

LABORATOIRES
Dubernet
œ n o l o g i e

CONSEIL EN VINIFICATION - ELEVAGE ET TRAVAIL DU VIN - ANALYSE
ANALYSE FINE - MICROBIOLOGIE DU VIN - AUDIT - EXPERTISE

SENTIA Free SO2 analyser



Dossier de validation

2 Novembre 2021

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1 Presentation of the method and intended use

Universal Biosensors Pty is an Australian listed company called. Sentia is a hand-held device that measures key compounds such as free sulphur in post fermentation red and white wine. Sentia offers significant advantages over other analysis products in the market: speed, portability (e.g. test at the barrel), ease of use, automatic calibration, and no use of reagents.

The Sentia Wine Analyzer is currently distributed in Australia, New Zealand, North America, Chile and South Africa.

The Sentia system uses square wave voltammetry which is utilised to measure electrical current as a function of voltage rather than time. When wine is added to the strip, it dissolves the dried down reagents on the strip. The dried down compounds automatically adjust the pH of the wine sample so that the hydrogen sulphite is converted to sulphur dioxide. This becomes directly reduced at the electrode when the square waveform is applied. The data obtained is analysed to generate “differential current vs voltage” data which contains a specific peak that correlates to the concentration of free SO₂ in the wine sample.

Universal biosensor has asked Laboratoires Dubernet, France, to carry out a validation study of the SENTIA system for the analysis of free SO₂

2 Expected performance

Paramètre	Free SO2
Paramétrages de la méthode	Type de détection.... Electrochimie

Type de matrices à analyser :	Vins rouges Vins blancs			
Performances requises:				
Exigences des clients :	LQ : 5 mg/L			
Données Bibliographiques :	Sr – r : 1,5 mg/L 4,5 mg/L			
Données réglementaires :				
Autre :				
Itinéraire de validation	Commentaires			
<p>Plans d'expérience</p> <p>1/ Total error profile</p> <p>6 samples ran 5 times with replicates Range 2 to 50 ppm, distributed equally</p> <p>The experiment is performed one time for white/rosé calibration and one time for red wines calibration.</p> <p>This total error profile is designed to test the LOQ value at the same time. The target values are defined on an average of 2 Franz Paul determinations.</p> <p>2/ Comparison to Franz Paul method and automated colorimetric method</p> <p>30 samples ran in replicates on SENTIA system, and once on Franz Paul method, and automated method.</p> <p>Regression for comparison.</p> <p>The experiment is performed one time for white/rosé calibration and one time for red wines calibration.</p> <p>Theses experiments design are described into the OENO SCMA 418/2003 OIV resolution.</p>				

3 Presentation of the plans of experiment and the calculations carried out

3.1 Accuracy profile

3.1.1 Plan of experiment

Prepare or choose $q \geq 3$ reference materials covering the scope of the method in terms of concentration for a given matrix.

Analyze each material in $n \geq 5$ series under conditions of intermediate fidelity and in the material stability time for the matrix under consideration. If the material is unstable carry out several preparations.

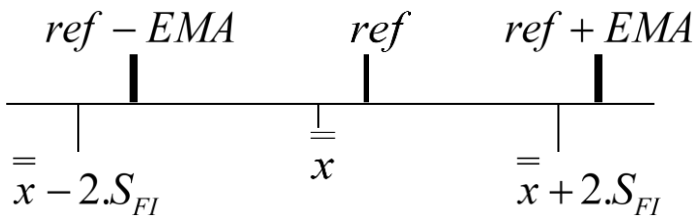
For each reference material and in each series, perform $p = 2$ repetitions under repeatability conditions.

3.1.2 Accuracy calculations

Pour chaque matériau de référence correspond à une niveau de concentration donné pour lequel on peut définir un $EMA_{\text{exactitude}}$ donné.

	Matériau 1	...	Matériau i	...	Matériau q
Valeur de référence	Ref_1	...	Ref_i	...	Ref_q
EMA	EMA_1	...	EMA_i	...	EMA_q
EMA%	$EMA\%_1 = \frac{EMA_1}{ref_1}$...	$EMA\%_i = \frac{EMA_i}{ref_i}$...	$EMA\%_q = \frac{EMA_q}{ref_q}$
Nombre de séries	n_1	...	n_i	...	n_q
Nombre de répétitions par série	p_1	...	p_i	...	p_q
Moyenne générale de chaque matériau	$\bar{x}_1 = \frac{\sum_{j=1}^{n_1} \sum_{i=1}^{p_1} x_{ji}}{n_1}$...	$\bar{x}_i = \frac{\sum_{j=1}^{n_i} \sum_{i=1}^{p_i} x_{ji}}{n_i}$...	$\bar{x}_q = \frac{\sum_{j=1}^{n_q} \sum_{i=1}^{p_q} x_{ji}}{n_q}$
Ecart relatif	$b\%_1 = \frac{\bar{x}_1 - ref_1}{ref_1} \cdot 100$...	$b\%_i = \frac{\bar{x}_i - ref_i}{ref_i} \cdot 100$...	$b\%_q = \frac{\bar{x}_q - ref_q}{ref_q} \cdot 100$
Écart-type de fidélité intermédiaire	S_{FI_1}	...	S_{FI_i}	...	S_{FI_q}
CV de fidélité intermédiaire en %	$CV(\%)_1 = 2 \cdot \frac{S_{FI_1}}{\bar{x}_1} \cdot 100$...	$CV(\%)_i = 2 \cdot \frac{S_{FI_i}}{\bar{x}_i} \cdot 100$...	$CV(\%)_q = 2 \cdot \frac{S_{FI_q}}{\bar{x}_q} \cdot 100$

