



# **OIV-OENO 661-2021 Collaborative study- Method validation for the determination of free sulphur dioxide, OIV-MA-AS323-04A1 (update). Update to the method validation for the determination of total sulphur dioxide, OIV-MA-AS323-04A2 (update)**

THE GENERAL ASSEMBLY,

IN VIEW OF the Article 2, paragraph 2 b) iv of the Agreement of 3<sup>rd</sup> April 2001 establishing the International Organisation of Vine and Wine,

AT THE PROPOSAL OF the “Methods of Analysis” Sub-Commission,

CONSIDERING the two draft resolutions already adopted in 2018 regarding the update to the method for the determination of sulphur dioxide, distinguishing the Type IV method for the determination of free sulphur dioxide (Resolution OIV-OENO 591A-2018) from the Type II method for the determination of total sulphur dioxide (Resolution OIV-OENO 591B-2018),

CONSIDERING the need for validation of the method for the determination of free sulphur dioxide, OIV-MA-AS323-04A1 (update), and the need for updated validation of the method for the determination of total sulphur dioxide, OIV-MA-AS323-04A2 (update),

DECIDES to complete methods OIV-MA-AS323-04A1 on free sulphur dioxide and OIV-MA-AS323-04A2 on total sulphur dioxide in the Compendium of International Methods of Wine and Must Analysis with the following collaborative study:

## **Collaborative study**

**Method validation for the determination of free sulphur dioxide, OIV-MA-AS323-04A1 (update). Update to the method validation for the determination of total sulphur dioxide, OIV-MA-AS323-04A2 (update)**

### **1. Scope of application**

An international collaborative study, in accordance with Resolution OIV-OENO 6-2000, for the validation of updates to the methods for the determination of free sulphur dioxide and total sulphur dioxide (OIV-MA-AS323-04A), based on the decision of the OIV “Methods of Analysis” Sub-Commission, April 2018.

### **2. Standard references**

- Update (draft) to the OIV-MA-AS323-04A methods,
- ISO 5725,
- Resolution OIV-OENO 6-2000.

### 3. Protocol

A total of 20 samples were prepared using homogeneous volumes of 10 wines from various wine regions in France and Portugal. Each sample was made up twice (the second as a blind duplicate), according to the double-blind principle.

The samples were prepared between 18 and 20 June 2018, then shipped without delay to the participating laboratories.

Sample no.	Blind duplicate no.	Nature of sample
A	1-14	Dry white wine
B	2-16	Dry white wine
C	3-19	Dry rosé wine
D	4-12	Dry rosé wine
E	5-20	Dry red wine
F	6-18	Dry red wine
G	7-11	Dry red wine
H	8-15	White liqueur wine
I	9-17	Red liqueur wine
J	10-13	Red liqueur wine

The analyses were carried out simultaneously by all participating laboratories between 16 and 20 July 2018. Samples were kept in refrigerated cabinets by all laboratories between the date of reception and the date of analysis, according to the protocols sent.

The following laboratories provided their results:

Laboratory	City	Country
Estación de Viticultura e Enoloxía de Galicia	Leiro (Ourense)	Spain

Laboratorio arbitral agroalimentario	Madrid	Spain
ASAE	Lisbon	Portugal
SCL Montpellier	Montpellier Cdex 5	France
HBLA und BA für Wein- und Obstbau	Klosterneuburg	Austria
Laboratorio de Salud Pública	Madrid	Spain
Laboratorio Agroambiental de Zaragoza	Zaragoza	Spain
Laboratoire SCL Bordeaux	Pessac Cedex - CS 98080	France
Unione Italiana Vini Servizi	Verona	Italy
Laboratorio Agroalimentario de Valencia	Burjassot (Valencia)	Spain
Agroscope	Nyon	Switzerland
Laboratoires Dubernet	Montredon des Corbières	France
Laboratoire Dioenos Rhône	Orange	France
Laboratoire Natoli	Saint Clément de Rivière	France

NB: The order of laboratories in the table does not correspond with the order in the following tables, in order to preserve the anonymity of results.

