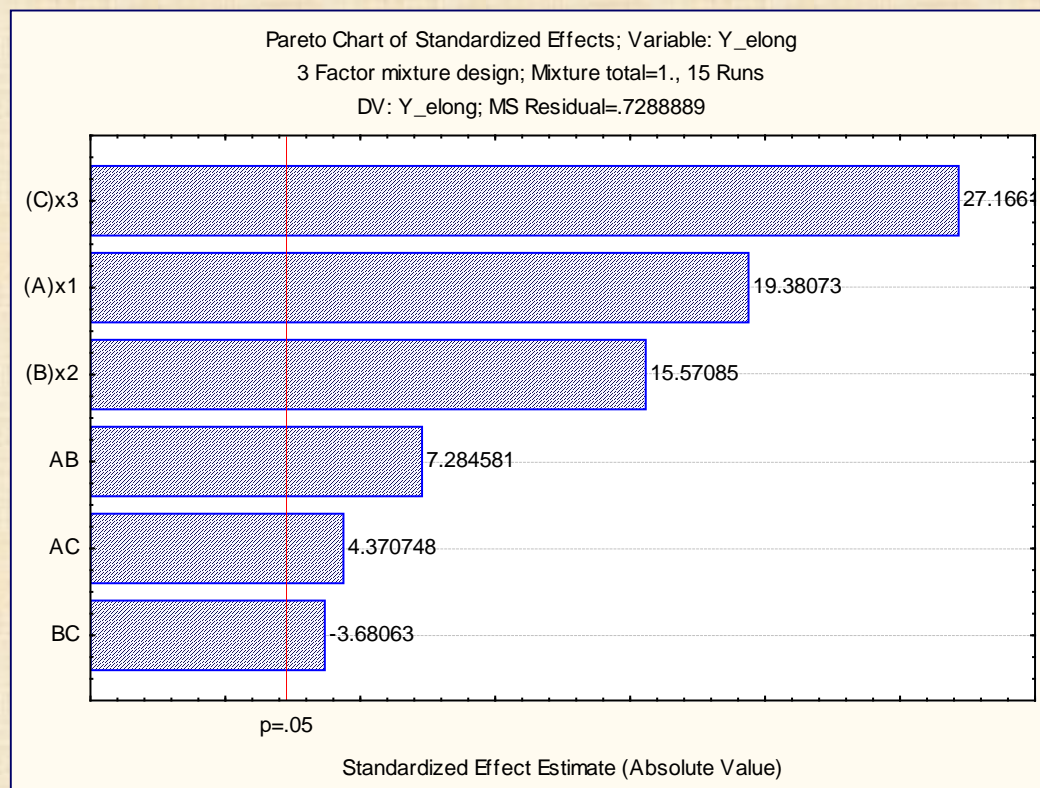
modèle quadratique

	SS	DF	MS	F	p
Model	128.30	5	25.66	35.20	0.00001
Total Error	6.56	9	0.73		
Lack of Fit	0.00	0	0.00		
Pure Error	6.56	9	0.73		
Total Adjusted	134.86	14	9.63		

Exemple – 13.1 (suite)

