Short Note No. 169/2014
Sulfur dioxide determination in shrimps

Distillation Unit K-355 or KjelFlex K-360
Sulfur dioxide determination in shrimps in accordance with the European legal regulation 2003/89/EC

The presented method for sulfur dioxide determination is based on the chemical degradation of sulfites into volatile sulfur dioxide (SO_2). SO_2 is separated from the sample matrix by steam distillation, with the Distillation Unit K-355 or KjelFlex K-360, into a known volume of iodine standard solution. The amount of sulfur dioxide is determined by means of a back titration with sodium thiosulfate standard solution.

1. Introduction

Sulfur dioxide, sulfurous acid, sodium-, potassium- or calcium-salts of sulfite, hydrogensulfite, and disulfite are used as preservatives and antioxidants in food. In Europe potassium disulfite, sulfur dioxide and sodium sulfite are allowed food additives. Nevertheless, due to the suspected adverse effects on human health, the use of sulfites is subject to regulatory legislation calling for the need for analytical methods to determine the levels present [3, 4]. The goal of the analysis is to meet the European legal regulation [1] which requires the ability to determine SO_2 at a level of 10 ppm.

2. Procedure

Detailed information concerning the basic principles for SO_2 determination are described in the SO_2 white-paper [2].

Recommended equipment: Distillation Unit K-355 or KjelFlex K-360, Mixer B-400 and a redox titrator.

Blanks: All chemicals are added except the sample. Blanks are treated in the same way as the samples for determination.

Samples: Frozen shrimps

Sample preparation:

Homogenize the frozen shrimps with a mixer. Weigh 100 g of the homogenized sample material into a crystallization dish. Transfer 10 - 20 g of the sample into a mortar containing a layer of sand. If the SO_2 amount is close to the limit of quantification (LOQ), 0.85 mg SO_2 per sample, the weight of the sample has to be increased.

Table 1: *Parameters for sample preparation*

Sample weight	100 g
Sample tube size	500 mL

As illustrated in Figure 1, coat the meat with sand, flatten and fold it several times until it consists of a layered structure of meat and sand. Transfer the layered lump into the 500 mL sample tube. Repeat the procedure with the rest of the sample material and finally wipe the crystallization dish with a paper tissue and add it to the sample tube as well.

The aim of this procedure is to separate the meat into small portions from which the SO_2 can be released during distillation. Without this preparation procedure, the meat will form dumplings with a cured surface during distillation preventing access to the SO_2.

homogenized *coated with sand* *folded*
Figure 1: *Forming meatballs coated with sand*

Preparation of the SO_2 absorption vessels

The two absorption vessels, shown in Figure 2, are filled with the liquids mentioned in Table 2. Then the vessels are connected to the Distillation Unit.

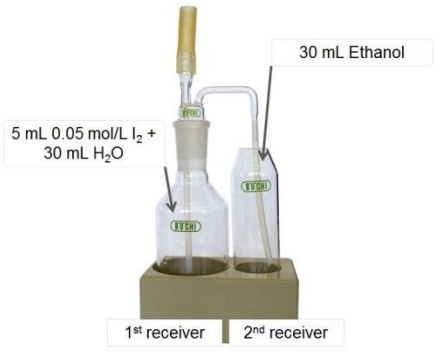

Figure 2: *SO_2 adsorption vessels.*

Table 2: *Filling of receiver vessels*

1st receiver		2nd receiver	
H_2O	30 mL	Ethanol 96 %	30 mL
I_2 0.05 mol/L	5 mL		

Hydrolyzation and distillation of the sample:

Table 3: *Parameters for distillation*

NaOH 1M	75 mL
Ethanol 5%	60 mL
H_3PO_4 85%	45 mL
Steam output	100 %

Distillation time 5:30 -7 minutes

Note: Hydrochloric acid must not be used as it corrodes the steel parts. Please use phosphoric acid instead.

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Add NaOH and ethanol to the sample. After hydrolyzing the sample for at least 10 minutes start the SO_2 method on the distillation unit. H_3PO_4 is added via the acid resistant pump to release SO_2.

The distillation is started immediately to prevent loss of I_2 and SO_2. The distillation process is stopped as soon as the distillate in the 1st receiver is filled up to the neck of the bottle (approx. 5:30 - 7 minutes), shown in Figure 3.

Figure 3: *Distillation is stopped when the level of the distillate reaches the neck of the bottle.*

During the distillation the sand-meat mixture will release the meat of low specific mass and it will rise toward the upper part of the sample tube. Due to its high specific mass the sand will be deposited in the lower part of the sample tube.

Titration:
The solutions of 1st and 2nd receiver are combined. The remaining iodine in the distillate is titrated with sodium thiosulfate solution. The endpoint is indicated by a color change from orange to colorless. The parameters for titration are described in table 4. The volume of the titrant is used for the calculation of the SO_2 content (see equations (1), (2) and table 4).

Table 4: *Parameters for titration*

Titration solution	$Na_2S_2O_3$ 0.01 mol/L
H_2SO_4 0.05 M for acidification	2 mL
Titration type	Redox
Equivalence point	Colorless

Result calculation:

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

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

Table 5: *Abbreviations*

Symbol	Definition	Unit
$W(SO_2)_{sample}$	Weight of SO_2 in the sample	mg
V^T_{blank}	Consumption of thiosulfate solution for the blank	mL
V^T_{sample}	0.01 mol/L thiosulfate consumption for the sample	mL
c^T	Concentration of the thiosulfate standard	mol/L
$M(SO_2)$	Molar mass SO_2 = 64.0648	g/mol
z	Redox valency of thiosulfate = 2	
$c(SO_2)_{sample}$	Determined SO_2 concentration in the sample (using the BUCHI SO_2 Method)	mg/kg
m_{sample}	Sample weight	g

Reporting:
The result calculation and reporting can be easily done using the App KjelReports which can be downloaded from iTunes, and google playstore for windows phone [5].

4. Conclusion

The Distillation Unit K-355 and KjelFlex K-360 are appropriate instruments for the distillation of SO2 in solid and liquid samples. For more information please view the application notes available on the BUCHI Website as well as the movies on the BUCHI YouTube channel [6].

5. References

[1] European Regulation 2003/89/EC
[2] BUCHI SO_2 white paper
[3] Norm DIN 32645:2008, DIN Deutsches Institut für Normung e.V., Berlin, Beuth Verlag GmbH, 10772 Berlin
[4] AOAC 990.28: Sulfites in Foods, Optimized Monier-Williams Method, First Action 1990, Final Action 1994, (1998)
[5] App KjelReports for result calculation and reporting from itunes, google playstore and for windows phone
[6] BUCHI YouTube channel

Operation Manuals
- Distillation Unit K-355
- KjelFlex K-360
- Mixer B-400