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## 7 Anexos

Anexo I: Gráficos de superfície de resposta para o micronebulizador PFA-100<sup>TM</sup>

Anexo II: Gráficos de superfície de resposta para o micronebulizador Miramist<sup>TM</sup>

Anexo III: Espectro de emissão das vizinhanças dos analitos estudados em ICP OES.

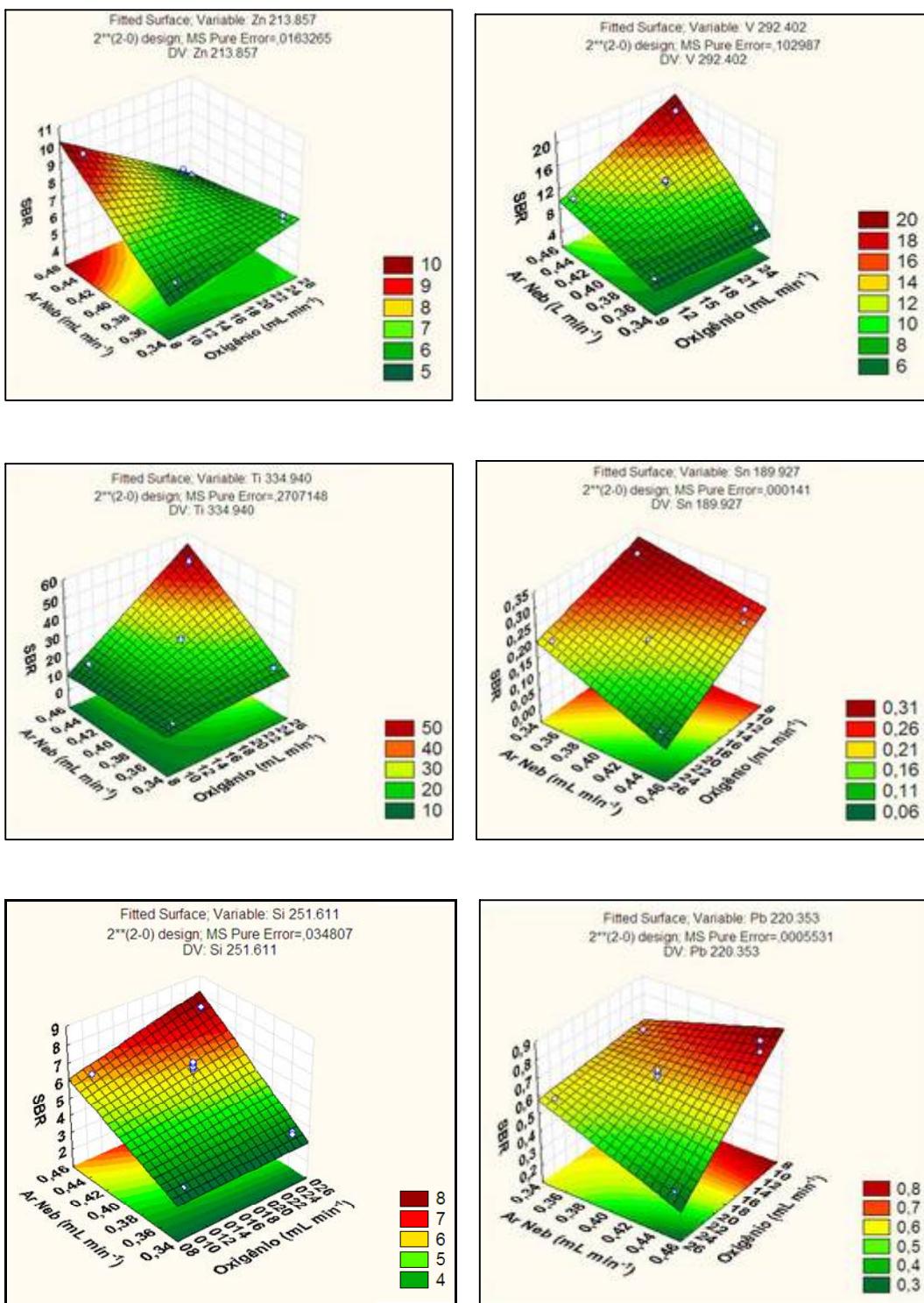
Anexo IV: Tabela dos parâmetros empíricos para o cálculo da pressão de vapor

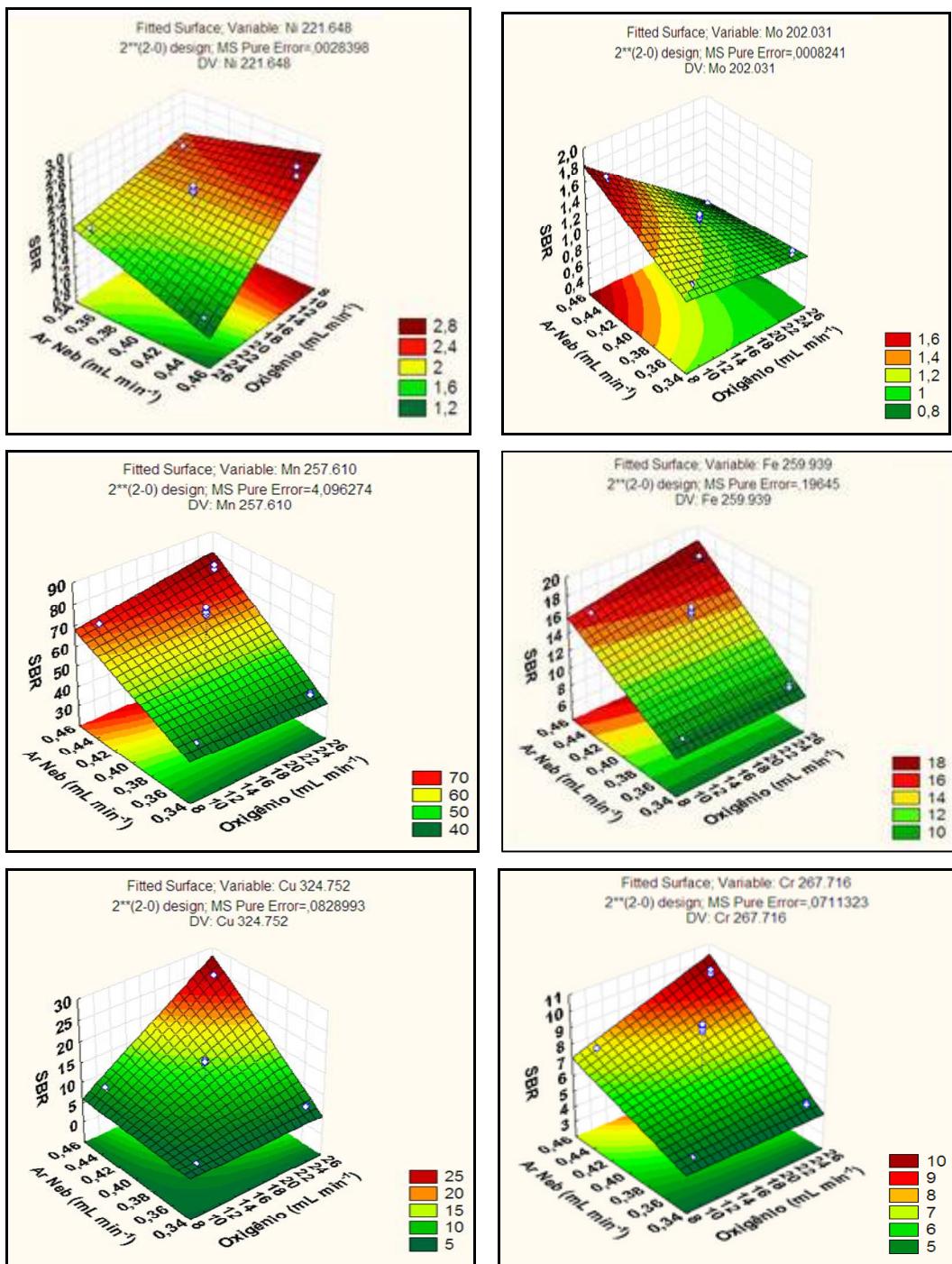
Anexo V: Gráficos da otimização das condições da célula de reação dinâmica