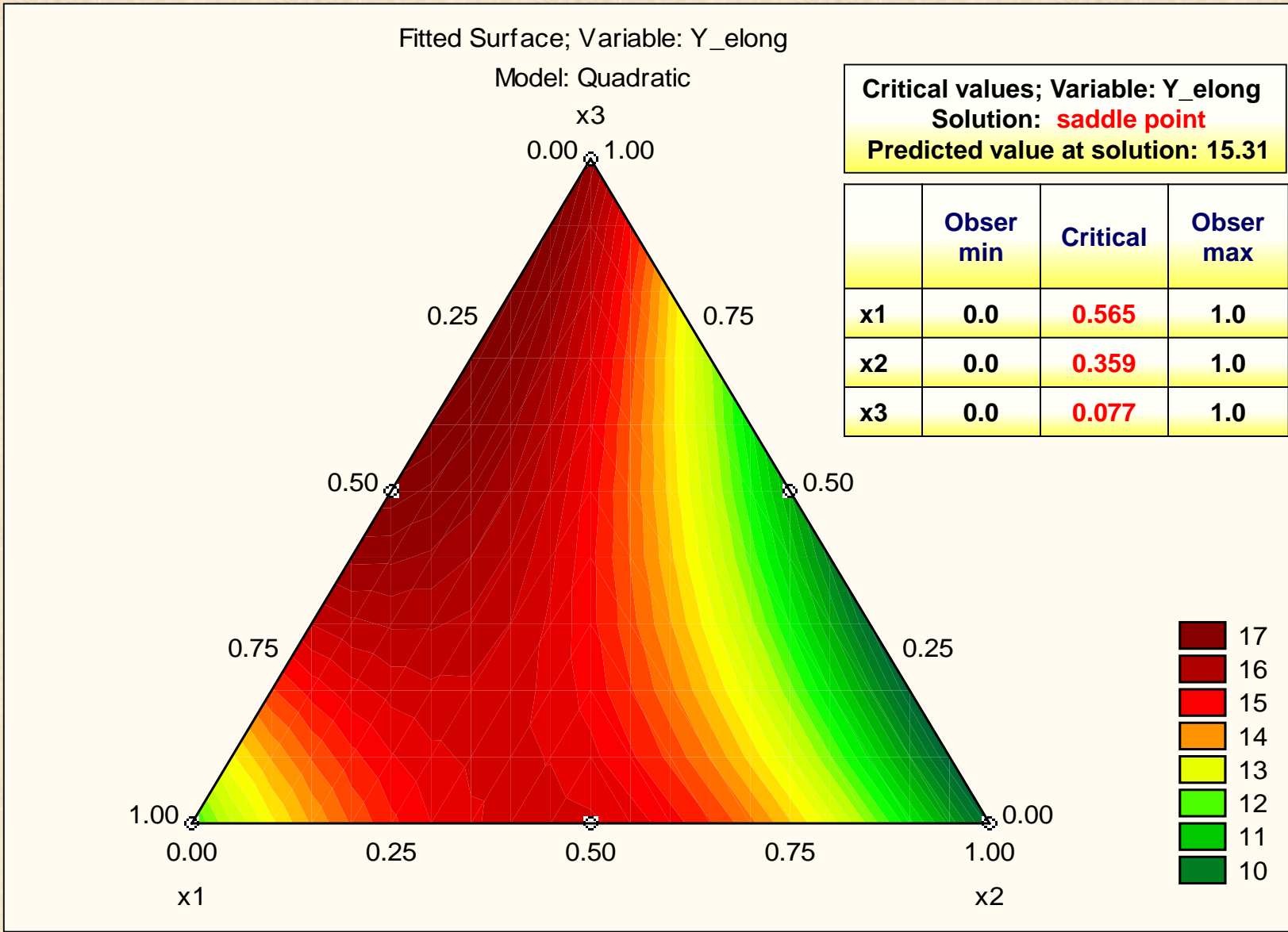
Coeffs R-sqr = 0,9514; Adj:0,9243

	Coeff	Std.Er	t(9)	p
(A)x1	11.7	0.6037	19.38	0.0000
(B)x2	9.4	0.6037	15.57	0.0000
(C)x3	16.4	0.6037	27.17	0.0000
AB	19.0	2.6082	7.28	0.0000
AC	11.4	2.6082	4.37	0.0018
BC	-9.6	2.6082	-3.68	0.0051

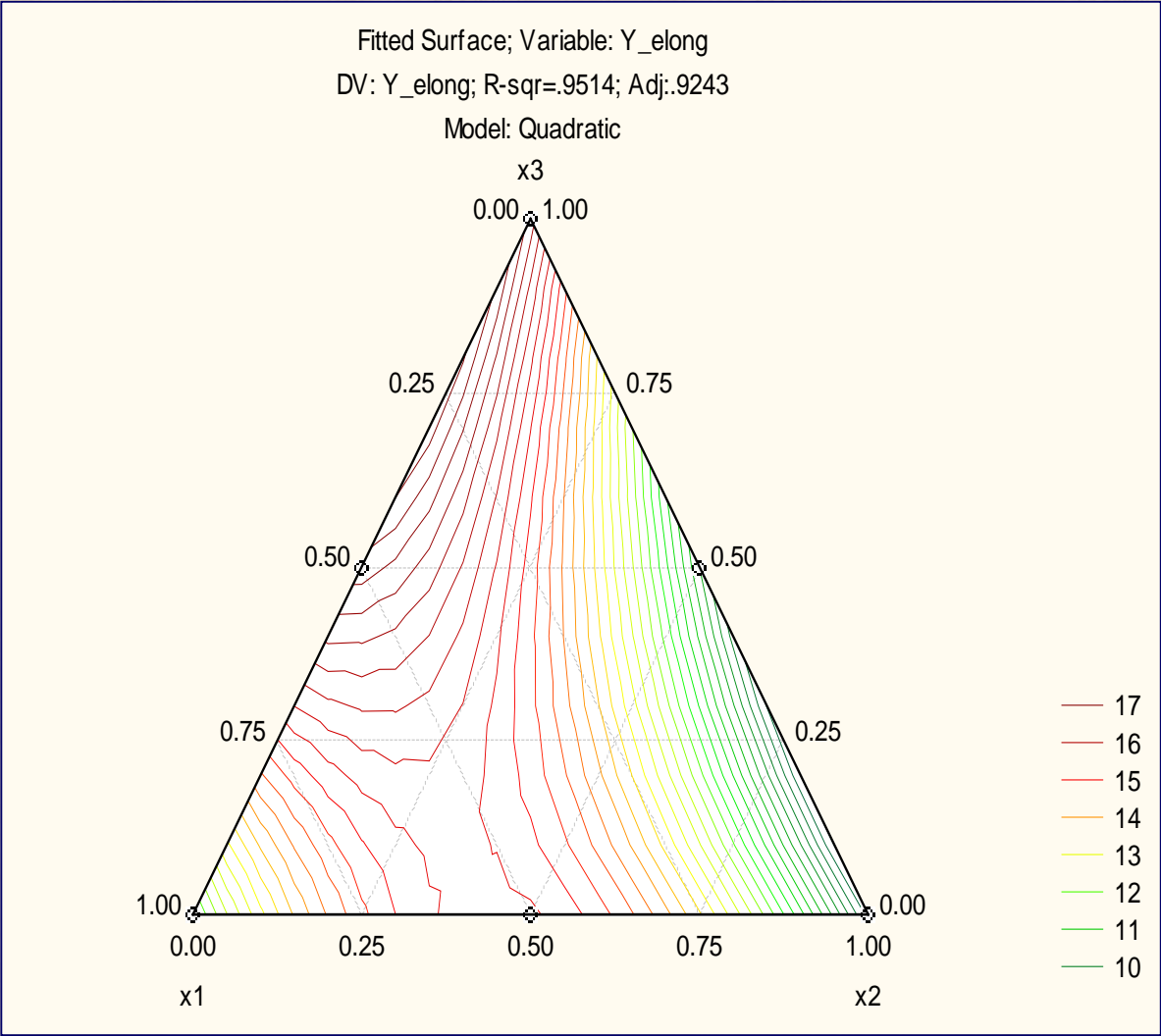


$$Y = 11.7 x_1 + 9.4 x_2 + 16.4 x_3 + 19.0 x_1 x_2 + 11.4 x_1 x_3 - 9.6 x_2 x_3$$