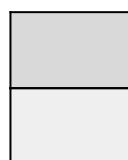
#### 4. Free sulphur dioxide

##### 4.1. Free SO<sub>2</sub> data

Free SO <sub>2</sub> (mg/L)	A	B	C	D	E	F	G	H	I	J
Sample	1 14	2 16	3 19	4 12	5 20	6 18	7 11	8 15	9 17	10 13
Labo 3		31 36	18 18	21 23	20 18	6 6	20 17	5 6		

Labo 5		37 35	21 24	24 25	20 20	8 7	20 20	3 4		
Labo 6	4 1	38 33	21 20	20 26	19 20	7 6	21 19	7 8	1 3	1 1
Labo 7	1 1	37 40	20 22	24 26	20 22	9 8	20 23	8 8	2 1	1 1
Labo 8		31 32	18 19	23 22	22 20	6 7	19 20	5 3	1 1	
Labo 9		35 34	23 19	25 24	21 24		17 17			
Labo 10	2 1	35 34	20 21	24 24	22 21	9 8	21 20	7 7	2 2	1 1
Labo 11	0 0	33 30	17 11	22 16	16 21	6 4	15 19	6 3	1 1	0 0
Labo 15		15 19	15 13	18 20	8 16	6 5	8 15	5 5		
Labo 17	0 0	37 38	24 26	28 28	26 23	8 8	24 22	7 7	1 2	0 0
Labo 18	0 4	33 31	21 11	23 27	15 19	6 4	9 20	3 4	1 1	0 0
Labo 20	0 0	32 32	20 19	21 21	29 21	8 8	20 18	12 4	1 1	0 0
Labo 21	2 1	33 38	19 15	25 22	19 21	6 6	19 20	8 7	2 1	0 0

Results left blank were rendered non-quantifiable (< limit of quantification).



Result removed by the COCHRAN test at 5%

Result removed by the GRUBBS test at 5%

#### 4.2. Free SO<sub>2</sub> results

Free SO <sub>2</sub> (mg/L)	A	B	C	D	E	F	G	H	I	J
No. of laboratories selected	7	9	11	10	10	12	11	11	9	8
No. of repetitions	2	2	2	2	2	2	2	2	2	2
Min.	0	31.5	14	19	17	5	17	3.5	1	0
Max.	2.5	38.5	25	28	24.5	8.5	23	8	2	1
Mean	0.9	34.2	19.8	23.4	20.6	6.8	19.6	5.7	1.4	0.4
Standard deviation	0.98	2.67	2.91	2.46	2.04	1.31	1.77	1.72	0.42	0.52



Repeatability variance	0.79	1.67	2.59	1.20	2.60	0.58	2.23	0.82	0.39	0.00
Inter-laboratory standard deviation	0.98	2.67	2.91	2.46	2.04	1.31	1.77	1.72	0.42	0.52
Reproducibility variance	1.35	7.97	9.76	6.64	5.46	2.00	4.25	3.38	0.37	0.27
Repeatability standard deviation	0.89	1.29	1.61	1.10	1.61	0.76	1.49	0.90	0.62	0.00
r limit	2.48	3.61	4.51	3.07	4.51	2.14	4.18	2.53	1.75	0.00
Repeatability %CV (k=2)	191	8	16	9	16	23	15	32	90	0
Reproducibility standard deviation	1.16	2.82	3.12	2.58	2.34	1.41	2.06	1.84	0.61	0.52
R limit	3.25	7.90	8.75	7.22	6.54	3.96	5.78	5.15	1.70	1.45
Reproducibility %CV (k=2)	250	16	32	22	23	42	21	64	87	276
Horwitz PRSD <sub>R</sub> (%)	16.18	9.40	10.21	9.95	10.15	12.00	10.22	12.30	15.23	18.55
Horwitz s <sub>R</sub>	0.15	3.22	2.02	2.33	2.09	0.81	2.00	0.70	0.21	0.07
Horwitz R	0.42	9.10	5.71	6.59	5.91	2.29	5.67	1.99	0.60	0.20
Horwitz Ratio	7.64	0.87	1.53	1.10	1.11	1.73	1.02	2.58	2.84	7.37