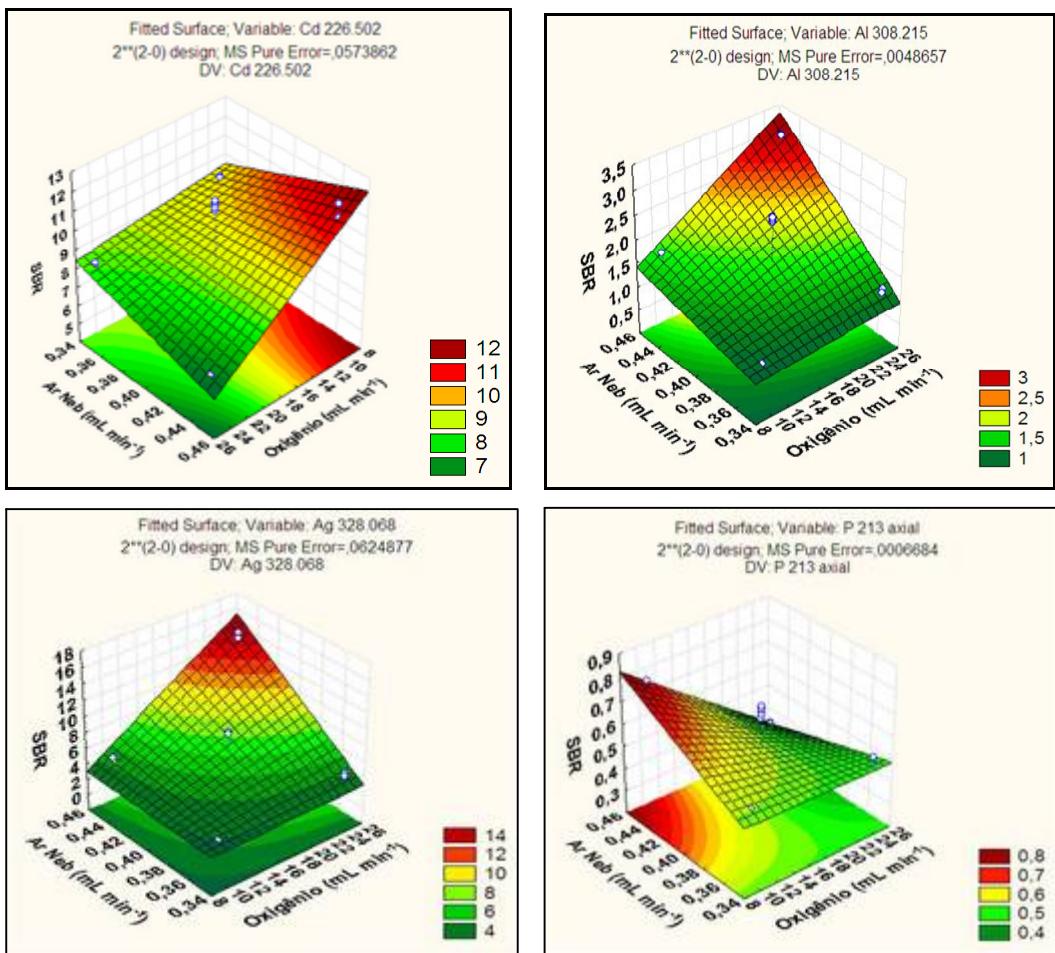
Anexo VI: Superfície de resposta e gráfico de Pareto para planejamento composto central em DRC-ICP-MS

Anexo VII: Comparativo entre as técnicas ICP OES e DRC-ICP-MS

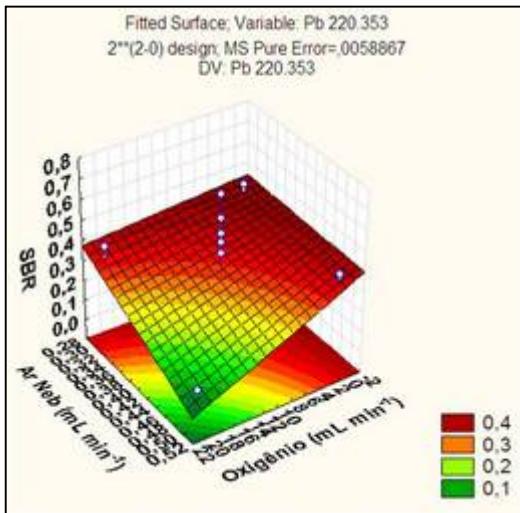
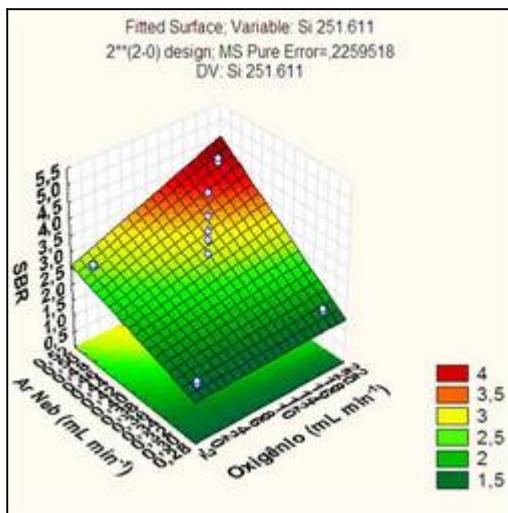
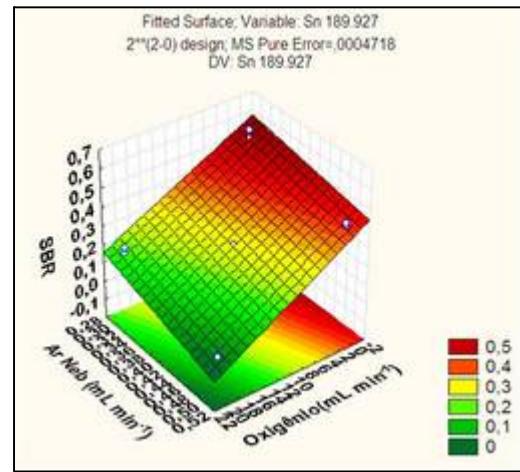
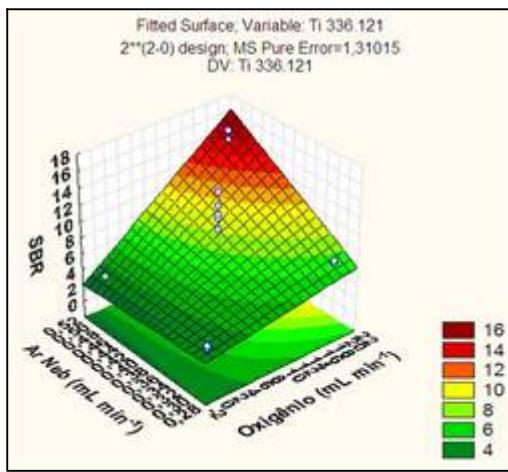
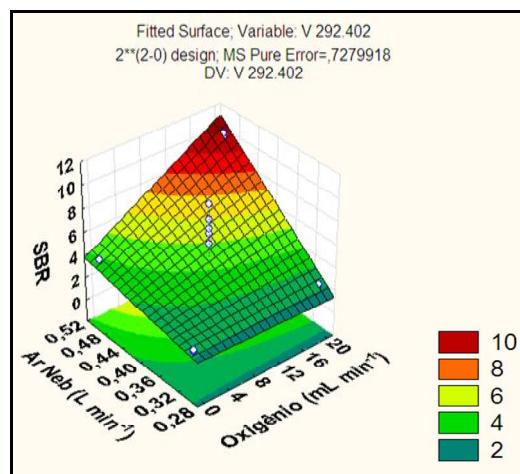
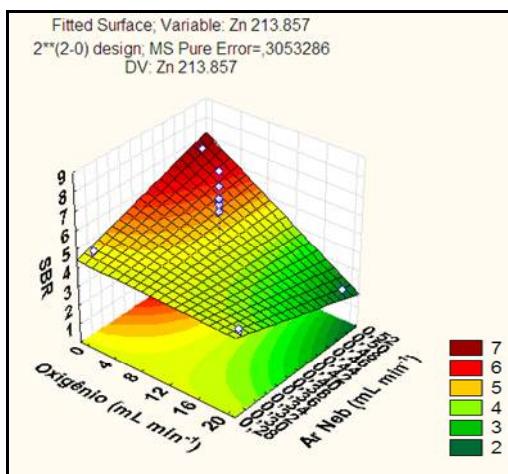
Anexo I: Gráficos de superfície de resposta para o micronebulizador PFA-100<sup>TM</sup>

