Application Note
No. 784/2021

Total SO_2 content determination in reference standards by BUCHI method

MultiDist and BasicDist with BUCHI SO_2 glass set: determination of total sulfur dioxide in reference standards sodium metabisulfite & HMS by the patented BUCHI Method with iodometric titration.

1. Introduction

Sulfites are widely used as a preservatives and antioxidants in foods and beverages. Exposure to high levels of sulfites can cause an allergic reaction. Given the health risks associated with sulfite exposure, its amount in beverages and foods is regulated in many countries. Regulations have set the maximum amount of sulfites used and required labelling practice to indicate the presence of sulfites.

Total SO_2 is defined as “the total of all the various forms of sulfur dioxide present in the sample, either in the free state or combined with their constituents” [1]. Its determination in solid samples poses a challenge because SO_2 is withheld in adducts and is released slowly during boiling. Recognized results are obtained by means of the generally accepted Optimized Monier-William’s method according to AOAC 990.28 [2] which suggests the use of nitrogen assisted boiling of the acidified sample to release the Total SO_2. The method presented in this study provides equally quantitative results with much less time required per sample and is based on the patented BUCHI Method that involvs steam distillation followed by a redox titration [3].

In this application note recovery results for two widely used reference standards for total sulfite analysis are presented. A representative concentration range of 0.5-10 mg/sample tube is selected to demonstrate the robust performance of BUCHI method by steam distillation.

The BUCHI method is based on acidification and steam distillation of the samples with ortho-phosphoric acid mixture to release SO_2. If HMS is analyzed, a predefined amount of NaOH is taken in the sample tube to facilitate hydrolysis. The released SO_2 is absorbed in I_2 solution placed in a special BUCHI SO_2 absorption glass set. The BUCHI SO_2 absorption glass consists of two inter-connected receiving flasks. In the first reciever a predefined volume of iodine standard solution is pipetted out and in the second reciever a certain volume of ethanol is taken to minimize possible loss of iodine.

Reaction of SO_2 with iodine solution:

$$SO_2 + I_2 + 4H_2O \rightarrow 2HI + SO_4^{2-} + 2H_3O^+$$

The determination is carried out by means of a redox back titration, where the excess of iodine is back titrated with a standard thiosulfate solution.

Titration of excess of iodine with sodium thiosulfate:

$$I_2 + 2\ Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

2. Equipment

- MultiDist (11K36532011)
- SO_2 absorption glass set (11073599)
- BUCHI Sample tubes 300 mL (037377)
- Metrohm EcoTitrator (11072748)
- Metrohm metal electrode Pt-Titrode (6.0431.100)
- Volumetric pipette 5 mL
- Measuring cylinder, 100 mL
- Glass beaker ~800 mL
- Analytical balance
- Micropipette 1mL, 5mL (Eppendorf)

3. Chemicals and materials

Chemicals:

- Ethanol absolute, analytical, Sigma-Aldrich (20821.321)
- Iodine solution 0.05 mol/L, Reag. Ph Eur, Reag. USP, Merck (1.09099.1000)
- Sodium thiosulfate solution 0.01 mol/L, volumetric, VWR (309337.1000)
- Orthophosphoric acid 85 %, Ph.Eur., VWR, (20621.330)
- Methanol, Reag. Ph.Eur., Merck (1.06009.2500)
- Sodium metabisulfite or Sodium disulphite VWR (27920.295)
- Formaldehyde-sodium bisulfite adduct, HMS, Sigma Aldrich (112704) mol/L NaOH
- Sulphuric acid 0.5 mol/L, VWR (30144.294)
- Deionized water
- Acid mixture: 400 mL deionized water, 500 mL methanol and 50 mL orthophosphoric acid were mixed well in a closed bottle by stirring for approx. 10 min.

For safe handling please follow all relevant MSDS!

4. Procedure

SO_2 determination involvs *in-situ* acidification of the sample by dosing an acid mixture, followed by distillation in two steam steps and simultaneous collection of the distillate in a BUCHI SO_2 absobtion glass set (Figure 1) containing iodine solution. After the distillation, the collected distillate is quantitatively transferred into a ~800 mL glass beaker and a redox titration is carried out to quantitatively determine the excess of iodine and thereby the quantity of the distilled SO_2 [3].

