

## Determination of total sulfur dioxide according to the patented BUCHI method

This method is designed to overcome the various problems found in the International Organization of Vine and Wine (OIV-18) method without compromising on results.

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### Abstract

Foodstuffs or alcoholic beverages contain allergenic substances. The manufacturer must indicate them in the product labelling according to the guideline 2003/89/EC, (Nov 2005). This guideline requires the labelling of twelve potential allergens, such as sulfur dioxide (SO<sub>2</sub>) and sulfites, at concentrations of more than 10 mg/kg or 10 mg/L. Sulfur dioxide is found in, among other substances, potato products, dried fruit, and wine - where it is used as an antimicrobial and antioxidant. In addition, SO<sub>2</sub> is used to 'improve' product appearance as it diminishes the darkening effect which can occur for example in potatoes or apples.

### BUCHI method vs. OIV method

For the determination of total SO<sub>2</sub> BUCHI developed a patented procedure.

The procedure includes steam distillation into specially designed SO<sub>2</sub> absorption vessels in which the SO<sub>2</sub> reacts with a defined volume of iodine standard solution. Subsequently the distillate is back-titrated with sodium thiosulfate standard solution using a titrator suitable of carrying out redox titrations. The patented method is designed to overcome the various problems found in the official International Organization of Vine and Wine (OIV) method without compromising on results.

The OIV SO<sub>2</sub> method is based on the entrainment of SO<sub>2</sub> from the sample into a titration vessel by means of a nitrogen stream. Simple steam distillation, as a possible alternative, does not produce results comparable to the OIV method without further optimization and adaption. The most important improvement stems from a calibration using a stabilized SO<sub>2</sub> standard containing acetaldehyde to simulate a wine matrix. The calibration reveals a good linear relationship between the determined SO<sub>2</sub> amounts and the known amounts of the standard solution associated with the correlation factor R<sub>2</sub> >0.998.

The linear equation  $y = a \cdot x + b$  is used as a correction in the calculations for total SO<sub>2</sub>. Typical values are: slope a: 1.05 – 1.15 and intercept: b: 0 – 0.4 (see Figure 7). a and b have to be individually determined for each distillation unit. The calibration is stable over months but to maintain quality, standards should be checked at regular intervals.

The detection limit (LOD) is 0.3 mg SO<sub>2</sub>/sample and the determination limit (LOQ) 0.9 mg SO<sub>2</sub>/sample. As a result of an interlaboratory survey involving four different Swiss laboratories ranges of repeatability were shown to be r: 0.6 – 0.8 mg SO<sub>2</sub>/L with a reproducibility of R: 3.6 – 5.5 mg SO<sub>2</sub>/L.

This shows that the patented BUCHI SO<sub>2</sub> method performs within the repeatability and reproducibility



Figure 1: Setup for SO<sub>2</sub> determination

limits stated for the official OIV SO<sub>2</sub> Method which are r = 6 and R = 15 mg SO<sub>2</sub>/L.

In addition SO<sub>2</sub> levels for a range of 40 to 220 mg SO<sub>2</sub>/L were found in eleven different wines and results were compared to the OIV SO<sub>2</sub> method. The BUCHI SO<sub>2</sub> method represents a fast and reliable technique for the determination of total SO<sub>2</sub> in wine, allowing proper labelling according to US and EU regulations.

### Which distillation unit can be used?

The instrument must feature an acid resistant pump to automatically dose strong acids to the sample in advance to the distillation. This feature is available on the Kjelflex K-360 and the Distillation Unit K-355. For further characterization of the two instruments please refer to the table below.

Table 1: Overview distillation units

Characteristics	Distillation Unit K-355	Kjelflex K-360
Sample dilution	•	•
Steam regulation	•	•
Dosage H <sub>2</sub> BO <sub>3</sub>	•	•
Dosage NaOH	•	•
Dosage of strong acids	•	optional
Aspiration (sample tube and reciever)	•	•
Result memory		500
Method memory	9	50
Communication with titrator*		•
Port for printer		•
Port for level sensors		•

\* Different titrators are possible to be connected (such as Metrohm, Mettler-Toledo, SCHOTT and Radiometer).