Exemple – 13.1 (suite)



Exemple – 13.1 (suite)



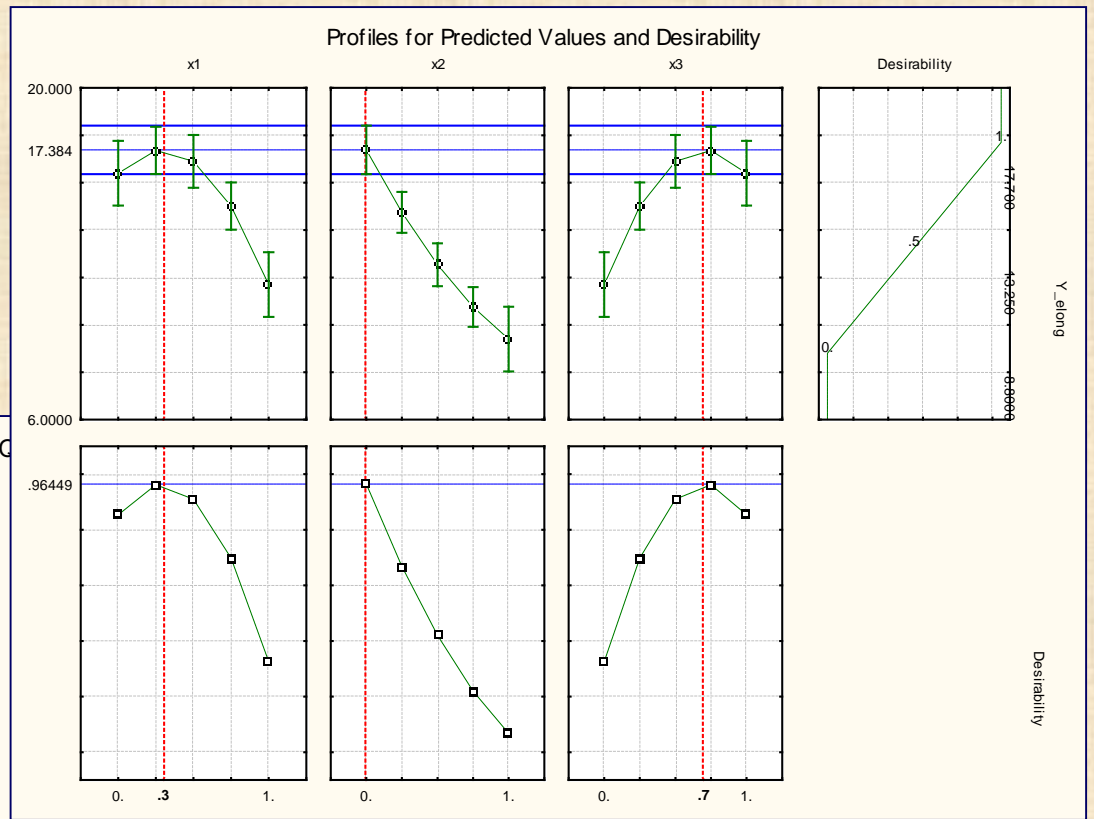
	Obs min	Critical	Obs max
x1	0.0	0.565	1.0
x2	0.0	0.359	1.0
x3	0.0	0.077	1.0

Critical values;
Variable: Y_elong

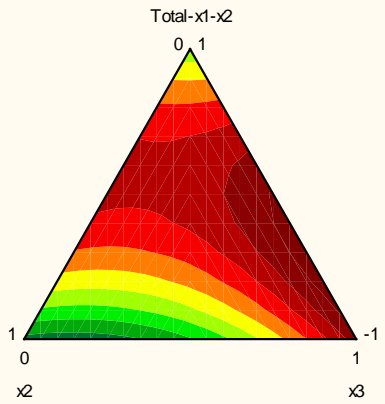
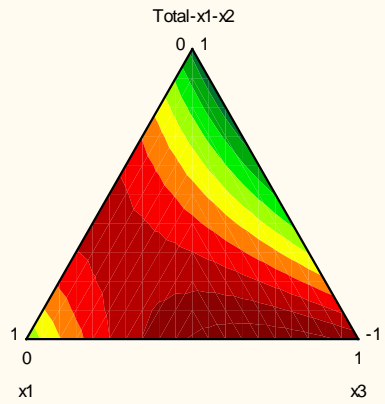
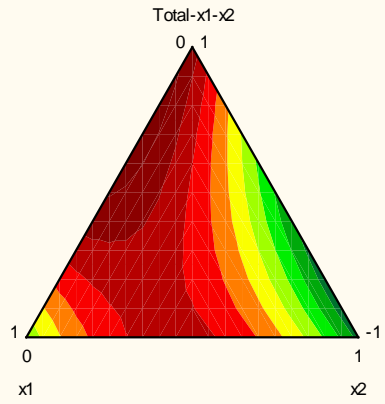
Solution: saddle point

Predicted value
at solution: 15.31

Exemple– 13.1 (suite)