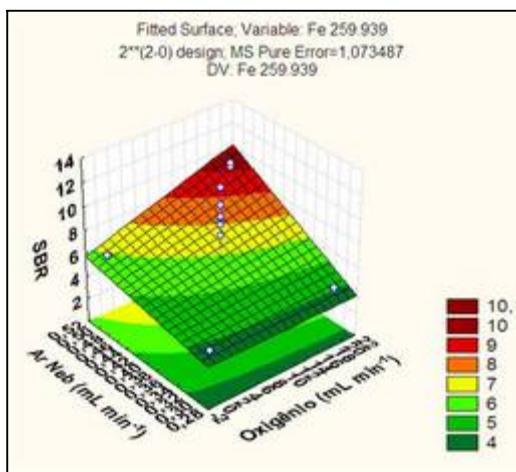
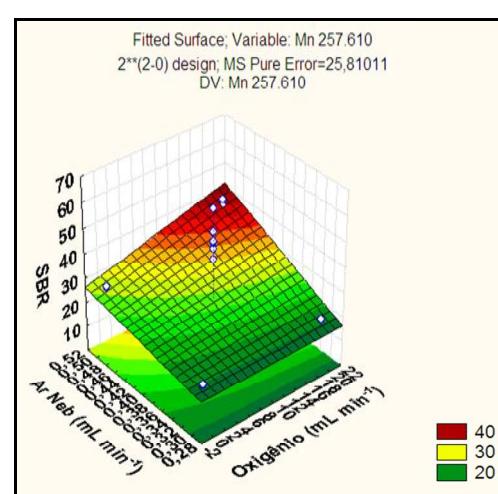
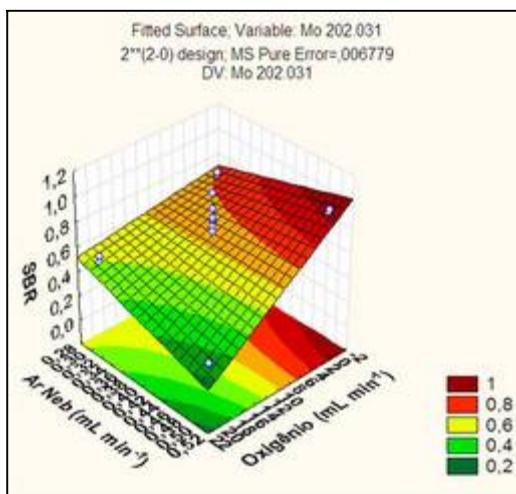
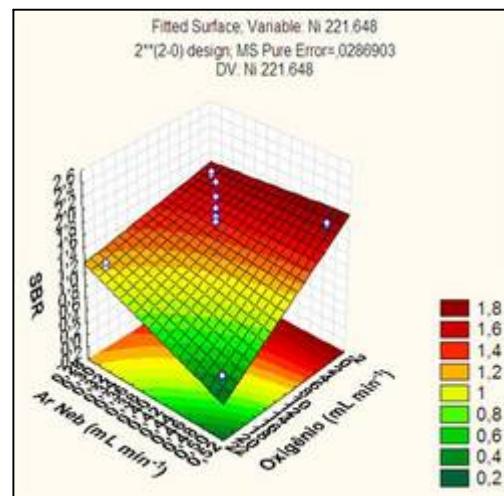
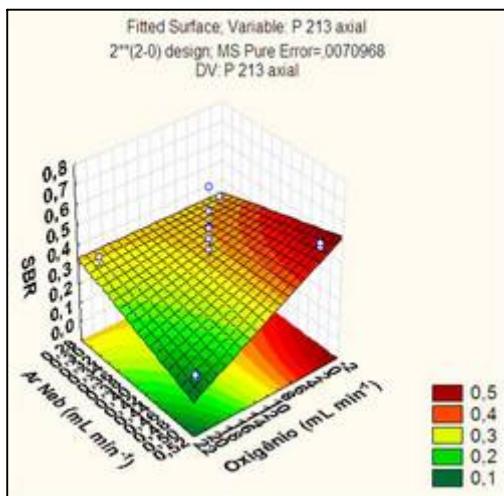


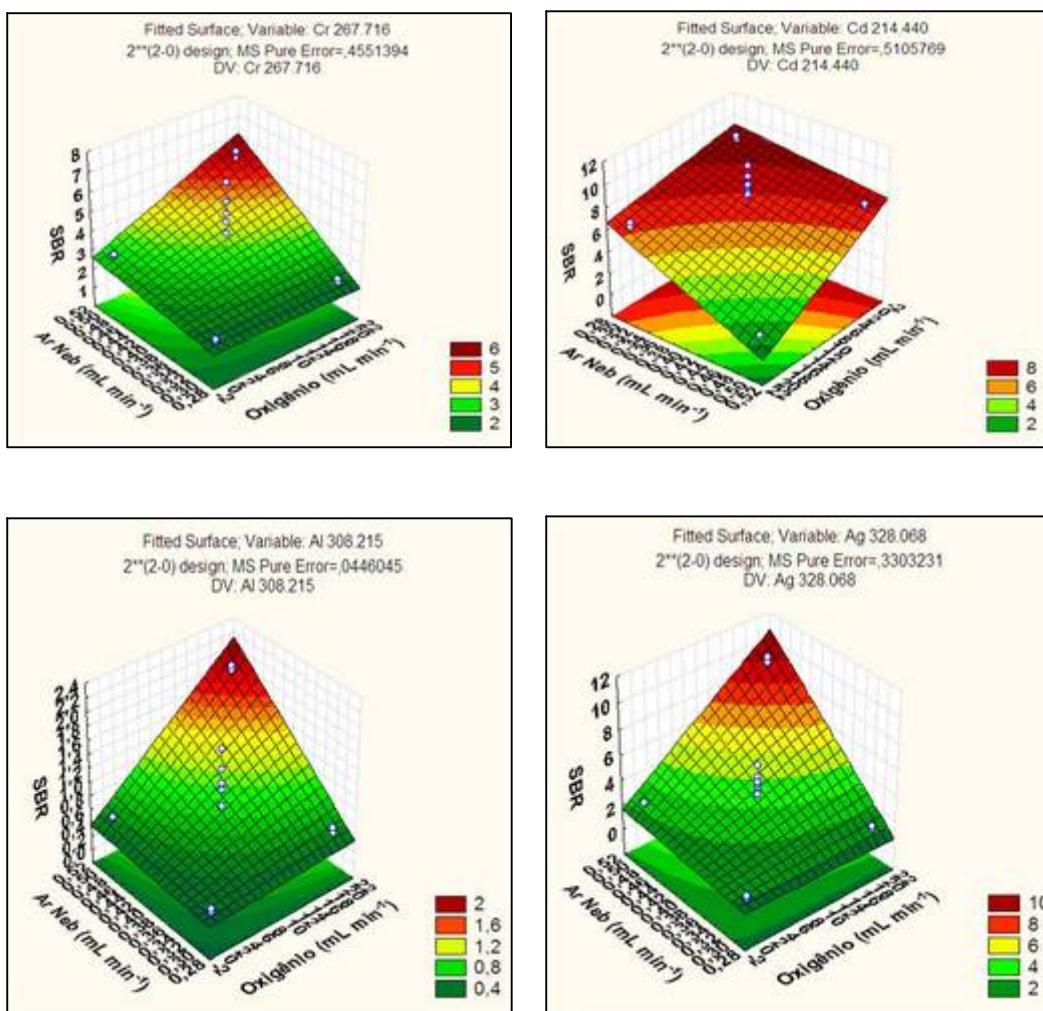




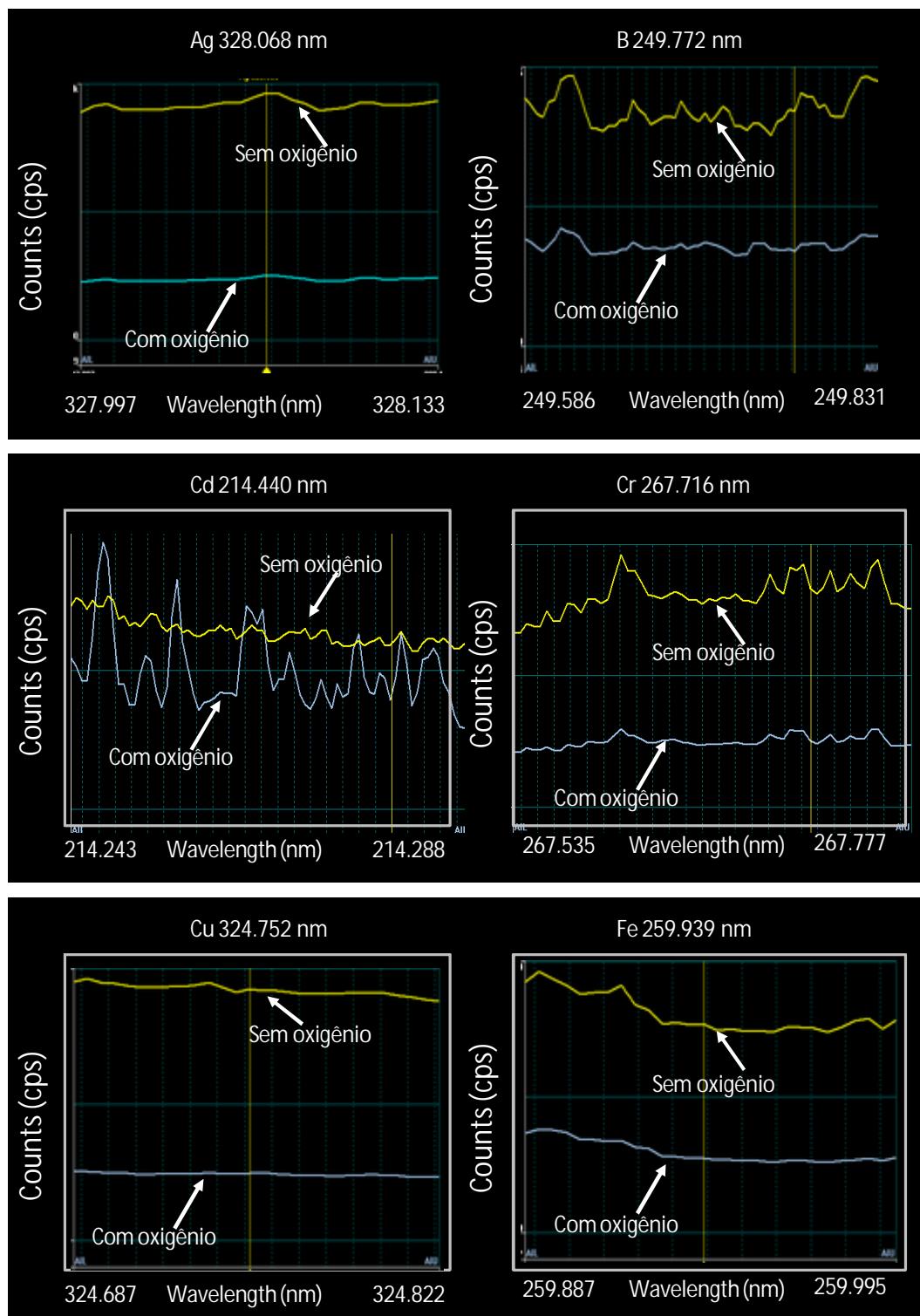
Anexo II: Gráficos de superfície de resposta para o micronebulizador Miramist™