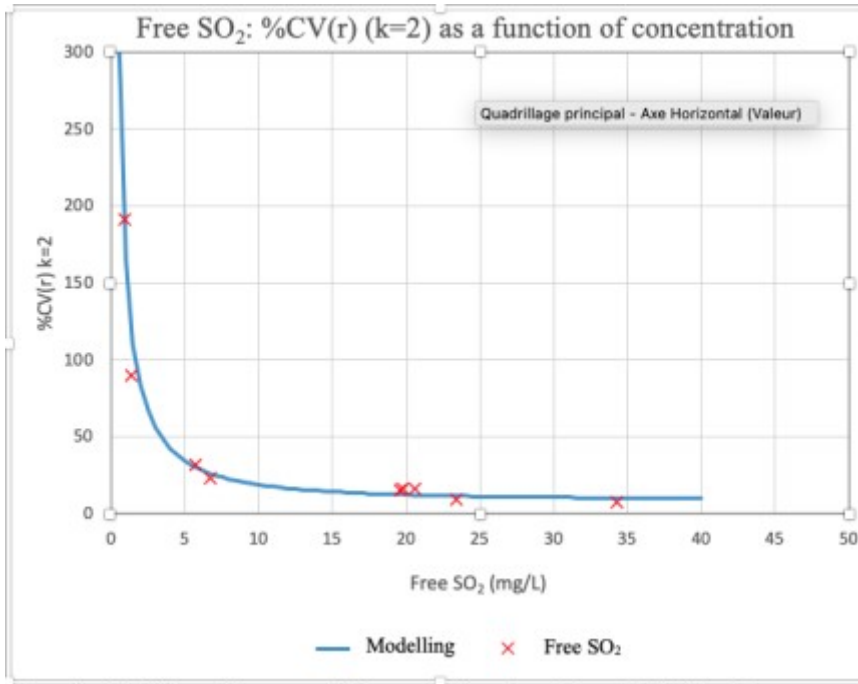


Figure 1: Modelling of the repeatability coefficient of variation, %CV(r) (k=2), as a function of the concentration, C:

$$\%CV(r) = \sqrt{\frac{164.55^2}{C^2} + 9^2}$$

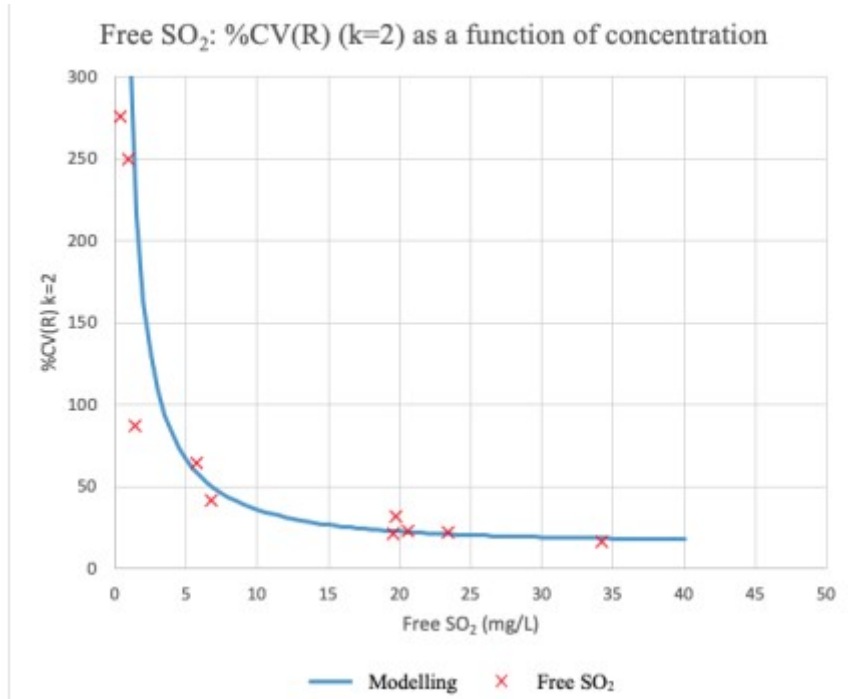


Figure 2: Modelling of the inter-laboratory reproducibility coefficient of variation, %CV(R) (k=2), as a function of concentration, C:

$$\%CV(r) = \sqrt{\frac{323,6^2}{C^2} + 16^2}$$

### 5. Total sulphur dioxide

#### 1. Total SO<sub>2</sub> data

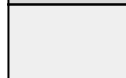
Total SO <sub>2</sub> (mg/L)	A		B		C		D		E		F		G		H		I		J	
Sample	1	14	2	16	3	19	4	12	5	20	6	18	7	11	8	15	9	17	10	13
Labo 3			128	127	72	73	128	131	61	59	28	28	57	56	102	102	47	45		
Labo 5			122	121	68	71	112	114	42	53	22	22	51	42	102	101	35	34		
Labo 6		1	128	131	72	72	126	131	53	54	22	20	42	49	98	99	31	34	3	1
Labo 7	3	3	131	131	70	74	130	131	54	59	26	23	46	48	106	101	37	40	1	1
Labo 8	2	1	125	127	72	72	129	128	58	57	22	23	46	45	97	99	42	39	1	1