Desirability Surface/Contours; Model: C



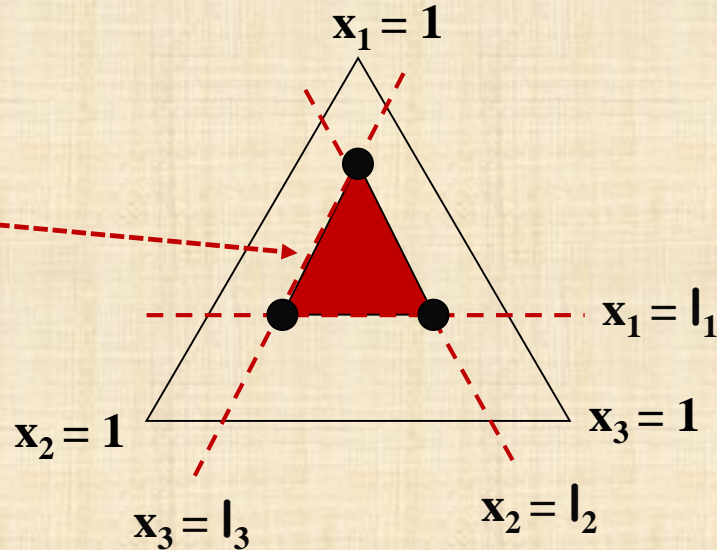
	Obs min	Critical	Obs max
x_1	0.0	0.565	1.0
x_2	0.0	0.359	1.0
x_3	0.0	0.077	1.0

MÉLANGES AVEC CONTRAINTES

cas 1 : bornes inférieures

$$0 < l_i \leq x_i \leq 1 \quad i = 1, 2, \dots, p$$

région faisabilité :
encore un simplexe



pseudo-composants

$$x'_i = (x_i - l_i) / (1 - L) \quad L = \sum l_i < 1$$

$$\sum x'_i = 1$$

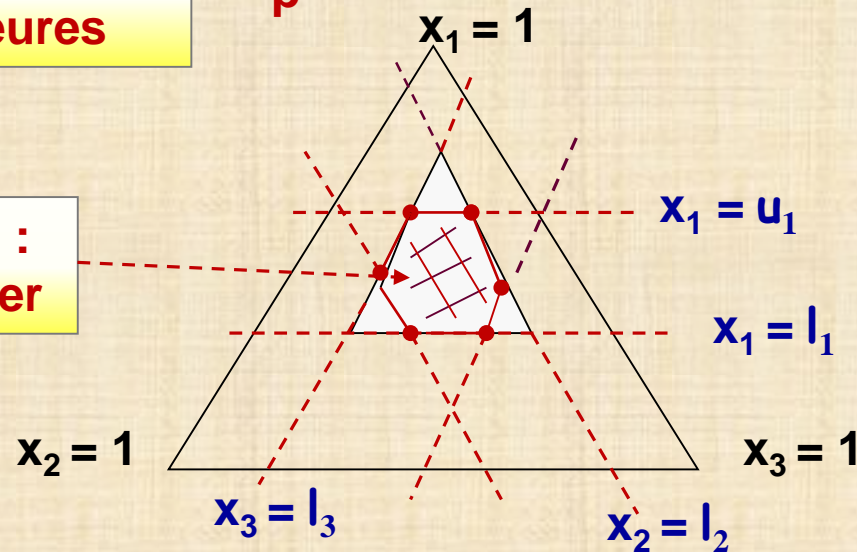
$$x_i = l_i + (1 - L) x'_i$$

MÉLANGES AVEC CONTRAINTES

cas 2 : bornes supérieures
bornes inférieures

$$0 < l_i \leq x_i \leq u_i < 1 \quad i = 1, 2, \dots, p$$

région faisabilité :
polygone irrégulier



pseudo-composants

$$x'_i = (x_i - l_i) / (u_i - l_i)$$

« recoded components »

$$0 \leq x'_i \leq 1$$

$$x_i = l_i + (u_i - l_i) x'_i$$

détermination sommets polygone : logiciel nécessaire
concept : design « D-optimal »