The verification of accuracy is done at each concentration level represented by the q materials studied, comparing the interval produced by the intermediate fidelity around the measured mean value, to the interval of the EMA_{accuracy} around the reference value of the material. Accuracy is accepted if the first interval falls within the second.



This is reflected in the verification of the following inequalities:

accuracy is verified if:

$$\bar{x} + 2.S_{FI} \leq ref + EMA$$

et

$$\bar{x} - 2.S_{FI} \geq ref - EMA$$

These quantities can just as well be expressed as a coefficient of variation:

Accuracy is accepted if:

$$b(\%) + CV(\%) \leq EMA(\%)$$

et

$$b(\%) - CV(\%) \geq -EMA(\%)$$

If the accuracy of the method is verified on the reference materials then the accuracy of the method is verified on the validation domain. Graphical formatting of the results is performed.

3.2 Calculation of intralaboratory repeatability

Répétabilité

Either:

$w_j = x_{j1} - x_{j2}$, the difference between the two repetitions of the $j^{ème}$ reply.

Alors,

$$s_r = \sqrt{\frac{\sum_{j=1}^n w_j^2}{2n}}$$

The repeatability standard deviation is expressed as s_r , and repeatability $r = 2.8.s_r$.

3.3 Comparison of the usual method with the OIV reference method

3.3.1 Basic protocol and calculations

In each range level, accuracy will be determined from a series of **60** test materials with analyte concentration values covering the range level under consideration.

Each test material will be duplicated by both methods under repeatability conditions.

The average values \bar{Mx}_i of the 2 measurements x_i and x'_i made by the usual method and the average values \bar{My}_i of the 2 measurements y_i and y'_i made by the reference method will be

calculated, then the difference d_i between the values Mx_i and My_i .

The results of the experiment can be recorded in the following table:

Matériau d'essai	x : Méthode usuelle		y : Méthode de référence		Moyennes		Différence d
	Rep1	Rep2	Rep1	Rep2	x	y	
1	x_1	x'_1	y_1	y'_1	Mx_1	My_1	$d_1 = Mx_1 - My_1$
...
i	x_i	x'_i	y_i	y'_i	Mx_i	My_i	$d_i = Mx_i - My_i$
...
n	x_n	x'_n	y_n	y'_n	Mx_n	My_n	$d_n = Mx_n - My_n$

Les calculs suivants seront mis en oeuvre

- La moyenne des résultats de la méthode usuelle M_x $M_x = \frac{1}{n} \sum_{i=1}^n Mx_i$

- La moyenne des résultats de la méthode de référence M_y $M_y = \frac{1}{n} \sum_{i=1}^n My_i$

- Calculer la moyenne des différences M_d $M_d = \sum_{i=1}^n \frac{d_i}{n} = M_x - M_y$

- Calculer l'écart type des différences S_d $S_d = \sqrt{\frac{\sum_{i=1}^n (d_i - M_d)^2}{n-1}}$

- Calculer le Z_{score} $Z_{score} = \frac{|M_d|}{S_d}$

Interprétation

- If Z_{score} is **less than** or equal to 2.0, it can be concluded that the accuracy of one method in relation to the other is satisfactory, in the level of range considered, with a risk of error $\alpha = 5\%$.

- If Z_{score} is **greater than** 2.0, it can be concluded that the usual method is not fair compared to the

reference method, in the range level considered, with a risk of error $\alpha = 5\%$.