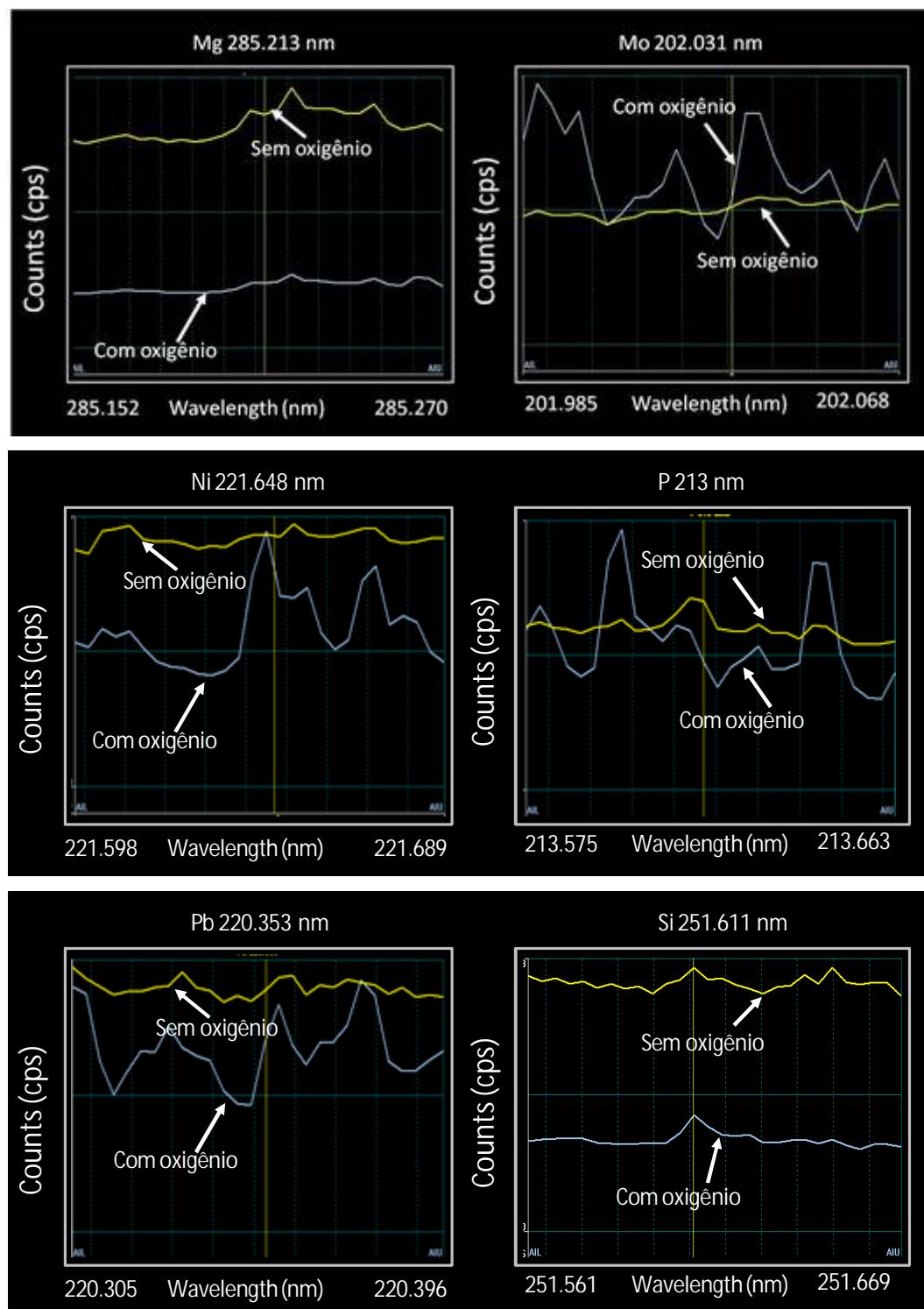


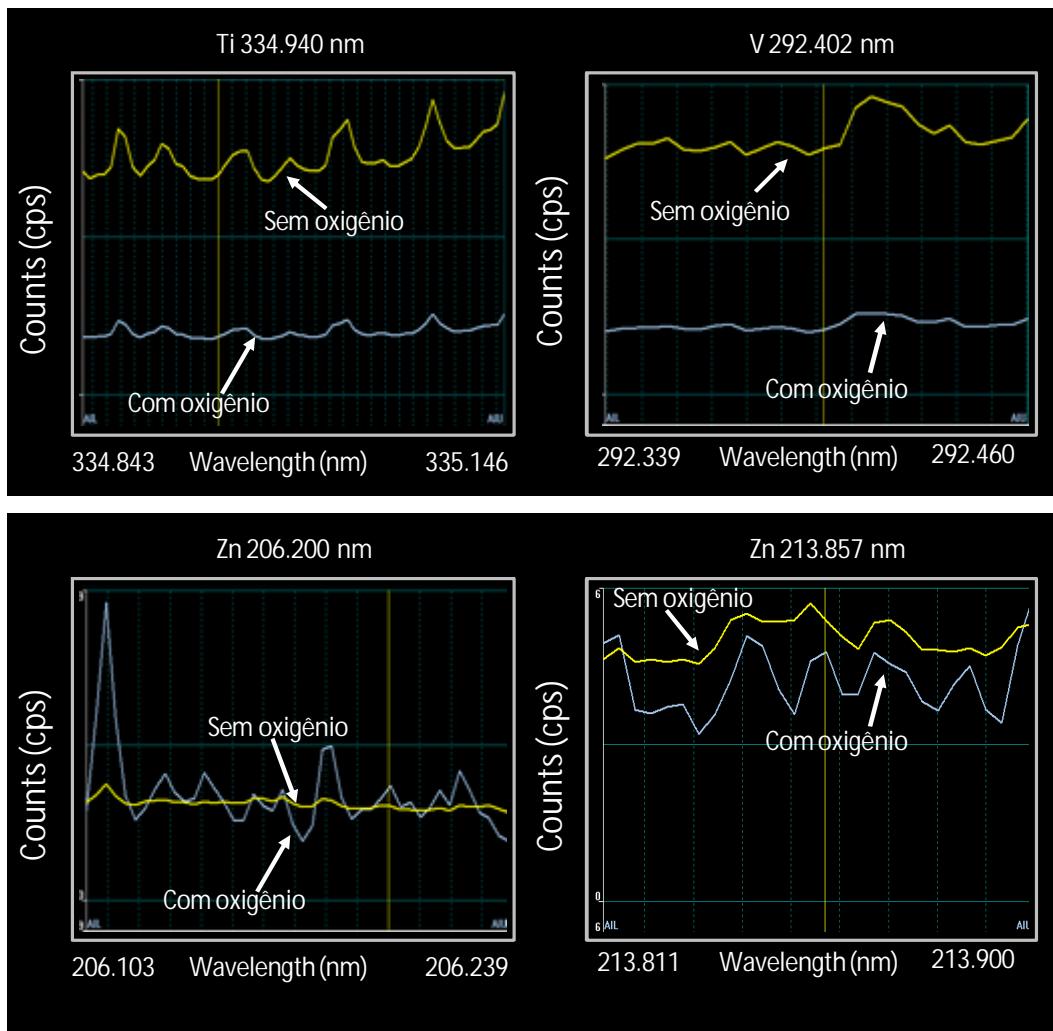




Anexo III: Espectro de emissão das vizinhanças dos analitos estudados em ICP OES.