Exemple – 13.2 – peinture

composition peinture voiture

x1 : % monomere

x2 : % crosslinker

x3 : % resin

Y_dur : dureté Knoop

Y_solid : % solid

$$x_1 + x_2 + x_3 = 1$$

$$5 \leq x_1 \leq 25$$

$$25 \leq x_2 \leq 40$$

$$50 \leq x_3 \leq 70$$

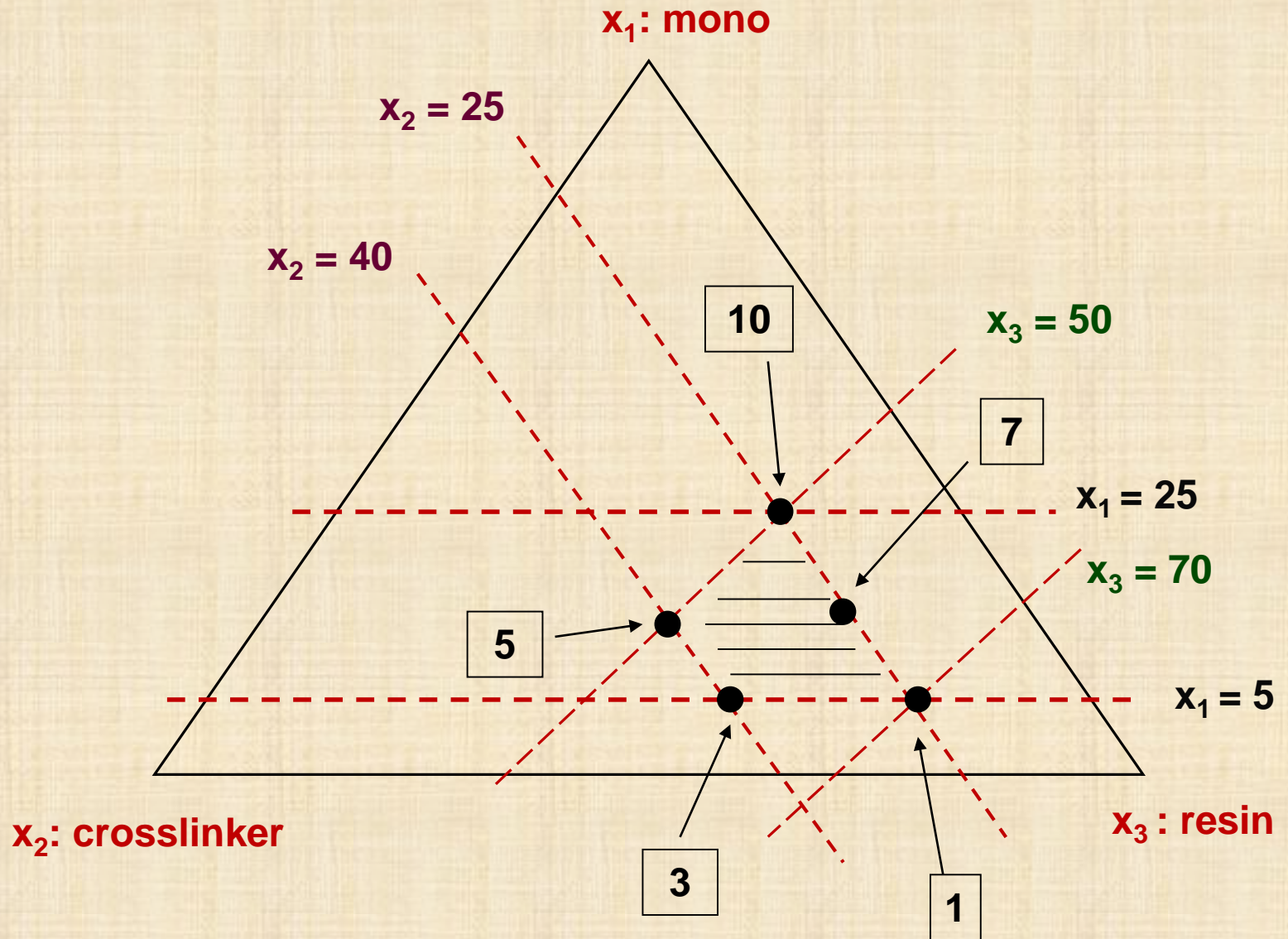
OBJECTIF

$$Y_{dur} \geq 25$$

$$Y_{solid} \leq 30$$

i	point	rep	x1	x2	x3	y_dur	y_solid
1	1	1	5.00	25.00	70.00	35	74.98
2	1	2	5.00	25.00	70.00	23	70.95
3	2	1	5.00	32.50	62.50	31	31.50
4	3	1	5.00	40.00	55.00	20	19.20
5	4	1	8.13	28.75	63.13	25	32.49
6	5	1	10.00	40.00	50.00	26	27.33
7	5	2	10.00	40.00	50.00	30	32.98
8	6	1	11.25	32.50	56.25	21	15.59
9	7	1	15.00	25.00	60.00	17	29.21
10	7	2	15.00	25.00	60.00	14	41.06
11	8	1	17.50	32.50	50.00	29	9.54
12	9	1	18.13	28.75	53.13	29	23.44
13	10	1	25.00	25.00	50.00	28	30.46
14	10	2	25.00	25.00	50.00	19	23.01

Exemple – 13.2 (suite)



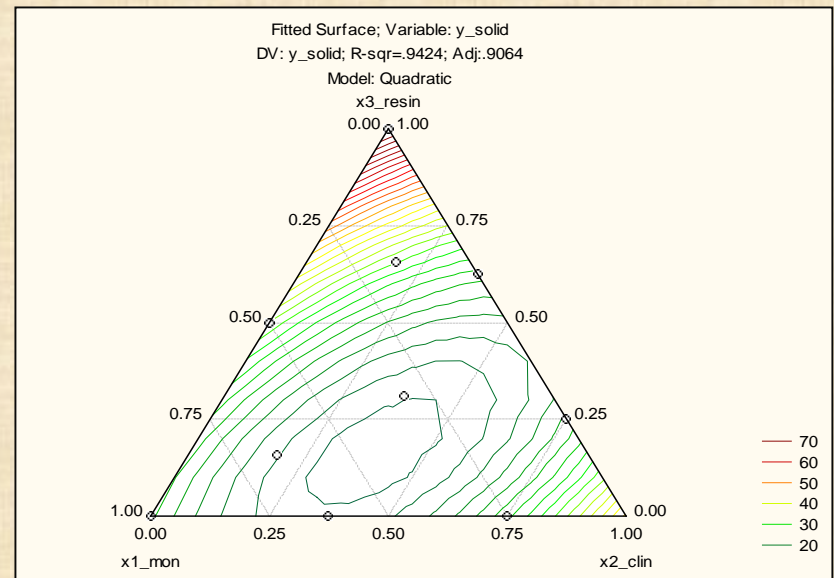
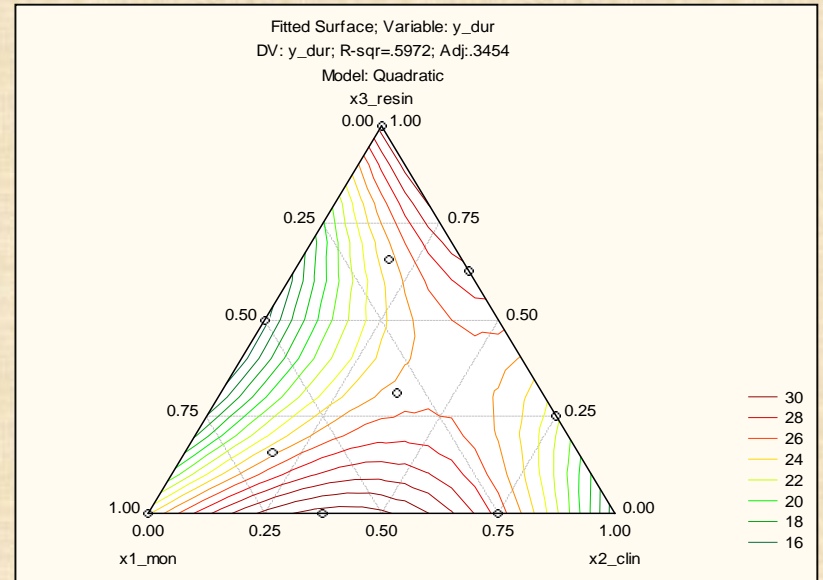
Exemple – 13.2 (suite)