4 Results

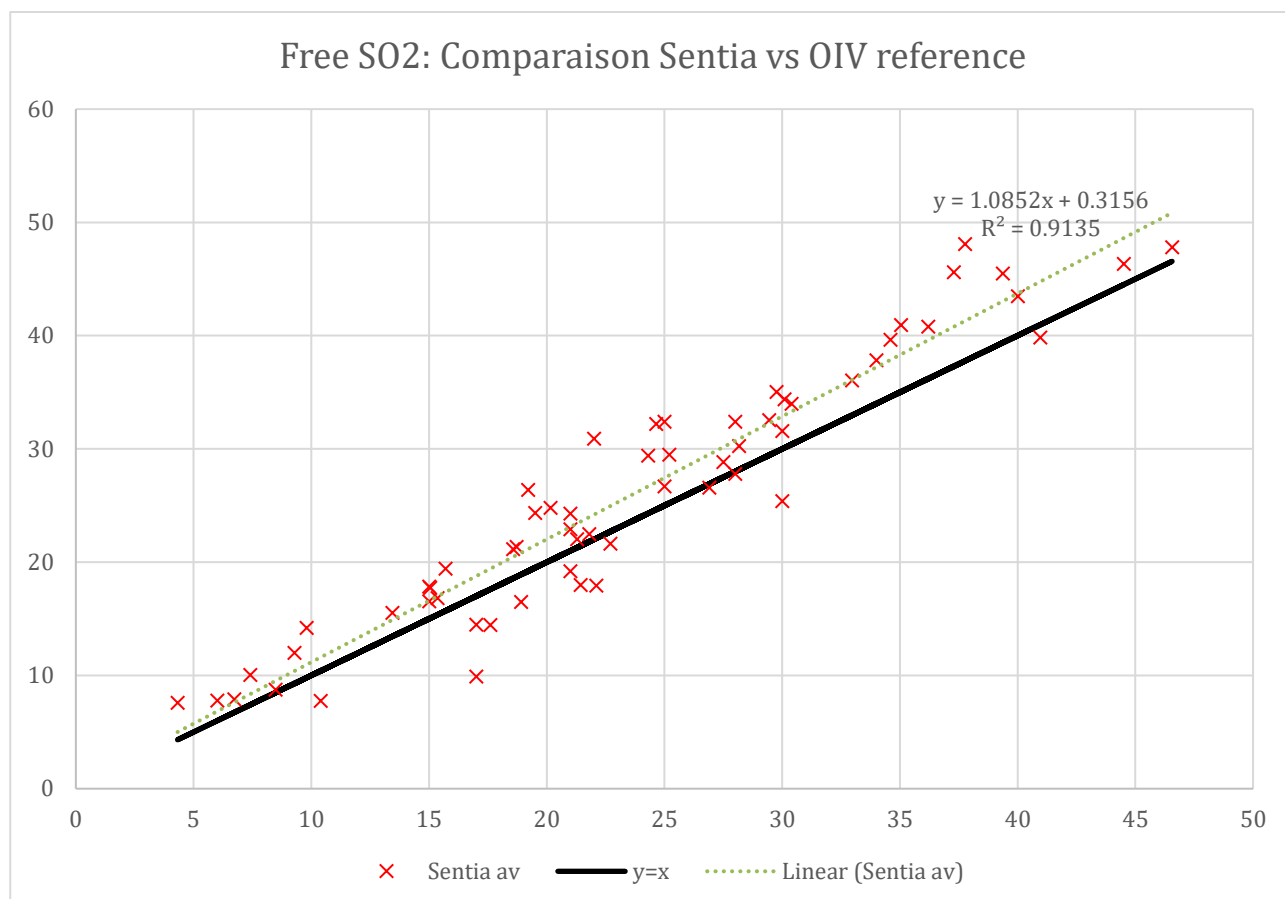
4.1 Raw results

Results in mg/L

n°	ID ech	Color	Date	Franz Paul (OIV)	Sentia 1	Sentia 2	Sentia av	Sequential
1	BL170921-1	white	17/9/21	34	38,2	37,5	37,85	37,8
2	BL170921-2	white	17/9/21	21	23,4	22,4	22,9	23
3	BL170921-3	white	17/9/21	40	44	43	43,5	42,8
4	RS170921-4	white	17/9/21	15	16,5	16,6	16,55	18,2
5	RS170921-5	white	17/9/21	28	30,3	25,3	27,8	27,5
6	RS170921-11	white	17/9/21	25	27	26,4	26,7	30,6
7	BL170921-12	white	17/9/21	21	19,4	19	19,2	24,1
9	BL230921-29	white	23/9/21	9,28	12	12	12	15
10	RS230921-32	white	23/9/21	30,1	34,4	34,4	34,4	32
11	BL230921-33	white	23/9/21	24,64	33,9	30,5	32,2	31
12	RS230921-34	white	23/9/21	28,16	31,3	29,2	30,25	29
14	RS230921-36	white	23/9/21	21	23,3	25,3	24,3	27
16	BL230921-38	white	23/9/21	22	29,9	31,9	30,9	27
17	BL230921-39	white	23/9/21	6,72	7,6	8,2	7,9	11
18	BL230921-40	white	23/9/21	39,36	42,8	48,2	45,5	43
19	BL2709-21-43	white	27/9/21	44,5	46,6	46,1	46,35	50,3
20	BL2709-21-44	white	27/9/21	27,5	29,7	28	28,85	29,6
21	BL2709-21-45	white	27/9/21	24,3	31,6	27,2	29,4	28,8
22	BL2709-21-46	white	27/9/21	17,6	16,3	12,6	14,45	21,2
23	BL2709-21-47	white	27/9/21	22,7	22,2	21,1	21,65	19,7
24	BL2709-21-48	white	27/9/21	21,8	22,6	22,4	22,5	27
26	PE-BL061021-2	white	6/10/21	15,36	17	16,7	16,85	24,7
27	PE-BL061021-3	white	6/10/21	21,28	23,4	20,7	22,05	28,5
28	PE-BL061021-4	white	6/10/21	30,4	30,5	37,5	34	40,2
29	PE-RS061021-5	Rose	6/10/21	4,32	7,6	7,6	7,6	7,3
30	PE-RS061021-6	Rose	6/10/21	40,96	43	36,7	39,85	42,3
31	BL111021-1	White	11/10/21	15,04	17,9	17,6	17,75	15,9
32	RS111021-2	Rose	11/10/21	32,96	36,2	35,9	36,05	34,6