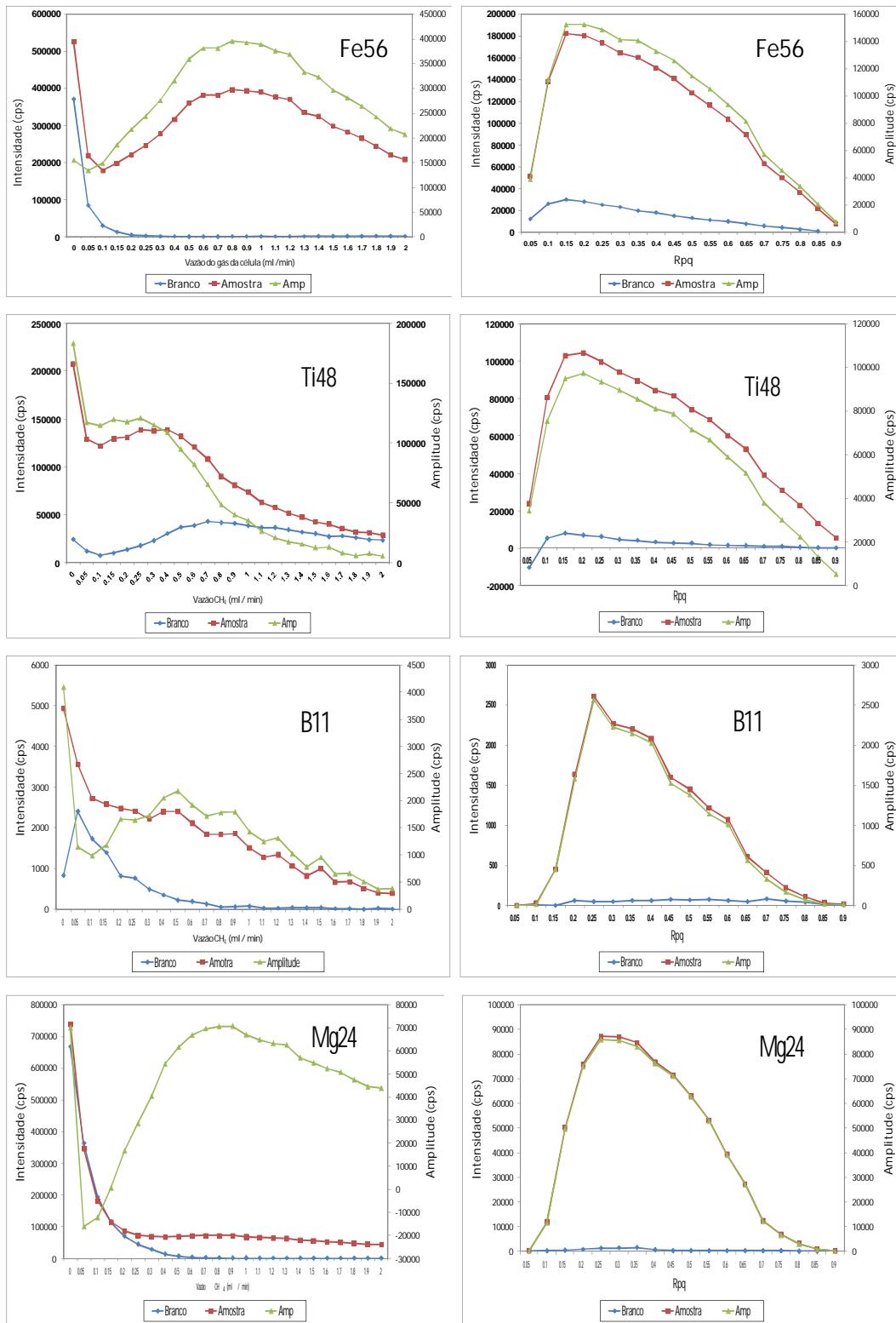


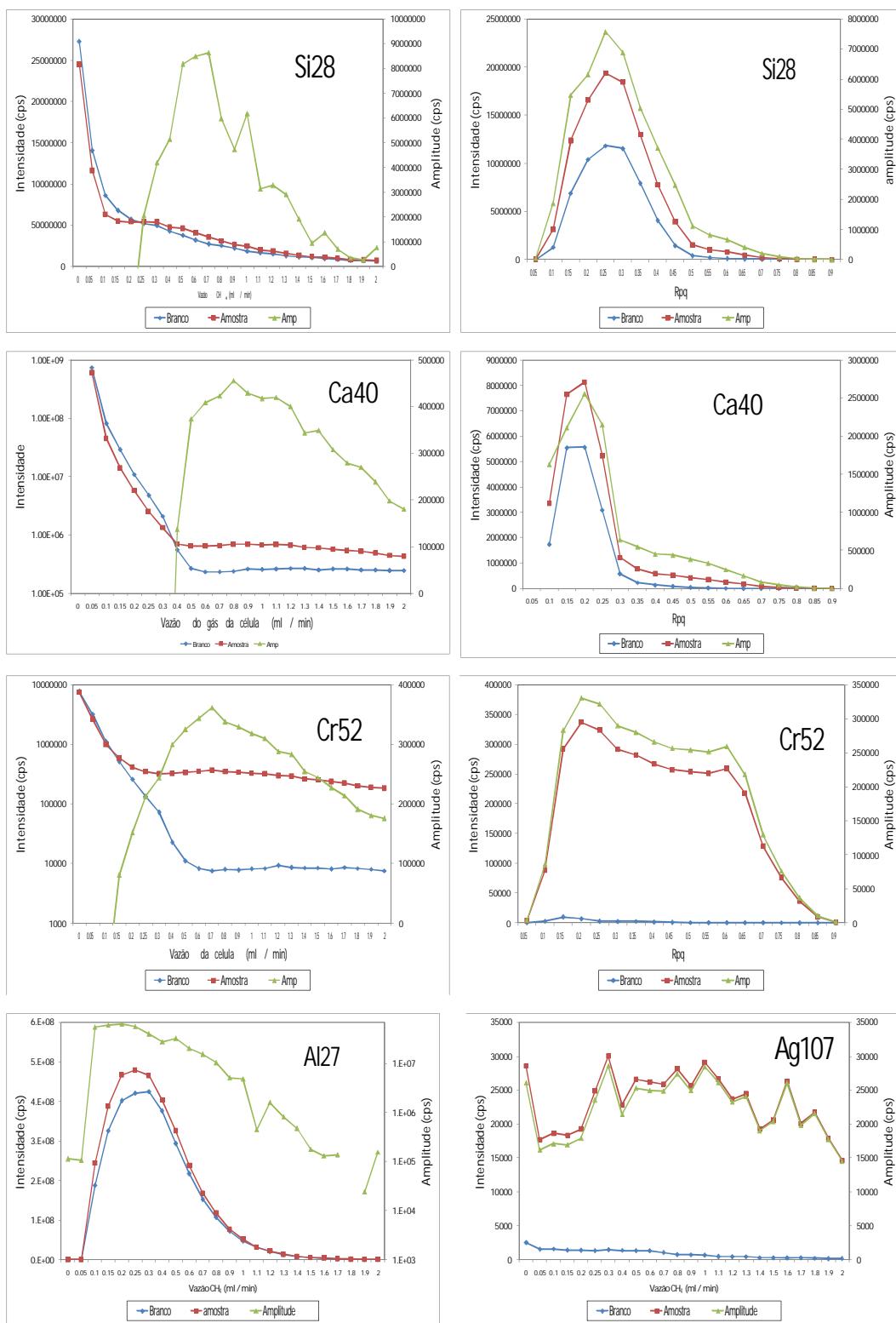
Anexo IV: Tabela dos parâmetros empíricos da equação de Antoine