Coeffs (recoded comps);
Var.:y_dur; R-sqr = 0.5972; Adj: 0.3454

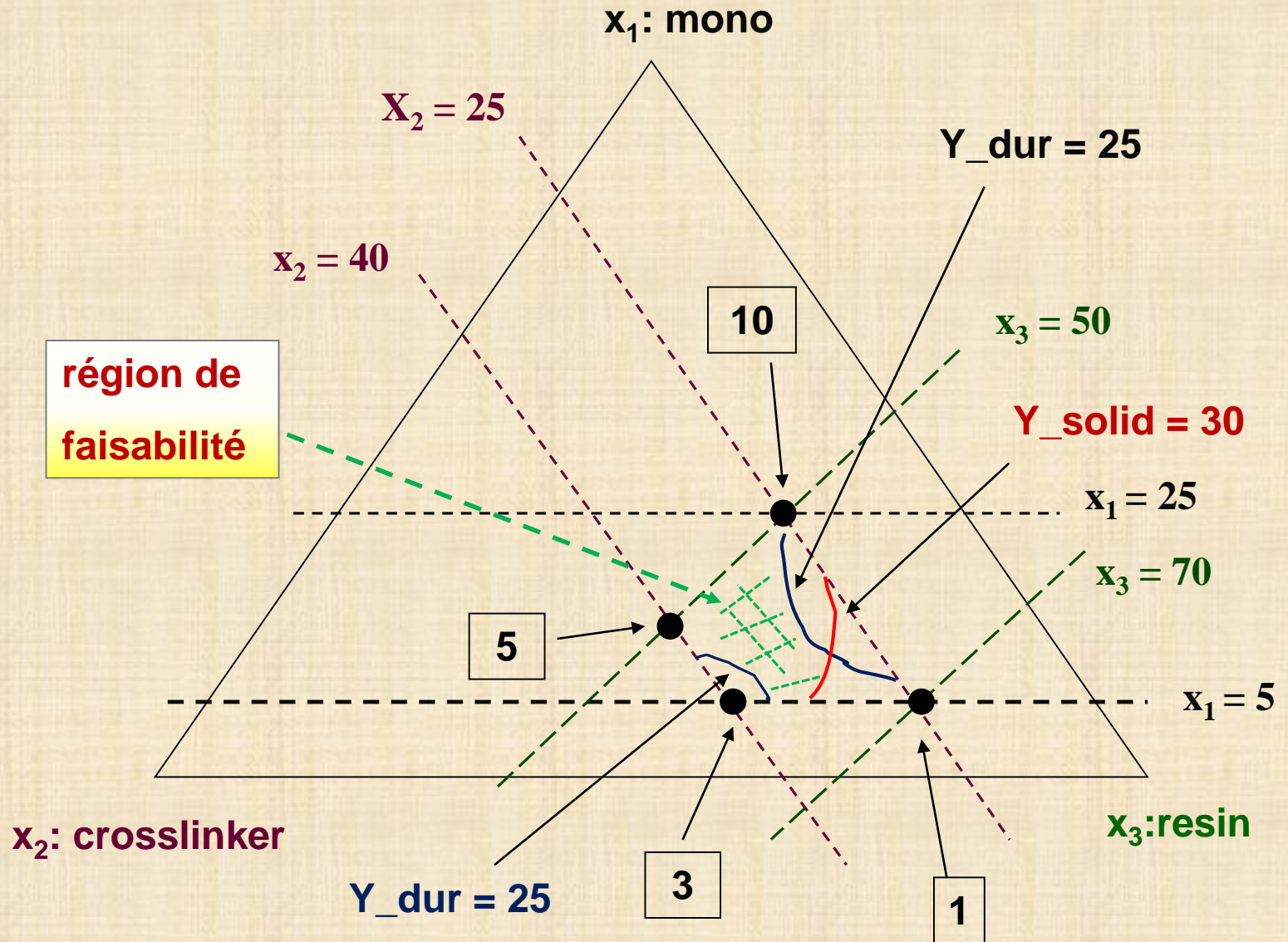
	Coeff.	Std.Err	t(8)	p
(A)x1_mon	23.81	3.36	7.09	0.0001
(B)x2_clin	16.40	7.69	2.13	0.0655
(C)x3_resin	29.45	3.36	8.77	0.0000
AB	44.43	25.32	1.75	0.1174
AC	-44.01	15.94	-2.76	0.0247
BC	13.81	23.32	0.59	0.5702