33	BL111021-3	White	11/10/21	46,56	46,8	48,8	47,8	47,6
34	BL111021-11	White	11/10/21	21,44	18,5	17,5	18	16,8
35	RG070921-1	Red	7/9/21	36,2	39,7	41,9	40,8	39,6
36	RG070921-2	Red	7/9/21	26,9	27,4	25,8	26,6	31,8
37	RG070921-3	Red	7/9/21	17	9,6	10,2	9,9	17,4
38	RG070921-4	Red	7/9/21	18,9	16,2	16,8	16,5	23,2
39	RG070921-5	Red	7/9/21	22,1	17,2	18,7	17,95	26,1
41	RG170921-7	Red	17/9/21	15	18,6	17,1	17,85	20,7
42	RG170921-8	Red	17/9/21	6	8,8	6,8	7,8	12,5
43	RG170921-9	Red	17/9/21	28	31,6	33,2	32,4	30,5
44	RG170921-10	Red	17/9/21	17	15,7	13,3	14,5	18,4
45	RG170921-13	Red	17/9/21	30	31,4	31,8	31,6	31,6
46	RG170921-14	Red	17/9/21	30	25,6	25,2	25,4	29
50	RG220921-25	Red	22/9/21	25	32,4	32,4	32,4	33,9
51	RG230921-25	Red	23/9/21	7,4	9,6	10,5	10,05	14,2
52	RG230921-26	Red	23/9/21	15,7	20	18,9	19,45	22,7
53	RG230921-27	Red	23/9/21	25,2	28,3	30,7	29,5	28,1
54	RG230921-28	Red	23/9/21	19,2	23,4	29,4	26,4	25,5
55	RG230921-30	Red	23/9/21	19,5	26,1	22,6	24,35	24,8
56	RG230921-31	Red	23/9/21	9,8	14,8	13,6	14,2	14,8
57	RG270921-41	Red	27/9/21	34,6	39,1	40,2	39,65	39,1
58	RG270921-42	Red	27/9/21	10,4	8,1	7,4	7,75	13,2
59	RG111021-4	Red	11/10/21	18,72	21	21,7	21,35	20,8

60	RG111021-5	Red	11/10/21	35,04	41	40,9	40,95	38,4
61	RG111021-9	Red	11/10/21	8,48	8,7	8,8	8,75	11,6
62	RG111021-10	Red	11/10/21	18,56	21,4	20,9	21,15	20,9
63	RG111021-12	Red	11/10/21	37,76	49	47,2	48,1	34,7
64	RG111021-13	Red	11/10/21	29,76	35,7	34,4	35,05	30
65	RG121021-1	Red	12/10/21	37,28	44,4	46,8	45,6	39,3
66	RG121021-2	Red	12/10/21	13,44	16,1	15	15,55	14,4
67	RG121021-3	Red	12/10/21	29,44	31,6	33,5	32,55	31,4
68	RG121021-4	Red	12/10/21	20,16	24,6	25	24,8	24,4