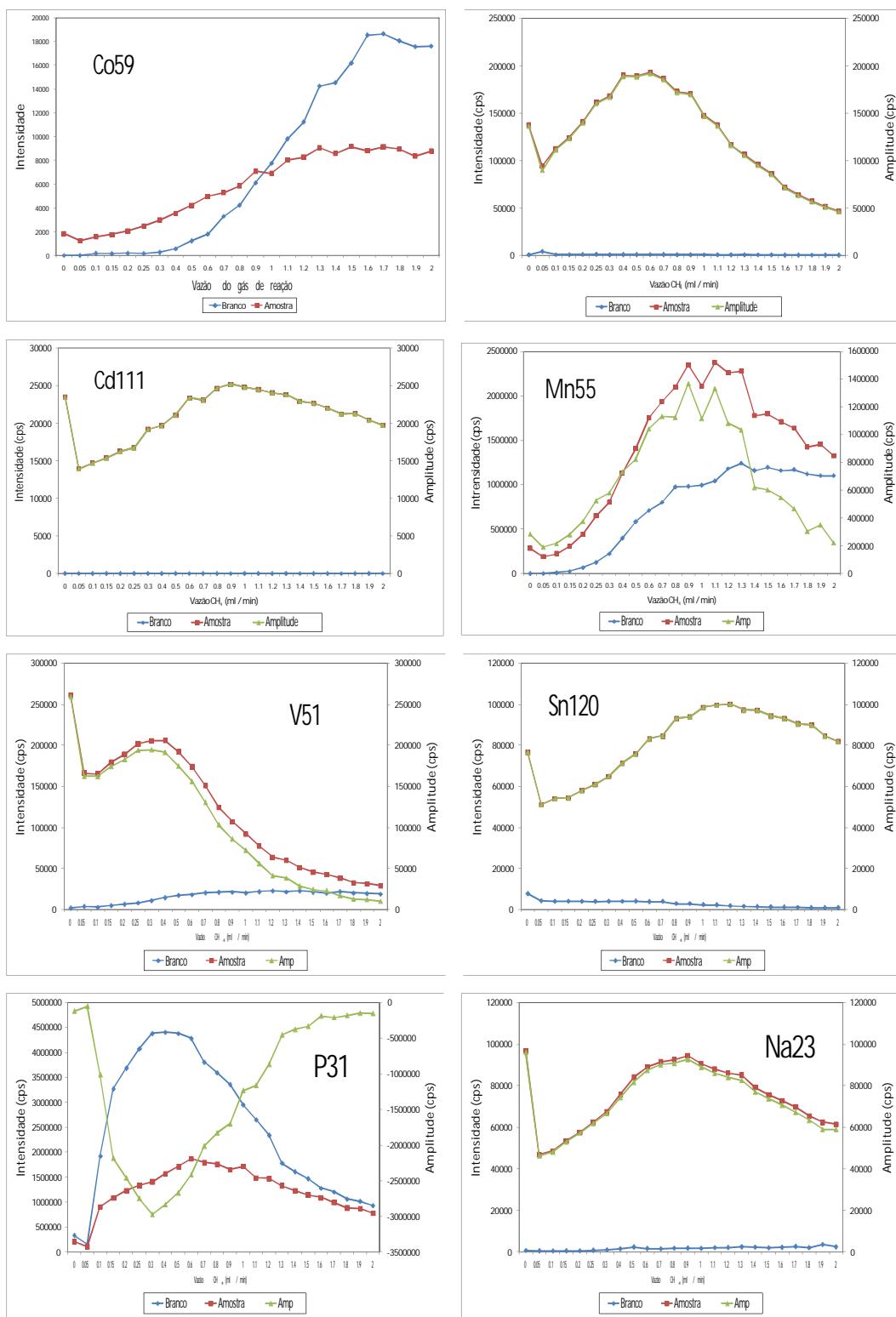
$$\log p = A - \frac{B}{C + T}$$

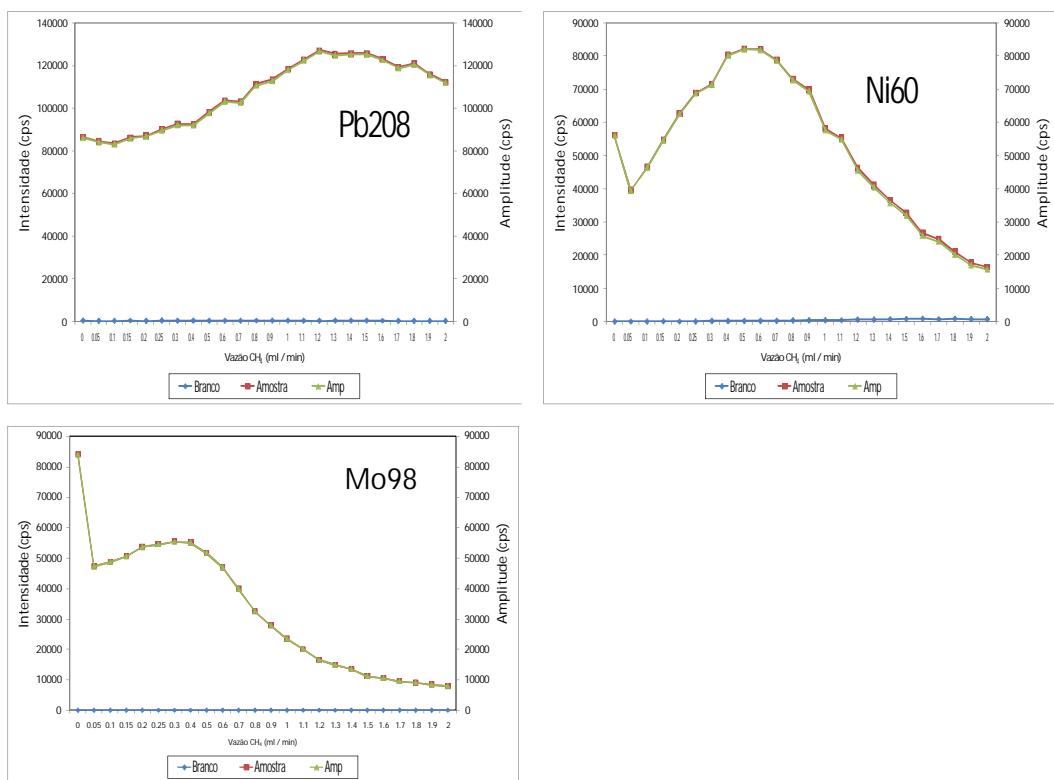
<b>Substância</b>	<b>Fórmula</b>	<b>A</b>	<b>B</b>	<b>C</b>
Acetona	C <sub>3</sub> H <sub>6</sub> O	7.02447	1161.00	224.00
Ácido acético	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	7.18807	1416.70	211.00
Água	H <sub>2</sub> O	7.96681	1668.21	228.00
Anilina	C <sub>6</sub> H <sub>7</sub> N	7.24179	1675.30	200.00
Benzeno	C <sub>6</sub> H <sub>6</sub>	6.90565	1211.03	220.79
i-Butano	C <sub>4</sub> H <sub>10</sub>	6.74808	882.80	240.00
n-Butano	C <sub>4</sub> H <sub>10</sub>	6.83029	945.90	240.00
Estireno	C <sub>8</sub> H <sub>8</sub>	6.92409	1420.00	206.00
Etanol	C <sub>2</sub> H <sub>6</sub> O	8.04494	1554.30	222.65
Éter dietílico	C <sub>4</sub> H <sub>10</sub> O	6.78574	994.20	220.00
Etilbenzeno	C <sub>8</sub> H <sub>10</sub>	6.95719	1424.26	213.21
Etilenoglicol		7.88080	1957.00	193.80
n-Heptano	C <sub>7</sub> H <sub>16</sub>	6.90240	1268.12	216.90
n-Hexano	C <sub>6</sub> H <sub>14</sub>	6.87776	1171.53	222.37
n-Octano	C <sub>8</sub> H <sub>18</sub>	6.92370	1355.13	209.52
i-Pentano	C <sub>5</sub> H <sub>12</sub>	6.78967	1020.01	233.10
n-Pentano	C <sub>5</sub> H <sub>12</sub>	6.85221	1064.63	232.00
Tolueno	C <sub>7</sub> H <sub>8</sub>	6.95464	1344.80	219.48
o-Xileno	C <sub>8</sub> H <sub>10</sub>	6.99891	1474.68	213.69
m-Xileno	C <sub>8</sub> H <sub>10</sub>	7.00908	1462.27	215.11
p-Xileno	C <sub>8</sub> H <sub>10</sub>	6.99052	1453.43	215.31