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## Sample and blank preparation

The sample preparation depends on the sample type:

### Liquid samples

E.g. beer, wine and others:

1. Homogenize sample by shaking and degassing, necessary to ensure reproducible results
2. Acidification  
Release SO<sub>2</sub> with a water, methanol and phosphoric acid mixture;  
NOTE: the mixture should be added automatically by means of the acid resistant pump
3. Generation of a calibration curve with a standard prior to the sample analysis

### Solid samples

E.g. dried fruits, shrimps and others:

1. Homogenize sample by grinding, mixing, drying or deep-freezing
2. Hydrolyzation with ethanol and sodium hydroxide  
NOTE: The two chemicals must be added one after the other
3. Acidification with phosphoric acid,  
NOTE: the acid should be added automatically by means of the acid pump
4. No calibration curve is necessary

### What is the required sample amount?

The sample amount needs to be selected depending on the expected SO<sub>2</sub> content, and in order that a LOQ of ≥0.85 mg SO<sub>2</sub>/sample is achieved.

This rule of thumb is valid for all liquid and solid samples.

### How is the minimum sample amount calculated?

Example:

Expected SO<sub>2</sub> content in dried pear halves: 200 mg/kg

$$m_{\text{sample}} \geq \frac{\text{LOQ SO}_2 \text{ per sample} \cdot 1000}{c(\text{SO}_2)} \quad [1]$$

$$m_{\text{sample}} \geq \frac{1 \text{ mg SO}_2 \text{ per sample} \cdot 1000}{200 \text{ mg/kg}} = \underline{\underline{5 \text{ g sample}}} \quad [2]$$

Table 2: Legend of abbreviations

Abbreviation	Description	Unit
m <sub>sample</sub>	Sample weight	g
LOQ	Limit of quantification	SO <sub>2</sub> /sample
c(SO <sub>2</sub> )	concentration	mg SO <sub>2</sub> /kg

Formula [1] is valid for the calculation of the minimum sample weight or volume of solid and liquid samples.

Table 3: Correlation of expected SO<sub>2</sub> concentration and sample weight

c(SO <sub>2</sub> ) [mg/kg]	m <sub>sample</sub> [g]
7 – 10	150 – 100
10 – 20	100 – 50
20 – 100	50 – 10
100 – 200	10 – 5
200 – 500	5 – 2
≥ 500	≤ 2

### How are liquid samples prepared?

1. Determination of the density of the sample.
2. If necessary the sample is degassed by use of an ultrasonic bath. Sample is measured and weighed into a glass beaker. Details are described in application note AN 066/2011 "Determination of Total SO<sub>2</sub> in Beer".
3. SO<sub>2</sub> is released from the sample matrix by a mixture of water, methanol and phosphoric acid (v/v/v 400:500:50). Generally, 50 mL of the mixture is added to the sample by means of the acid resistant pump.
4. Distillation is started immediately after the addition of the mixture.

### How are solid samples prepared?

1. If necessary the sample is homogenized by mixing or grinding.
2. Sample is weighed into a glass beaker.
3. Solid matrices are hydrolyzed with a mixture of sodium hydroxide and ethanol. The required volume of the chemicals to be added is depending on the expected c(SO<sub>2</sub>) and m<sub>sample</sub> and can be calculated from the table below.

Table 4: Required volume of liquids depending on the mass of sample

m <sub>sample</sub> [g]	5 % Ethanol [mL]	1 M NaOH [mL]	85 % H <sub>3</sub> PO <sub>4</sub> [mL]
< 20	20	25	15
20 - 40	40	50	30
40 - 80	60	75	45

After hydrolyzing the solid samples for at least 10 minutes the sample is transferred completely into a 500 mL sample tube and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) is added via the acid resistant pump to release the SO<sub>2</sub>. Distillation is started immediately to prevent loss of I<sub>2</sub> (from the receiver) and SO<sub>2</sub> (from the sample).