4.2 Comparison Sentia vs OIV reference method



N= 60 samples of regular white and red wines

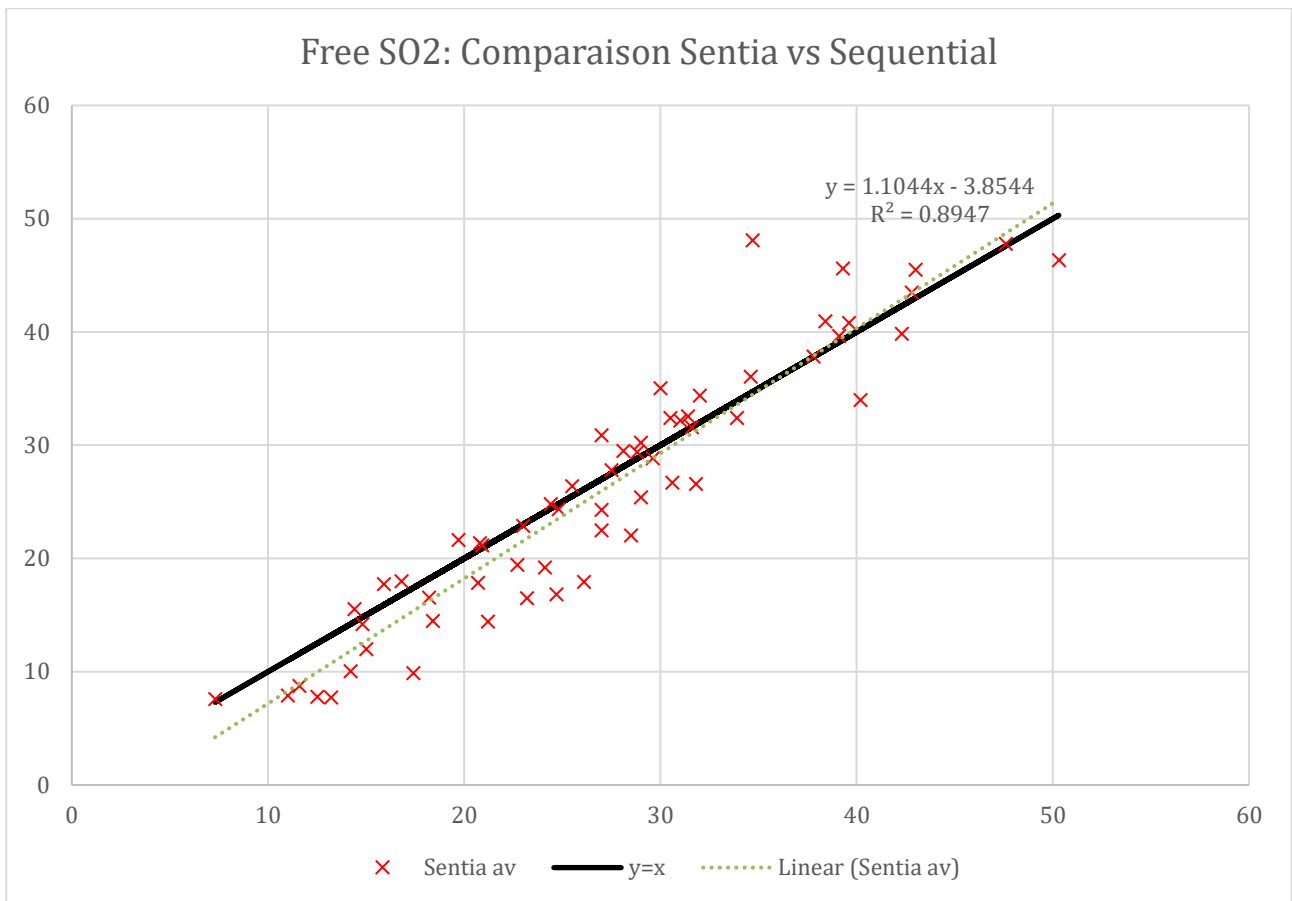
Md (écart moyen) = 2,32 mg/L

Sd (Écart type écart moyen) = 3, 43 mg/L

Z_Score = 0,67

Conclusion: the differences are statistically insignificant

4.3 Comparison Sentia vs colorimetric automated accredited method



N= 60 samples of regular white and red wines

Md (écart moyen) = -1,04 mg/L

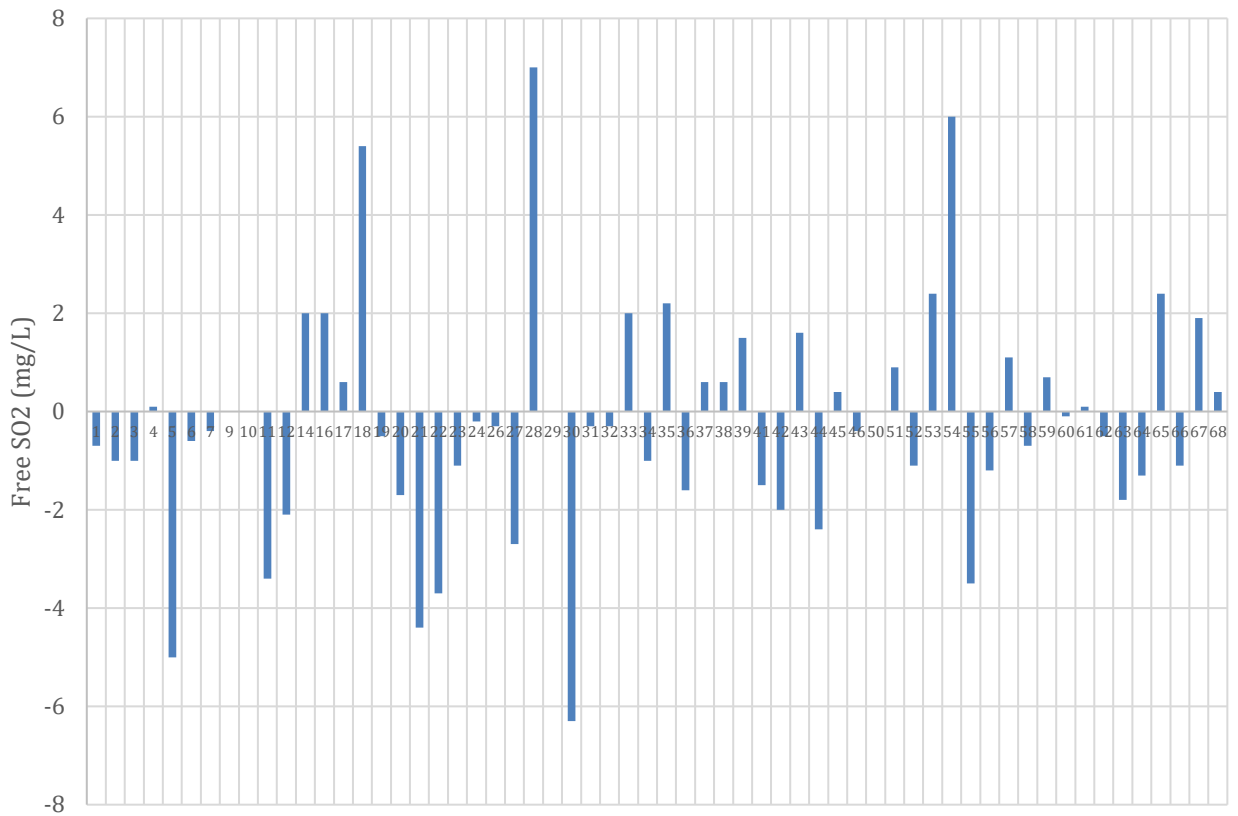
Sd (Écart type écart moyen) = 3,81 mg/L

Z_Score = - 0,27

Conclusion: the differences are statistically insignificant

4.4 Repeatability

Sentia repeatability differences between replicates



Repeatability Standard error

Sr = 1,63 mg/L

Repeatability

R : 4,47 mg/L

4.5 Accuracy Profile

4.5.1 White and rosé

Reference value is assigned by OIV reference method

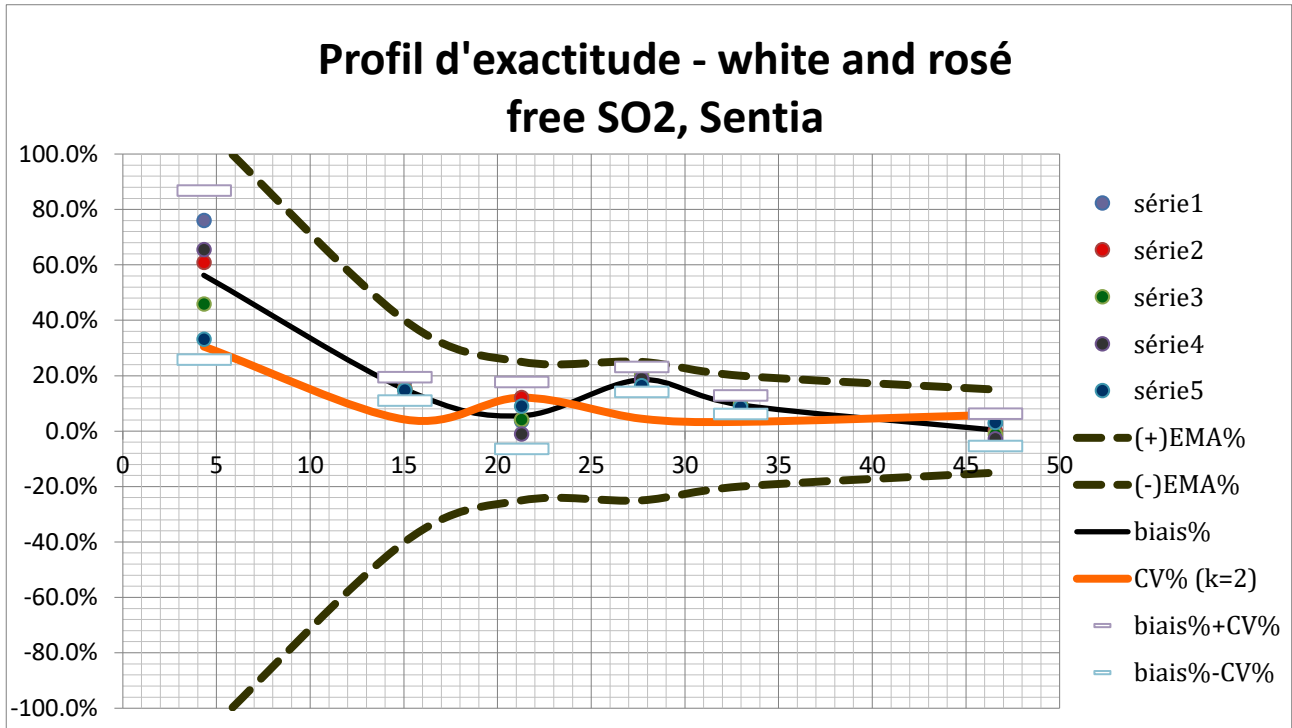
FQ7-0-5_B

Méthode	SENTIA
Paramètre	SO2 libre
Date	06/10/2021 au 11/10/2021