### Anexo V: Gráficos da otimização das condições da célula de reação dinâmica

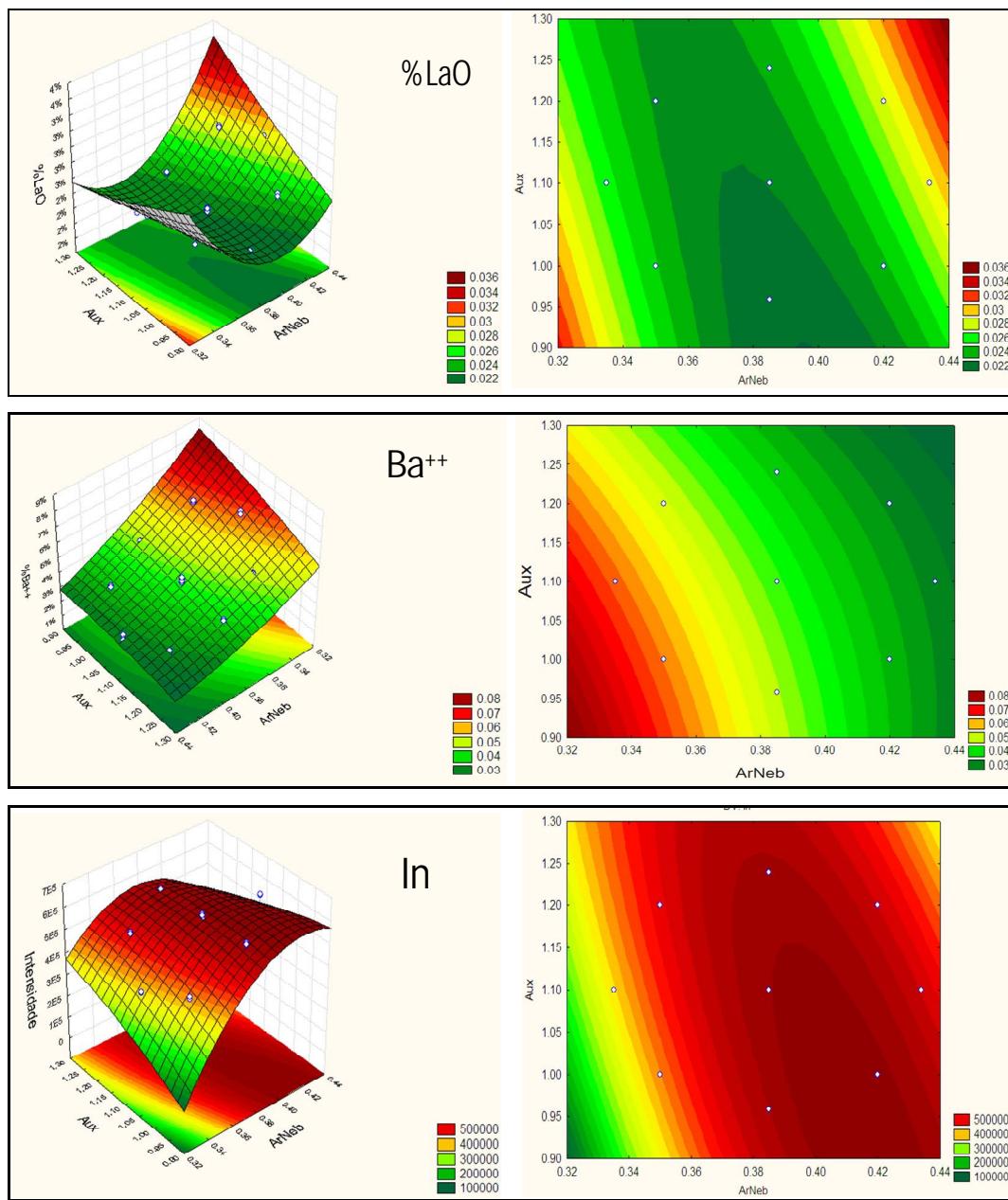


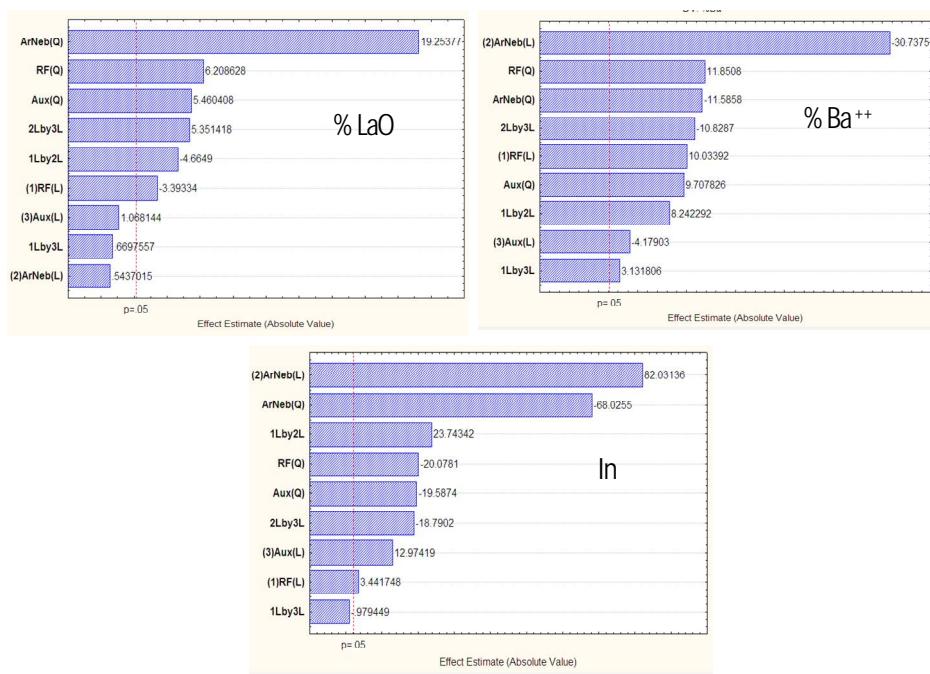






Anexo VI: Superfície de resposta e gráfico de Pareto para planejamento composto central em DRC-ICP-MS





## Anexo VII: Comparativo entre as técnicas ICP OES e DRC-ICP-MS

Para comparação dos resultados e consequente validação dos mesmos, foi realizado um teste estatístico de hipótese baseado na distribuição de *t* de *Student*. Para aplicar-se este teste de hipóteses, primeiramente deve-se realizar o teste F de *Snedecor* para verificar se as variâncias dos métodos são diferentes, segundo a seguinte fórmula:

$$F = \frac{s^2_1}{s^2_2}$$

Onde  $s^2_1$  e  $s^2_2$  são as variâncias dos resultados obtidos por ICP OES e DRC-ICP-MS, sendo que a maior variância deve ser colocada no numerador. O valor de F tabelado com  $n_1-1$  graus de liberdade no numerador e  $n_2-1$  graus de liberdade no denominador, é obtido através da distribuição F.

Se o teste F não for significante, isto é, o valor do  $F_{calculado}$  for menor do que o  $F_{Tabelado}$ , pode-se considerar que as variâncias são iguais e a aplicação do teste t pode ser efetuada empregando-se o  $s_{combinado}$  através da fórmula:

$$t_{calculado} = \frac{|\bar{x}_1 - \bar{x}_2|}{\sqrt{s^2 \left( \frac{1}{n_1} + \frac{1}{n_2} \right)}}$$

$$\text{Onde } s^2 = [(n_1-1) \times s^2_1 + (n_2-1) \times s^2_2] / (n_1+n_2 - 2)$$

Compara-se o valor de  $t_{calculado}$  com o valor de  $t_{Tabelado}$ , que é obtido para  $n_1+n_2 - 2$  graus de liberdade. Se o valor do  $t_{calculado}$  é menor do que o  $t_{Tabelado}$  no nível de confiança 95%, então, não há evidência estatística de que as médias são diferentes. Se o teste F for significante em relação ao  $F_{Tabelado}$ , então, não pode-se considerar as variâncias das médias em estudo como sendo iguais e, dessa forma, o teste de hipótese segue a seguinte fórmula:

$$t_{calculado} = \frac{|\bar{x}_1 - \bar{x}_2|}{\sqrt{\frac{s^2_1}{n_1} + \frac{s^2_2}{n_2}}}$$

Tabela 17: Teste de hipótese para validação dos resultados obtidos pela técnica ICP OES empregando micronebulizador PFA-100

Elemento	NIST 1085b		ICP OES (PFA-100)		Rec (%)	Teste F snedecor			Teste T $\sigma^2$ iguais	
	Media	IC	Media	IC		$\sigma^2$ MRC	$\sigma^2$ PFA-100	F <sub>calculated</sub>	S <sub>combinado</sub>	t <sub>calculated</sub>
Al	300,4	9,30	301,60	8,20	100,4	86,49	67,24	1,29	76,87	-0,17
Ag	304,6	8,90	288,80	14,40	94,8	79,21	207,36	2,62	143,29	1,62
Cu	295,6	8,50	291,00	6,90	98,4	72,25	47,61	1,52	59,93	0,73
Cd	302,9	5,10	288,69	6,18	95,3	26,01	38,19	1,47	32,10	3,07
Mn	289		291,70	4,70	100,9					
V	297,8	4,60	298,80	9,80	100,3	21,16	96,04	4,54	58,60	-0,16
P	299,9	7,20	305,60	12,40	101,9	51,84	153,76	2,97	102,80	-0,69
Pb	297,7	6,80	277,40	14,00	93,2	46,24	196,00	4,24	121,12	2,26
Ni	295,9	7,40	290,50	5,82	98,2	54,76	33,87	1,62	44,32	0,99
Mo	296		285,00	6,15	96,3					
Zn	296,8	6,80	293,46	4,40	98,9	46,24	19,36	2,39	32,80	0,71
Fe	301,2	5,00	296,10	6,00	98,3	25,00	36,00	1,44	30,50	1,13
Ti	301,1	2,90	291,43	4,00	96,8	8,41	16,00	1,90	12,21	3,39
Ba	314		294,80	2,50	93,9					
Ca	298		292,90	4,90	98,3					
Mg	297,3	4,10	293,60	5,70	98,8	16,81	32,49	1,93	24,65	0,91
Cr	302,9	3,90	301,70	5,80	99,6	15,21	33,64	2,42	24,43	0,02

\* t<sub>tab</sub> para amostras com variâncias iguais a 4 graus de liberdade = 2,78

\* t<sub>tab</sub> para amostras com variâncias diferentes a 3,25 graus de liberdade = 3,18

Tabela 18: Teste de hipótese para validação dos resultados obtidos pela técnica ICP OES empregando micronebulizador Miramist

Elemento	NIST1085b		ICP OES (Miramist)		Rec (%)	Teste F snedecor			Teste t $\sigma^2$ iguais		Teste t $\sigma^2$ diferentes	
	Media	IC	Media	IC		$\sigma^2$ MRC	$\sigma^2$ PFA-100	F calculado	S combinado	t calculado	t calculado	t calculado
Al	300,4	9,3	293,5	1,7	98	86,5	2,8	31,1	44,6			1,3
Ag	304,6	8,9	295,2	3,3	97	79,2	11,2	7,1	45,2	1,7		
Cu	295,6	8,5	282,5	6,7	95	72,3	45,3	1,6	58,8	2,1		
Cd	302,9	5,1	288,9	2,8	95	26,0	7,8	3,3	16,9	4,2		
Mn	289		289,5	10,3	100	0,0						
V	297,8	4,6	294,7	6,0	99	21,2	36,0	1,7	28,6	0,7		
P	299,9	7,2	309,5	3,0	103	51,8	8,8	5,9	30,3	-2,1		
Pb	297,7	6,8	266,8	11,4	90	46,2	130,0	2,8	88,1	4,0		
Ni	295,9	7,4	279,2	3,7	94	54,8	13,5	4,1	34,1	3,5		
Mo	296		280,0	2,9	95	0,0	8,3		4,2			
Zn	296,8	6,8	293,4	3,7	99	46,2	13,4	3,5	29,8	0,8		
Fe	301,2	5	292,6	2,3	97	25,0	5,2	4,8			2,7	
Ti	301,1	2,9	285,6	4,9	95	8,4	24,4	2,9	16,4	4,7		
Ba	314		285,8	4,5	91							
Ca	298		284,9	6,9	96							
Mg	297,3	4,1	290,5	5,2	98	16,8	26,7	1,6	21,8			
Cr	302,9	3,9	296,0	2,0	98	15,2	4,0	2,4	9,6	0,02		