Distillation & Titration

- System preparation: Mount an empty sample tube into MultiDist and place a conical flask under the condenser to collect the distillate. Run a preheating followed by a priming step (choosing a priming method same as the method for analysis), alternatively use the prep function on the home screen (make sure that the right Priming method is selected)
- BUCHI SO2 absorbtion glass set: It is recommended to use the BUCHI SO2 absorption glass set to collect the distillate in the first receiver (5 mL 0.05 mol/L Iodine solution + 50 mL DI water) and to minimize possible loss of iodine use the second reciever containing absolute ethanol (30 mL Ethanol) (Figure 1).
- Blank preparation: An empty sample tube serves as a blank for this experiment. Use a new sample tube for each blank. Mount the sample tube on the distillation unit and perform the distillation. Collect the distillate with the BUCHI absobtion glass set.
- Reference standard preparation: A fresh (daily) stock solution of a reference standard is recommended.

Sodium metabisulfite:

To prepare a 10 mg/mL stock solution of SO_2 e.g., 1.5057 g sodium metabisulfite (Purity = 98.6%) is carefully weighed, dissolved, and diluted with DI water to 100 mL in a volumetric flask.

HMS:

To prepare a 5 mg/mL stock solution of SO_2 e.g., 1.053 g HMS (Purity = 95%) is carefully weighed, dissolved, and diluted with DI water to 100 mL in a volumetric flask.

When analysing HMS, 100 mL 0.1 M NaOH is previously taken in a 300 mL sample tube before adding the stock solution of HMS to facilitate hydrolysis. In case of sodium metabisulfite no addition of NaOH is required.

Different aliquots of this stock solution were pipetted out with a micropipette for each reference standard determination.

Distillation:

The following method parameters (Table 1) were used for distillation on MultiDist followed by a redox titration with Metrohm EcoTitrator. The detailed configuration and method parameters for the iodometric titration are shown in (Appendix A).