opérateurs	série1	FG
	série2	FG
	série3	FG
	série4	FG
	série5	FG

Nature du matériau	RS061021-5 Matériau 1		BL111021-1 Matériau 2		BL061021-3 Matériau 3		BL071021-1 Matériau 4		RS111021-2 Matériau 5		BL111021-3 Matériau 6	
	VIN ROSE		VIN BLANC		VIN BLANC		Vin BLANC		VIN BLANC		VIN ROSE	
Valeur de référence	4,32		15,04		21,28		27,68		32,96		46,56	
EMA%	110 %		40 %		25 %		25 %		20 %		15 %	
	Matériau 7		Matériau 2		Matériau 3		Matériau 4		Matériau 4		Matériau 6	
	rep1	rep2	rep1	rep2	rep1	rep2	rep1	rep2	rep1	rep2	rep1	rep2
Série1	7,60	7,60	17,90	17,60	23,40	20,70	32,70	33,00	36,20	35,90	46,80	48,80
Série2	6,70	7,20	16,90	17,80	24,00	23,70	33,00	32,60	37,00	36,60	45,60	47,60
Série3	5,30	7,30	17,30	17,30	23,30	21,00	33,70	32,90	35,90	36,40	45,35	46,70
Série4	7,30	7,00	17,10	16,80	21,20	20,90	34,20	31,60	35,60	35,60	44,90	45,60
Série5	4,50	7,00	17,30	17,20	22,90	23,50	32,30	32,10	35,00	36,60	48,10	47,90
Moy	6,75		17,32		22,46		32,81		36,08		46,735	