\*  $t_{tab}$  para amostras com variâncias iguais a 4 graus de liberdade = 2,78

\*  $t_{tab}$  para amostras com variâncias diferentes a 3,25 graus de liberdade = 3,18

Tabela 19: Teste de hipótese para comparação entre os micronebulizadores Miramist e PFA-100 pela técnica de ICP OES

Elemento	Miramist		PFA-100		Rec (%)	Teste F snedecor		Teste T $\sigma^2$ iguais		Teste T $\sigma^2$ diferentes
	Media	IC	Media	IC		$\sigma^2$ Miramist	$\sigma^2$ PFA-100	F <sub>calculated</sub>	S <sub>combinado</sub>	
Al	293,5	1,7	301,6	8,2	103	2,8	67,2	24,2	35,0	-1,7
Ag	295,2	3,3	288,8	14,4	98	11,2	207,4	18,5	109,3	0,8
Cu	282,5	6,7	291,0	6,9	103	45,3	47,6	1,1	46,4	-1,5
Cd	288,9	2,8	288,7	6,2	100	7,8	38,2	4,9	23,0	0,1
Mn	289,5	10,3	291,7	4,7	101					
V	294,7	6,0	298,8	9,8	101	36,0	96,0	2,7	66,0	-0,6
P	309,5	3,0	305,6	12,4	99	8,8	153,8	17,5	81,3	0,5
Pb	266,8	11,4	277,4	14,0	104	130,0	196,0	1,5	163,0	-1,0
Ni	279,2	3,7	290,5	5,8	104	13,5	33,9	2,5	23,7	-2,9
Mo	280,0	2,9	285,0	6,2	102					
Zn	293,4	3,7	293,5	4,4	100	13,4	19,4	1,4	16,4	-0,02
Fe	292,6	2,3	296,1	6,0	101	5,2	36,0	6,9	20,6	-1,0
Ti	285,6	4,9	291,4	4,0	102	24,4	16,0	1,5	20,2	-1,6
Ba	285,8	4,5	294,8	2,5	103					
Ca	284,9	6,9	292,9	4,9	103					
Mg	290,5	5,2	293,6	5,7	101	26,7	32,5	1,2	29,6	-0,7
Cr	296,0	2,0	301,7	5,8	102	4,0	33,6	2,4	18,8	0,02

\* t<sub>tab</sub> para amostras com variâncias iguais a 4 graus de liberdade = 2,78

\* t<sub>tab</sub> para amostras com variâncias diferentes a 3,25 graus de liberdade = 3,18

Tabela 20: Teste de hipótese para validação dos resultados obtidos pela técnica DRC-ICP-MS

Isótopo	Este Trabalho		MRC 1085b		Teste F snedecor			Teste T $\sigma^2$ iguais		Teste T $\sigma^2$ diferentes	
	Média	IC	Média	IC	$\sigma^2$ ICPMS	$\sigma^2$ MRC	F <sub>calc</sub>	S <sub>comb</sub>	t <sub>calc</sub>	t <sub>calc</sub>	
<sup>27</sup> Al	290,67	3,72	300,4	9,3	13,9	86,5	6	50	-1,68		
<sup>107</sup> Ag	467,83	20,9	304,6	8,9	437,0	79,2	6	258	12,44		
<sup>63</sup> Cu	277,37	11,17	295,6	8,5	124,8	72,3	2	99	-2,25		
<sup>111</sup> Cd	300,45	5,03	302,9	5,1	25,3	26,0	1	26	-0,59		
<sup>114</sup> Cd	302,16	10,61	302,9	5,1	112,6	26,0	4	69	-0,11		
<sup>55</sup> Mn	313,05	3,63	289								
<sup>51</sup> V	284,41	1,61	297,8	4,6	2,6	21,2	8	12	-4,76		
<sup>23</sup> Na	301,9	39,42	305,2	7,	1554,2	49,0	32			-0,14	
<sup>208</sup> Pb	281,03	12,67	297,7	6,8	160,6	46,2	3	103	-2,01		
<sup>60</sup> Ni	285,59	6,7	295,9	7,4	44,8	54,8	1	50	-1,79		
<sup>58</sup> Ni	286,4	2,14	295,9	7,4	4,6	54,8	12	30	-2,14		
<sup>96</sup> Mo	290,79	8,21	296								
<sup>98</sup> Mo	292,63	6,	296								
<sup>64</sup> Zn	267,49	8,95	296,8	6,8	80,0	46,2	2	63	-4,52		
<sup>66</sup> Zn	267,19	13,54	296,8	6,8	183,3	46,2	4	115	-3,38		
<sup>56</sup> Fe	292,67	,17	301,2	5,	0,03	25,0	827			-2,95	
<sup>48</sup> Ti	275,36	1,1	301,1	2,9	1,2	8,4	7	5	-14,38		
<sup>138</sup> Ba	312,45	5,12	314								
<sup>40</sup> Ca	354,28	24,56	298								
<sup>24</sup> Mg	352,96	38,45	297,3	4,1	1478,7	16,8	88	748		2,49	
<sup>52</sup> Cr	301,73	4,35	302,9	3,9	13,9	15,2	1	115		-2,95	

\* t<sub>tab</sub> para amostras com variâncias iguais a 4 graus de liberdade = 2,78

\* t<sub>tab</sub> para amostras com variâncias diferentes a 3,25 graus de liberdade = 3,18

Tabela 21: Teste de hipótese para comparação entre as técnicas ICP OES e DRC-ICP-MS

Isótopo	DRC-ICP-MS (mg kg <sup>-1</sup> )		ICP OES (mg kg <sup>-1</sup> )		Teste F snedecor		Teste T σ <sup>2</sup> iguais		Teste T σ <sup>2</sup> diferentes	
	Media	IC	Media	IC	σ <sup>2</sup> ICP-MS	σ <sup>2</sup> ICP OES	Fcalc	Scomb	t calc	Tcal
<sup>27</sup> Al	290,67	3,72	301,6	8,2	13,87	67,24	4,85	40,56	-2,10	
<sup>107</sup> Ag	467,83	20,90	288,8	14,4	436,97	207,36	2,11	322,17	12,22	
<sup>63</sup> Cu	277,37	11,17	291,0	6,9	124,83	47,61	2,62	86,22	-1,80	
<sup>59</sup> Co	33,30	9,69								
<sup>111</sup> Cd	300,45	5,03	288,7	6,2	25,32	38,19	1,51	31,75	2,56	
<sup>114</sup> Cd	302,16	10,61	288,7	6,2	112,65	38,19	2,95	75,42	1,90	
<sup>55</sup> Mn	313,05	3,63	291,7	4,7	13,21					
<sup>51</sup> V	284,41	1,61	298,8	9,8	2,59	96,04	37,14			-2,51
<sup>208</sup> Pb	281,03	12,67	277,4	14,0	160,57	196,00	1,22	178,28	0,33	
<sup>60</sup> Ni	285,59	6,70	290,5	5,8	44,83	33,87	1,32	39,35	-0,96	
<sup>58</sup> Ni	286,40	2,14	290,5	5,8	4,56	33,87	7,43	19,22	-1,15	
<sup>96</sup> Mo	290,79	8,21	285,0	6,1	67,34	37,82	1,78	52,58	0,98	
<sup>98</sup> Mo	292,63	6,00	285,0	6,1	36,04	37,82	1,05	36,93	1,54	
<sup>64</sup> Zn	267,49	8,95	293,5	4,4	80,01	19,36	4,13	49,69	-4,51	
<sup>66</sup> Zn	267,19	13,54	293,5	4,4	183,33	19,36	9,47	101,34	-3,20	
<sup>56</sup> Fe	292,67	0,17	296,1	6,0	0,03	36,00	1191,10			-0,99
<sup>48</sup> Ti	275,36	1,10	291,4	4,0	1,20	16,00	13,31	8,60	-6,71	
<sup>138</sup> Ba	312,45	5,12	294,8	2,5	26,20	6,25	4,19	16,23	5,37	
<sup>40</sup> Ca	354,28	24,56	292,9	4,9	603,39	24,01	25,13			4,24
<sup>24</sup> Mg	352,96	38,45	293,6	5,7	1478,66	32,49	45,51			2,64
<sup>52</sup> Cr	301,74	4,35	301,7	5,8	13,87	33,64	2,42	8,60	0,02	

\* t<sub>tab</sub> para amostras com variâncias iguais a 4 graus de liberdade = 2,78

\* t<sub>tab</sub> para amostras com variâncias diferentes a 3,25 graus de liberdade = 3,18