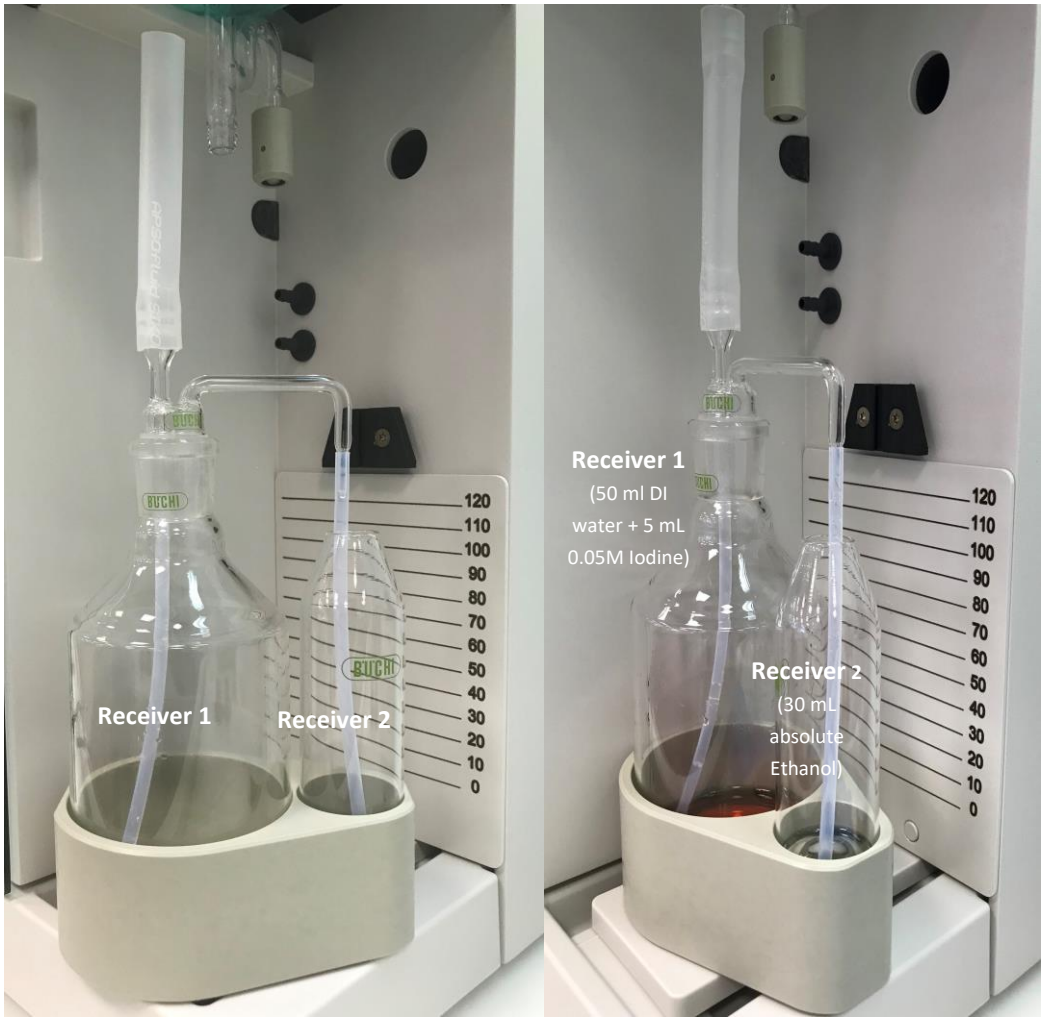

Figure 1: BUCHI SO_2 absorption glass set (left), BUCHI SO_2 absorption glass set with relevant solutions in Receiver1 and Receiver2 correctly attached to the distillate outlet (right)

Table 1: Distillation parameters on MultiDist.

Method parameters MultiDist

Distillation & Titration Parameters			
Reaction detection	Off	MaxAccuracy mode	On
H_2O volume	0 mL	Chiller/Tap water	Chiller F-314
NaOH volume	0 mL	Set temperature	15°C
Acid volume	100 mL	AutoDist mode	Off
Reaction time	5 s		
Steam Steps	2	For a separate redox titration on Metrohm EcoTitrator	
Steam Power 1	10 %	Titration mode	DET U
Startime 2	300 s	Sensor type	Redox (Pt)
Steam Power 2	100 %	Titrant	$Na_2S_2O_3$ 0.01 mol/L
Distillation Time	600 s	(For more details refer to Appendix A)	
Level Detection	Off		
Stirrer speed distillation	0		
Titration type	No titration		
Receiving solution volume	-		
Stirrer speed titration	-		
Titration start time	-		
Sample Tube Aspiration	30s (for blank & reference standard)		
Reciever Aspiration	-		

1. The aliquots of the reference standard stock solution were pipetted out into a 300 mL sample tube with or without addition of NaOH depending on the reference standard used.
2. The sample tube was mounted in the MultiDist unit.
3. The BUCHI SO_2 glass set up was prepared and mounted on to the outlet of the condenser.
4. The distillation was started according to Table 1.
5. After the distillation, the BUCHI SO_2 glass set up was removed, and the content of both vessels was poured together into an 800 mL beaker. The vessels and the tubes were rinsed carefully (thrice) into an 800 mL beaker using deionized water.
6. The 800 mL beaker containing the distillate was acidified with 2 mL 0.5 mol/L sulphuric acid & titrated immediately using the method in Appendix A.
7. In this study, a Metrohm EcoTitrator was used. Alternatively, this titration could also be done manually without a titrator using starch as an indicator added at the very end of the titration (at pale yellow colouration). Colour will change to blue. The end point manual titration is blue to colourless. The titrant volume needs to be noted after the titration.
8. After the experiment it is advised to rinse the pumps in use in the distillation unit with DI water.