Série1	Matériau 1		Matériau 2		Matériau 3		Matériau 4		Matériau 5		Matériau 6	
	75,9%	75,9%	19,0%	17,0%	10,0%	-2,7%	18,1%	19,2%	9,8%	8,9%	0,5%	4,8%

Série2	55,1%	66,7%	12,4%	18,4%	12,8%	11,4%	19,2%	17,8%	12,3%	11,0%	-2,1%	2,2%
Série3	22,7%	69,0%	15,0%	15,0%	9,5%	-1,3%	21,7%	18,9%	8,9%	10,4%	-2,6%	0,3%
Série4	69,0%	62,0%	13,7%	11,7%	-0,4%	-1,8%	23,6%	14,2%	8,0%	8,0%	-3,6%	-2,1%
Série5	4,2%	62,0%	15,0%	14,4%	7,6%	10,4%	16,7%	16,0%	6,2%	11,0%	3,3%	2,9%
Fidélité	Matériau 1	Matériau 2	Matériau 3	Matériau 4	Matériau 5	Matériau 6						
Sr	1,02908	0,31623	1,14543	0,87693	0,55317	1,01747						
r	2,88142	0,88544	3,20719	2,45539	1,54888	2,84892						
Sx	0,72887	0,28636	1,08766	0,39433	0,45634	1,16855						
SFI	1,02993	0,36332	1,35610	0,73485	0,60104	1,37227						
CV% (k=2)	30,52 %	4,20 %	12,08 %	4,48 %	3,33 %	5,87 %						



4.5.2 Red wines

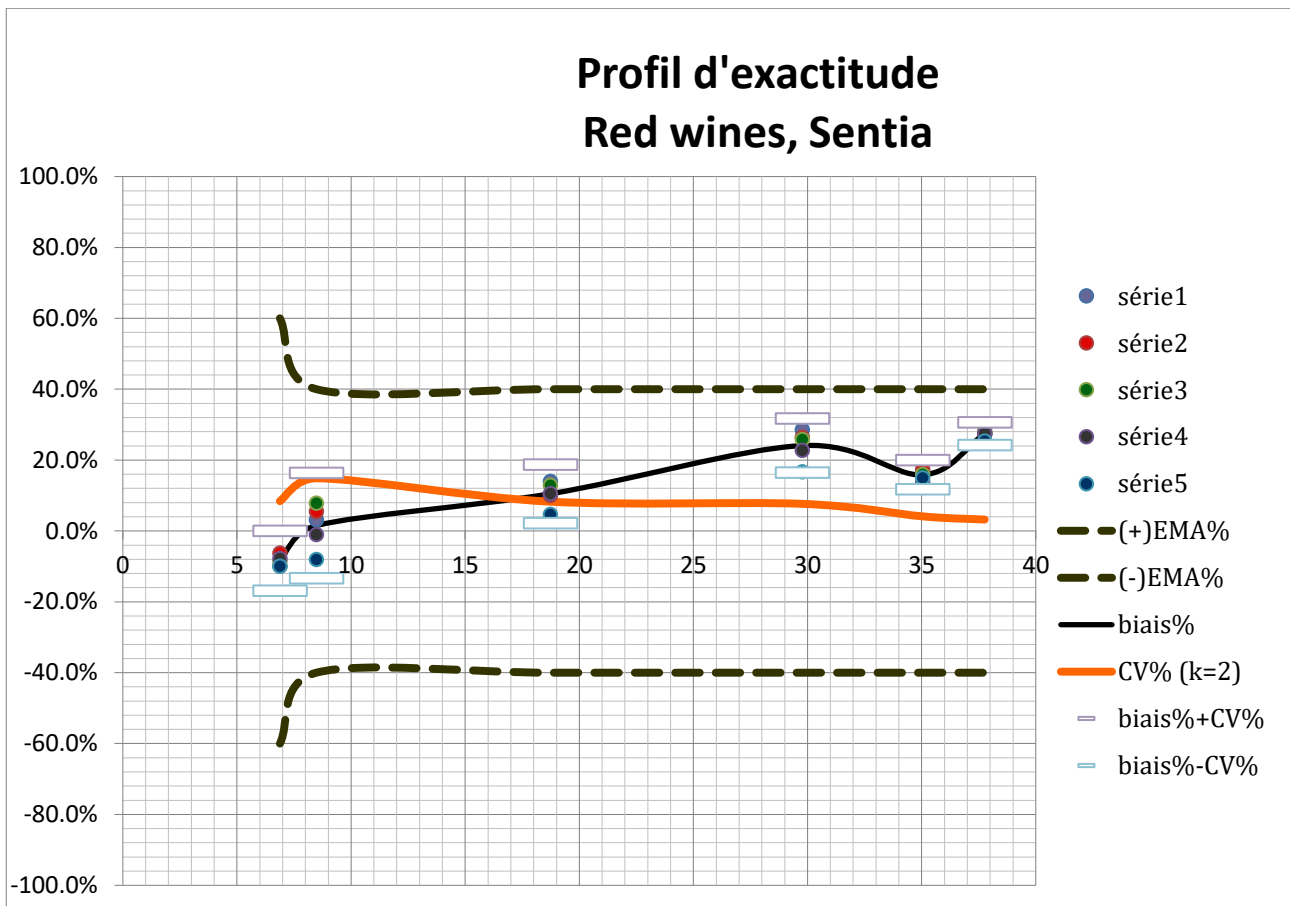
Reference value is assigned by OIV reference method