### Note: Hydrochloric acid must not be used.

The use of HCl will lead to corrosion of the steel parts in the distillation instrument

If HCl is recommended in a procedure please substitute it with phosphoric acid solution.

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Figure 2: Chemicals required for preparation of solid samples

### How are the blanks prepared?

- Beer:  
Water/methanol/H<sub>3</sub>PO<sub>4</sub> mixture + 5 % ethanol solution corresponding to the sample's volume
- Wine:  
Water/methanol/H<sub>3</sub>PO<sub>4</sub> mixture + 12 % ethanol solution corresponding to the sample's volume
- Solid samples:  
NaOH/ethanol/H<sub>3</sub>PO<sub>4</sub> mixture + 10 mL distilled water

### Preparation of the distillation unit and the absorption vessels

#### Distillation Unit:

- K-355 and K-360: The phosphoric acid or phosphoric acid mixture should be added using the acid resistant pump. Calibrate the pump with the acid or acid mixture before first dosing to ensure correct volume dosage.
- Create a method for the SO<sub>2</sub> distillation including the volume of the reagent dosage, the steam output and the distillation time.
- Preheat the distillation unit three times to heat up the glassware and the instrument.



Figure 3: Kjelflex K-360 with SO<sub>2</sub> absorption vessel

### How is the SO<sub>2</sub> absorption vessel prepared?

#### 1<sup>st</sup> receiver:

- 5 mL 0.05 mol/L iodine standard solution + 30 mL distilled water
- To avoid iodine losses close the receiver containing the iodine solution and the iodine solution bottle immediately after pipetting

#### 2<sup>nd</sup> receiver:

- 30 mL ethanol (96%)
- Ethanol absorbs iodine vapors from 1<sup>st</sup> receiver, and therefore prevents iodine loss

The SO<sub>2</sub> absorption vessels are connected to the condenser outlet of the distillation unit



Figure 4: SO<sub>2</sub> absorption vessel

### What needs to be considered to achieve the best distillation conditions?

#### How much distillate needs to be collected?

The distillation process is stopped as soon as the distillate in the 1<sup>st</sup> receiver is filled up to the neck of the bottle (approx. 5:30 - 7 minutes). Distillation time is expected to be longer for liquid samples with high water content than for solid samples. The distillation volume has to be identical for all the samples in the series.



Figure 5: 1<sup>st</sup> receiver filled with distillate to the bottle neck

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### How is the quality check of the iodine solution performed?

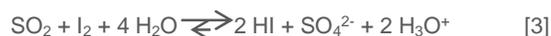
The quality check should be performed before starting the blank and the sample measurements and also if the thiosulfate solution is renewed during an experiment.

5 mL of 0.05 mol/L iodine solution are titrated (without distillation in advance) with freshly prepared 0.01 mol/L thiosulfate solution. A typical result is **49 - 50 mL**. If the determined value is below 49 mL it is recommended to prepare a fresh thiosulfate solution and/or to use a new freshly opened iodine solution.

### What is the chemical background of the redox titration?

**Iodometric titration:** reaction of SO<sub>2</sub> with I<sub>2</sub>

The distilled SO<sub>2</sub> reacts with the iodine standard solution in a redox reaction according to equation [3].



**Back-titration:** excess I<sub>2</sub> reacts with thiosulfate standard solution

After the distillation the residual iodine is determined according to a redox-titration using sodium thiosulfate standard solution as shown in equation [4].



### How is the titration carried out?

- The iodine containing liquids from the 1<sup>st</sup> and 2<sup>nd</sup> receivers are rinsed into a 600 mL glass beaker. The connecting glassware and both receiver vessels are rinsed with water into the same beaker
- The glass beaker is filled up to 400 mL with distilled water
- The solution in the beaker is acidified with ~ 2 mL of 0.5 mol/L H<sub>2</sub>SO<sub>4</sub> and stirred
- A freshly prepared 0.01 mol/L sodium thiosulfate standard solution must be used for titration. This solution has to be stored in the fridge and is stable for 3 weeks only