5. Calculation

$$W(SO_2)_{sample} = \frac{(V^T_{blank} - V^T_{sample}) \bullet c^T \bullet M(SO_2)}{z} \quad (1)$$

$$c(SO_2)_{sample} = \frac{W(SO_2)_{sample} \cdot 1000}{m_{sample}} \quad (2)$$

$M(SO_2)$: Molar mass SO_2 = 64.0648 [g/mol]
$W(SO_2)_{standard}$: Weight of SO_2 calculated from $V_{standard}$ [mg SO_2]
V^T_{blank}: 0.01 mol/L thiosulfate consumption for blank [mL]
c^T: Concentration of thiosulfate (titrant) [mol/L]
z: Redox valency of thiosulfate = 2
$W(SO_2)_{sample}$: Determined weight of SO_2 in sample [mg SO_2]
V^T_{sample}: Titrant volume for sample [mL]
$c(SO_2)_{sample}$: Determined SO_2 concentration in sample (by BUCHI SO_2 method) [ppm SO_2]
m_{sample}: Sample weight [g]

6. Results

6.1 Determining Limit of detection (LOD) and Limit of quantification (LOQ)

The “blank method” from DIN 32645 was used for the determination of the detection limit (LOD) and the quantification limit (LOQ) [4].

Ten blanks were determined, the results are presented in Table 2.

Table 2: Results of the blank determination

	V_{Blank} [mL]	Average [mL]	SD [mL]	RSD [%]
1	47.960	48.098	0.129	0.268
2	47.988			
3	47.987			
4	48.037			
5	48.280			
6	48.223			
7	48.151			
8	48.075			
9	48.292			
10	47.987			

The following equation (3) was used to calculate the limit of detection (LOD)

$$LOD = \phi n;\alpha \bullet SD \quad (3)$$

LOD = 0.387 mg

ϕn;α: factor 3.0; depending on the number of blanks (n=10) and the level of significance (α=0.01)
SD: standard deviation of the blank determination (SD=0.129 ml) [4]
Depending on the LOD, the limit of quantification (LOQ) can be calculated, see equotation (4).

$$LOQ = k \bullet \phi n;\alpha \bullet SD \quad (4)$$

LOQ = 1.159 mg

k: factor 3

6.2. Recovery results for reference standards: Sodium metabisulfite and HMS

The obtained SO_2 concentrations of both samples are shown in Table 3 and 4.

Table 3: Results Blanks and Reference substance for reference standard sodium metabisulfite

	Volume of 10 mg/mL stock soln. [mL]	SO_2 [mg]	Titrated volume [mL]	SO_2 / sample [mg]	Average Blank [mL]	Recovery Purity corrected [%]	Average Recovery [%]	Relative Standard Deviation [%]
Blank-1	-	-	48.225	-	48.418	-		0.307
Blank-2	-	-	48.559	-				
Blank-3	-	-	48.576	-				
Blank-4	-	-	48.311	-				
Ref 1-1	0.05	0.507	46.884	0.492		98.24	89.97	
Ref 1-2	0.05	0.507	47.142	0.409		81.70		
Ref 2-1	0.1	1.015	45.730	0.861		86.06	93.46	
Ref 2-2	0.1	1.015	45.268	1.009		100.85		
Ref 3-1	0.2	2.030	42.558	1.877		93.80	91.61	
Ref 3-2	0.2	2.030	42.831	1.790		89.42		
Ref 4-1	0.4	4.060	36.743	3.740		93.43	93.05	
Ref 4-2	0.4	4.060	36.838	3.709		92.67		
Ref 5-1	0.8	8.119	24.507	7.660		95.68	95.20	
Ref 5-2	0.8	8.119	24.750	7.582		94.71		
Ref 6-1	1.0	10.149	16.681	10.167		101.60	96.28	
Ref 6-2	1.0	10.149	20.002	9.103		90.97		