Var.:y_solid; R-sqr = 0.9424; Adj:0.9064

	Coeff.	Std.Err	t(8)	p
(A)x1_mon	26.53	3.96	6.70	0.0002
(B)x2_clin	46.52	9.07	5.13	0.0009
(C)x3_resin	73.22	3.96	18.49	0.0000
AB	-75.44	29.86	-2.53	0.0355
AC	-56.20	18.81	-2.99	0.0174
BC	-154.30	27.51	-5.61	0.0005



Exemple – 13.2 (suite)



Exemple – 13.3 - biotechnologie

Multiple Factor Design for Reactive Mixture Selection for Use in Reactive Walls in Mine Drainage Treatment

I.Cocos, G.Zagury, B.Clément, R. Samson, *Water Research vol. 32, 2002, pp. 167-177*

Plan de mélange avec contraintes

	$0 < \text{wood chips (X1)} < 30$	(1)
	$0 < \text{leaf compost (X2)} < 30$	(2)
	$10 < \text{poultry manure (X3)} < 20$	(3)
	$0 < \text{oxidized tailing (X4)} < 8$	(4)
	$0 < \text{silica sand (X5)} < 8$	(5)
	$30 < X1 + X2 < 40$	(6)
	$5 < X4 + X5 < 8$	(7)
contrainte	$X1 + X2 + X3 + X4 + X5 = 58$	(8)

Exemple – 13.3 (suite)

Plan expérimental - 17 essais en duplicata n = 2

réacteur	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
X1	30	30	0	0	30	10	30	10	30	30	3	3	30	30	10	10	17.87
X2	0	0	30	30	10	30	10	30	3	3	30	30	10	10	30	30	17.87
X3	20	20	20	20	10	10	10	10	20	20	20	20	13	13	13	13	15.75
X4	8	0	8	0	8	8	0	0	5	0	5	0	5	0	5	0	3.25
X5	0	8	0	8	0	0	8	8	0	5	0	5	0	5	0	5	3.25

Mesures

Y : taux de réduction (mg/l /) sulfate après 5, 9, 13, 17, 21, 25, 33, 41 jours

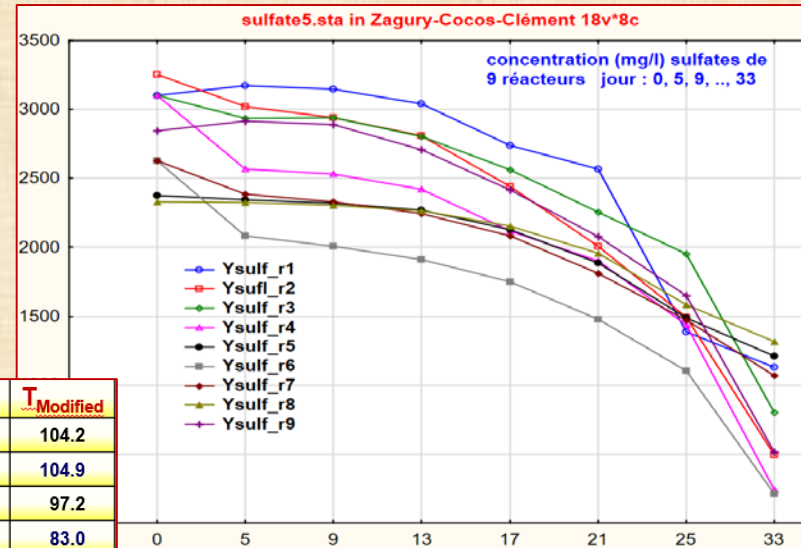
autres mesures : pH, sulfide, cuivre, ...

Plan en **mesures répétées** avec le **facteur INTRA TEMPS** (0, 5, 9, ..., 41)

Analyse : avec la pente période 0-41 jours

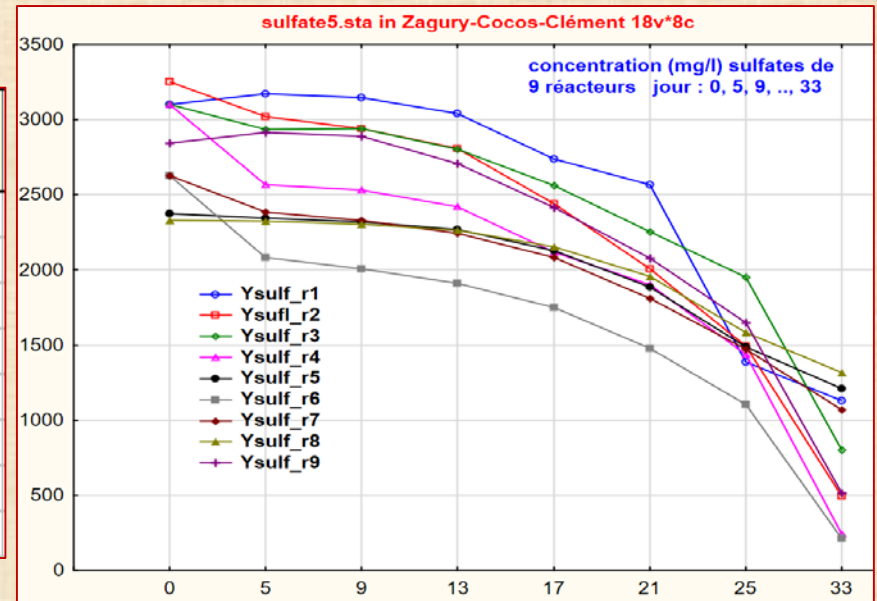
T₀₋₄₁ taux de decomposition (pente)