Figure 6: Titration setup with Pt-electrode

- Titrator e.g. Metrohm Titrimo Plus 877 with Pt-electrode
- Titration method: redox back-titration of I<sub>2</sub> by Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution.
- The start and stop criteria for the titration is selected for every experiment in accordance with the expected titrant consumptions. e.g. 30 mL start volume, 53 mL stop volume
- Endpoint: visible as a color change from orange to colorless
- Positions for the selected endpoints have to be chosen in a reproducible manner
- Write down the titrated volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution
- Typical titrant consumptions for **blanks** are **47 - 49 mL** (sd < 0.7 mL). Carry out 2 to 4 reproducible blank determinations

### How are the results calculated?

The SO<sub>2</sub> concentration of the sample is calculated according to formula [5] and [6].

$$W(\text{SO}_2)_{\text{sample}} = \frac{(V_{\text{blank}}^T - V_{\text{sample}}^T) \cdot c^T \cdot M(\text{SO}_2)}{z} \quad [5]$$

$$c(\text{SO}_2)_{\text{sample}} = \frac{W(\text{SO}_2)_{\text{sample}} \cdot 1000}{V_{\text{sample}}} \quad [6]$$

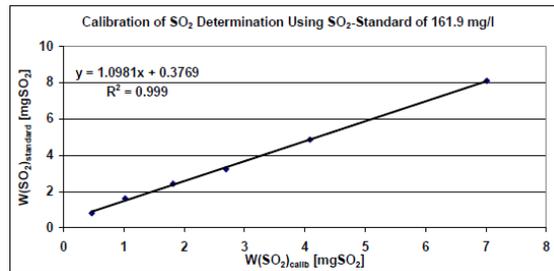
Table 5: Legend of abbreviations

Abbreviation	Description	Unit
M(SO <sub>2</sub> )	Molar mass SO <sub>2</sub> = 64.06	g/mol
M(Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> )	Molar mass Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> = 126.16	g/mol
V <sub>blank</sub> <sup>T</sup>	Consumption of thiosulfate solution for the blank	mL
c <sup>T</sup>	Concentration of the thiosulfate standard	mol/L
z	Redox valency of thiosulfate = 2	
W(SO <sub>2</sub> ) <sub>sample</sub>	Determined content of SO <sub>2</sub>	mg
V <sub>sample</sub> <sup>T</sup>	0.01 mol/L thiosulfate consumption for the sample	mL
c(SO <sub>2</sub> ) <sub>sample</sub>	Calculated SO <sub>2</sub> concentration in the sample (using the BUCHI SO <sub>2</sub> Method)	mg/L
V <sub>sample</sub>	Sample volume	mL
W(SO <sub>2</sub> )	Weight of SO <sub>2</sub> in the sample	mg

For liquid samples the calibration curve has to be included in the calculation. A SO<sub>2</sub> standard is determined and results are plotted in a graph. The linear equation is used for the calculation. Details are described in the AN 066/2011 SO<sub>2</sub> in beer.

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**Figure 7:** Calibration curve for the determination of total SO<sub>2</sub> and the linear equation correlating the measured SO<sub>2</sub> amounts (x-axis) to the theoretical SO<sub>2</sub> contents (y-axis).

To calculate and report the results the app KjelReports is available free of charge for iOS, Android and Windows. It can be downloaded from the iTunes and the google playstore. For more information use the [BUCHI mobile apps](#).



**Figure 8:** Tablet PC with the app KjelReports

### Summary

The determination of total SO<sub>2</sub> in liquid and solid samples using the KjelFlex K-360 or Distillation Unit K-355 provides reliable and reproducible results. The results of the patented BUCHI SO<sub>2</sub> method are in line with the results of the OIV-18 method.

### Where to find additional information?

- Instrument information:  
[Instrument information K-360](#)  
[Instrument information K-350 and K-355](#)
- Application Notes:  
[BUCHI application finder](#)
- Information and download of apps:  
[BUCHI mobile apps](#)
- YouTube BUCHI channel:  
[SO<sub>2</sub> determination in liquid samples](#)  
[SO<sub>2</sub> determination in solid samples](#)