Table 4: Results Blanks and Reference substance for reference standard HMS

	Volume of 5 mg/mL stock soln. [mL]	SO_2 [mg]	Titrated volume [mL]	SO_2 / sample [mg]	Average Blank [mL]	Recovery Purity corrected [%]	Average Recovery [%]	Relative Standard Deviation [%]
Blank-1	-	-	47.737	-	47.813			0.173
Blank-2	-	-	47.800	-				
Blank-3	-	-	47.901	-				
Ref 1-1	0.2	1.006	45.159	0.850		88.94	87.97	
Ref 1-2	0.2	1.006	45.216	0.832		87.00		
Ref 2-1	0.4	2.516	40.883	2.220		92.88	95.03	
Ref 2-2	0.4	2.516	40.563	2.322		97.18		
Ref 3-1	0.8	3.522	38.130	3.102		92.70	93.13	
Ref 3-2	0.8	3.522	38.041	3.130		93.56		
Ref 4-1	1.6	5.031	33.770	4.499		94.12	93.05	
Ref 4-2	1.6	5.031	34.088	4.397		91.98		
Ref 5-1	2	10.063	20.429	8.772		91.77	91.74	
Ref 5-2	2	10.063	20.442	8.768		91.72		

7. Comparison to standard methods

Based on the findings of this study, the optimized BUCHI method was compared to the standard method shown in Table 5. HCl should not be used with the Dist Line because of possible corrosion of steel parts. For this reason, ortho-phosphoric acid was used instead.

Table 5: Comparison of the methods AOAC 990.28 to the BUCHI SO_2 Method.

Parameter	AOAC 990.28	BUCHI SO_2 Method
SO_2 entrainment	N_2-stream	Steam
Acidification	90 mL HCL 4N	100 mL acid mixture
Distillation time	102 min	10 min
Solution in receiver	H_2O_2 in water	Aqueous I_2-solution and ethanol
Titration type	Acid-base	Redox back titration
Titrant	NaOH	$Na_2S_2O_3$
Titrated analyte	H_2SO_4	I_2
Reference standard	HMS	Sodium metabisulfite & HMS
Required recovery	>80% at 10 ppm	>85% recovery in the range 1-10 mg SO_2. e.g., 1 mg SO_2/100 g sample would be 10 ppm and would fit in the performance requirements. The LOQ acc. to blank method is 1.159 mg

8. Conclusion

The recoveries for reference standard sodium metabisulfite & HMS were above 85% in the range of 1 -10 mg SO_2 /sample tube (absolute amount). In this typical concentration range if the sample weight is adjusted accordingly the performance requirement from AOAC 990.28 is satisfied.

BUCHI method for total SO_2 determination is recommended especially in presence of volatile acids in the sample with low SO_2 concentrations.

9. References

Operation Manual of MultiDist/BasicDist

[1] Compendium of International Methods of Analysis – OIV, Sulfur dioxide, Method OIV-MA-AS323-04A

[2] AOAC Official Method 990.28, Sulfites in Foods, Optimized Monier-Williams Method

[3] European Patent EP 2 515 098 A1, Verfahren und Vorrichtung zur SO_2-Gehaltsbestimmung in Getränken und Lebensmitteln, Büchi Labortechnik AG.

[4] DIN 32 645 Nachweis-, Erfassungs- und Bestimmungsgrenze

10. Appendix

A: Configuration of titrator Metrohm EcoTitrator

Titration mode: DET U

Menu → Parameters → Start conditions

Activation pulse	Off
Start delay time	0 s
Start volume	0.0000 mL
Dosing rate	Max. mL/min
Pause	0 s
Request sample ID	Off
Request sample size	Off
Hold at request	On

Menu → Parameters → Titration parameters

Titration rate	Optimal
Temperature	25.0 °C
Sensor	Metal electrode
Solution	$Na_sS_2O_3$ 0.01 mol/L
Stirrer	On
Stirring rate	12
Titration rate	Optimal

Menu → Parameters → Stop conditions

Stop volume	100.000 mL
Stop meas. Value	Off
Stop EP	1
Volume after EP	1 mL
Stop time	Off
Filling rate	Max. mL /min

Menu → Parameters → Evaluation

Window	Off
EP criterion	5
EP recognition	All
Fixed EP1 at	Off
Fixed EP2 at	Off

The other settings should be adjusted to the customer's needs (calculations, reporting, statistics).