Méthode	SENTIA		opérateurs	série1	FG
Paramètre	SO2 libre			série2	FG
Date	07/10/21			série3	FG
				série4	FG
				série5	FG

RG071021-2	RG111021-9	RG11021-4	RG071021-3	RG111021-5	RG111021-12
Matériau 1	Matériau 2	Matériau 3	Matériau 4	Matériau 5	Matériau 6
vin rouge	vin rouge	vin rouge	vin rouge	vin rouge	vin rouge
6,88	8,48	18,72	29,76	35,04	37,76
60 %	40 %	40 %	40 %	40 %	40 %

date	Matériau 1		Matériau 7		Matériau 2		Matériau 4		Matériau 4		Matériau 4	
	rep1	rep2	rep1	rep2	rep1	rep2	rep1	rep2	rep1	rep2	rep1	rep2
07/10/21	6,10	6,30	8,70	8,80	21,00	21,70	38,50	38,00	41,00	40,90	49,00	47,20
07/10/21	6,40	6,50	9,10	8,80	21,00	20,20	38,00	37,30	41,70	40,60	48,90	47,50
07/10/21	6,40	6,20	9,20	9,10	21,40	20,90	38,10	36,80	41,60	39,70	48,00	49,40
07/10/21	6,50	6,20	8,90	7,90	20,70	20,70	36,70	36,40	40,90	38,90	48,20	48,20
07/10/21	5,70	6,70	8,40	7,20	18,60	20,60	34,50	35,00	40,40	40,20	47,50	47,20

6,3	8,61	20,68	36,93	40,59	48,11
Matériau 1	Matériau 2	Matériau 3	Matériau 4	Matériau 5	Matériau 6
-11,3%	-8,4%	2,6%	3,8%	12,2%	15,9%
-7,0%	-5,5%	7,3%	3,8%	12,2%	7,9%
-7,0%	-9,9%	8,5%	7,3%	14,3%	11,6%
-5,5%	-9,9%	5,0%	-6,8%	10,6%	10,6%
-17,2%	-2,6%	-0,9%	-15,1%	-0,6%	10,0%
Matériau 1	Matériau 2	Matériau 3	Matériau 4	Matériau 5	Matériau 6
0,34351	0,50498	0,73348	0,52631	0,94181	0,85147
0,96183	1,41393	2,05376	1,47366	2,63706	2,38411
0,10607	0,53080	0,67879	1,36272	0,50175	0,48528
0,26505	0,63973	0,85425	1,41262	0,83382	0,77330
8,41 %	14,86 %	8,26 %	7,65 %	4,11 %	3,21 %



5 Comments on results

The comparison with the OIV reference method shows compliant results on the SENTIA system, both for white, rosé and red wines. Very diverse wines were used, some of which were very rich in polyphenols. We can therefore see the robustness of the method.

The slight bias between the SENTIA system and the OIV reference method is also related to the use of the new version of the reference method, the results of which are significantly lower than the "classical" version of the reference method, before its revision by the OIV. This same type of bias is also observed with the usual colorimetric method. It should therefore not be considered as a major defect.

The repeatability of the method is correct. A little worse than the repeatability of the reference method. The user experience seems to be decisive in the quality of this repeatability. In particular, the test taking of the sample is an essential critical point to be well defined and controlled.

6 Conclusions

In view of the experiments conducted, the quality of the results of the determination of free SO₂ in wines by the SENTIA system seems to us to be very good. Very comparable to the OIV reference method, or to the usual ISO 17025 accredited method, the SENTIA system clearly shows an

extremely interesting new way of analysis of free SO₂.

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