Labo 9		120 128	77 75	132 108	71 59	21 25	44 47	110 99	38 48	
Labo 10	2 2	130 130	74 76	130 130	61 61	28 32	55 56	103 104	43 44	3 4
Labo 11	4 3	119 125	71 74	118 118	39 40	18 21	45 41	89 94	26 38	2 2
Labo 14	3 3	129 128	72 72	127 129	58 58	32 29	50 49	102 101	42 41	3 4
Labo 15		134 136	76 78	134 136	60 58	39 27	52 61	110 106	51 50	
Labo 17	3 3	134 132	82 76	136 133	59 50	24 23	46 44	107 105	35 38	0 0
Labo 18	5 3	130 129	78 73	133 133	62 59	29 32	58 52	105 105	50 48	2 2
Labo 20	1 1	128 131	72 74	130 130	58 56	26 28	48 45	98 93	41 43	0 0
Labo 21	0	124 125	69 72	124 126	45 51	19 20	42 42	97 97	35 34	0 1

Results left blank were rendered non-quantifiable (< limit of quantification).



Result removed by the COCHRAN test at 5%



Result removed by the GRUBBS test at 5%

## 5.2. Total SO<sub>2</sub> results

Total SO <sub>2</sub> (mg/L)	A	B	C	D	E	F	G	H	I	J
No. of laboratories selected	7	12	13	13	8	13	10	13	12	9
No. of repetitions	2	2	2	2	2	2	2	2	2	2
Min.	1	121.5	69.5	113	53.5	19.5	42	91.5	32.5	0
Max.	3.5	135	77	135	61	30.5	56.5	108	50.5	3.5
Mean	2.4	128.8	73.0	128.0	58.3	24.7	47.6	100.9	40.8	1.5
Standard deviation	0.93	3.63	2.20	6.24	2.42	4.04	4.89	4.61	5.80	1.35
Repeatability variance	0.14	1.46	3.27	2.35	1.44	3.04	2.30	3.96	2.21	0.17
Inter-laboratory standard deviation	0.93	3.63	2.20	6.24	2.42	4.04	4.89	4.61	5.80	1.35





Reproducibility variance	0.94	13.93	6.49	40.11	6.57	17.84	25.03	23.28	34.72	1.90
Repeatability standard deviation	0.38	1.21	1.81	1.53	1.20	1.74	1.52	1.99	1.49	0.41
r limit	1.1	3.4	5.1	4.3	3.4	4.9	4.2	5.6	4.2	1.1
Repeatability %CV (k=2)	31	2	5	2	4	14	6	4	7	54
Reproducibility standard deviation	0.97	3.73	2.55	6.33	2.56	4.22	5.00	4.82	5.89	1.38
R limit	2.7	10.5	7.1	17.7	7.2	11.8	14.0	13.5	16.5	3.9
Reproducibility %CV (k=2)	80	6	7	10	9	34	21	10	29	184
Horwitz PRSD <sub>R</sub> (%)	14.00	7.70	8.39	7.71	8.68	9.87	8.95	7.99	9.16	15.05
Horwitz s <sub>R</sub>	0.34	9.92	6.13	9.86	5.06	2.44	4.26	8.06	3.73	0.23
Horwitz R	0.96	28.05	17.33	27.90	14.31	6.91	12.04	22.80	10.56	0.64
Horwitz Ratio	2.82	0.37	0.41	0.64	0.50	1.71	1.16	0.59	1.56	6.04