React.	T ₀₋₄₁	T _{Modified}	React.	T ₀₋₄₁	T _{Modified}
1.1	85.8	115.1	1.2	77.9	104.2
2.1	86.5	100.3	2.2	87.6	104.9
3.1	85.4	128.2	3.2	70.8	97.2
4.1	78.0	74.6	4.2	79.8	83.0
5.1	53.2	82.3	5.2	57.8	78.9
6.1	66.5	68.2	6.2	64.6	64.3
7.1	63.1	63.1	7.2	58.4	79.7
8.1	35.6	45.9	8.2	52.0	82.6
9.1	77.7	100.7	9.2	79.1	118.1
10.1	84.8	132.2	10.2	84.0	125.5
11.1	81.6	129.4	11.2	77.0	119.9
12.1	83.6	153.5	12.2	84.3	156.3
13.1	61.6	95.8	13.2	64.0	97.2
14.1	71.7	131.8	14.2	67.8	102.7
15.1	63.4	93.1	15.2	63.0	96.1
16.1	58.8	92.6	16.2	58.8	107.0
17.1	70.7	150.2	17.2	67.6	150.3

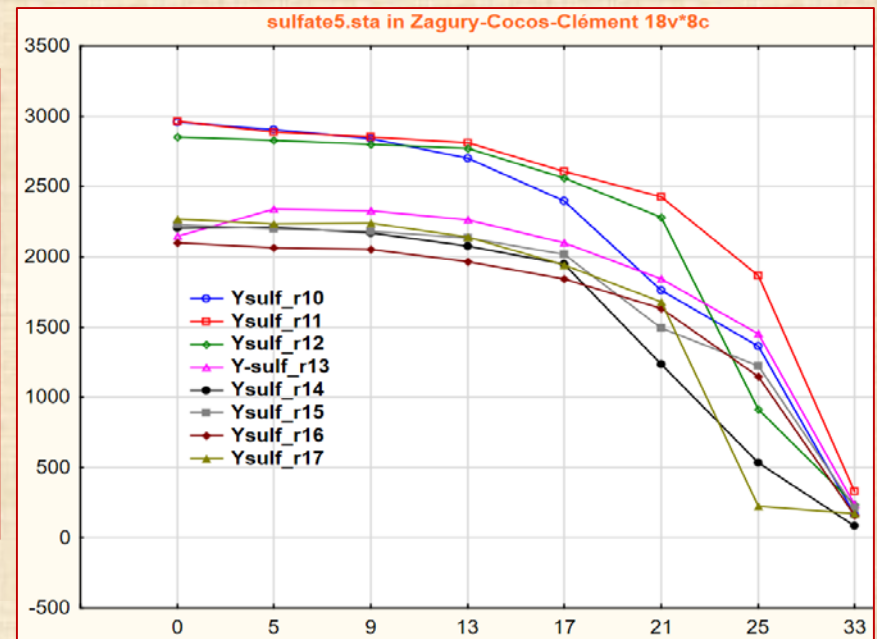


Exemple – 13.3 (suite)

1	2	3	4	5	6	7	8	9	10
time	Ysulf_r1	Ysulf_r2	Ysulf_r3	Ysulf_r4	Ysulf_r5	Ysulf_r6	Ysulf_r7	Ysulf_r8	Ysulf_r9
0	3101	3254	3100	3100	2377	2629	2628	2330	2843
5	3173	3022	2934	2567	2347	2085	2386	2325	2914
9	3147	2941	2941	2532	2319	2008	2331	2304	2892
13	3042	2810	2805	2419	2272	1910	2247	2265	2709
17	2740	2443	2564	2120	2128	1752	2086	2156	2416
21	2568	2008	2256	1901	1889	1480	1814	1957	2080
25	1390	1496	1953	1438	1489	1105	1471	1583	1647
33	1129	496	801	242	1211	213	1071	1319	515



11	12	13	14	15	16	17	18	19
time	Ysulf_r10	Ysulf_r11	Ysulf_r12	Y-sulf_r13	Ysulf_r14	Ysulf_r15	Ysulf_r16	Ysulf_r17
0	2959	2962	2852	2149	2207	2228	2100	2271
5	2903	2887	2827	2342	2212	2196	2066	2236
9	2842	2855	2802	2328	2167	2180	2052	2242
13	2702	2813	2771	2265	2077	2133	1968	2140
17	2397	2607	2559	2099	1948	2020	1841	1945
21	1760	2427	2280	1843	1235	1494	1630	1680
25	1363	1864	912	1450	533	1223	1147	225
33	164	332	239	236	83	215	164	173



Exemple – 13.3 modélisation

Modèle 1

$$Y1 = \sum_{i=1}^5 \alpha_i X_i + \sum_{i \neq j} \sum_{j=1}^5 \alpha_{ij} X_i X_j \quad (1)$$

Modèle 2

$$Y2 = \beta_0 + \sum_{i=1}^5 \beta_i Z_i + \sum_{i=1}^5 \beta_{ii} Z_i^2 + \sum_{i < j} \sum_{j=1}^5 \beta_{ij} Z_i Z_j \quad (2)$$

$$Z_i = X_i / X_3$$

$$X_3 \geq 10$$

$$i, j = 1, 2, 4, 5$$

^

$$Y1 = 2.205 X_3 - 0.057 X_2 X_5 + 9.065 X_3 X_5 \quad R^2 = 0.86$$

^

$$Y2 = 79.04 - 9.34 Z_1 Z_2 - 11.11 Z_2 Z_5 + 23.26 Z_5 + 5.05 Z_2 Z_4 \quad R^2 = 0.89$$

$$Z_1 Z_2 = X_1 X_2 / X_3^2$$

max Y si : X_3 min et $X_1 X_2$ max