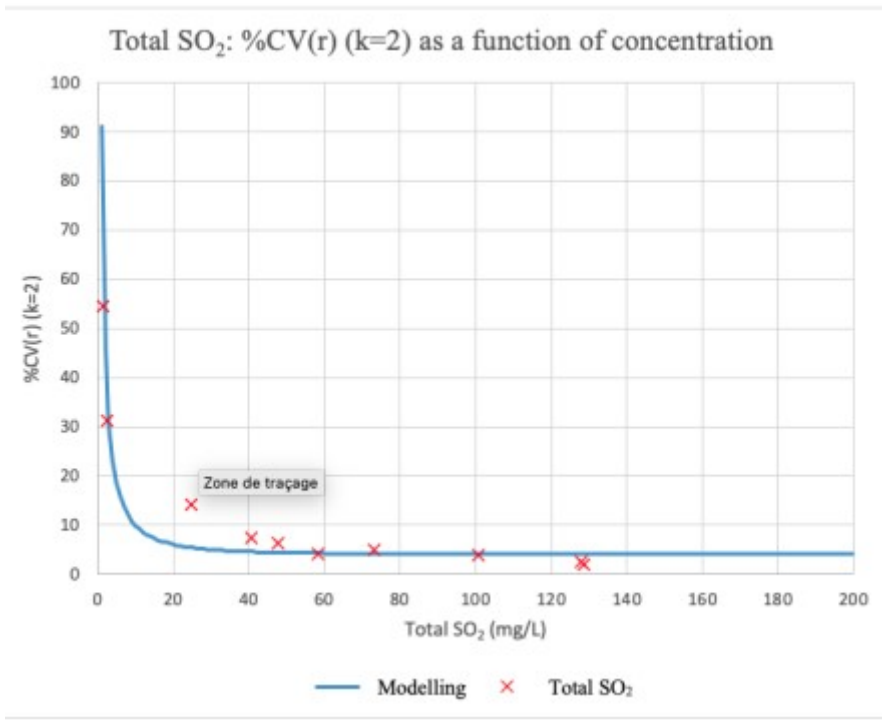


Figure 3: Modelling of the repeatability coefficient of variation, %CV(r) (k=2), as a function of concentration, C:

$$\%CV(r) = \sqrt{\frac{91^2}{C^2} + 4^2}$$

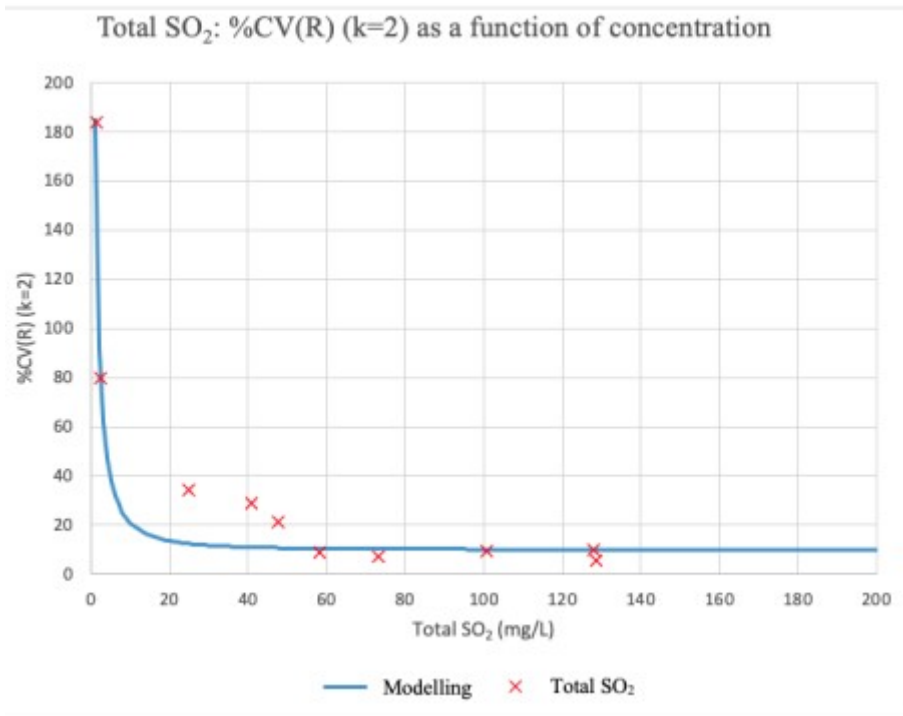


Figure 4: Modelling of the inter-laboratory reproducibility coefficient of variation, %CV<sub>R</sub> (k=2), as a function of concentration, C:

$$\%CV(r) = \sqrt{\frac{184.9^2}{C^2} + 10^2}$$