Application Note

090/2012

Distillation Unit K-355

Determination of Total SO_2 in Certified Potato Powder Reference

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SHORT NOTE

Determination of Total SO_2 in Certified Potato Powder Reference

The translation of the classical methods of Total SO_2 determination to modern steam distillation requires adaptions of the reagents releasing SO_2 from varied complex food matrices, and the different mechanisms transporting SO_2 from the distillation tube into the receiving vessel have to be taken into account. In order to replace classical methods of SO_2 determinations in food samples alkaline hydrolysis of the bisulfite adducts and steam distillation of SO_2 is described in the present paper using the typical example of potato powder.

Introduction

Classical methods for the determination of Total SO_2 in food are based on the optimized Monier-Williams Method [1]. In a specific apparatus SO_2 is entrained from the sample by means of nitrogen flow into H_2O_2 solution forming H_2SO_4. The sulphuric acid is titrated with NaOH standard solution and the SO_2 calculated.

The approach chosen for steam distillations using BUCHI distillers consists of three steps:

- Reaction of sample with suitable reagent to release SO_2 from matrix
- Use of steam as transport media to separate SO_2 from sample tube into receiving vessel
- Use of selective redox titration for determination of SO_2

A distillation method for SO_2 determinations in wine and beer, representing weak matrices, is reported in BUCHI Application Notes [2], [3]. In samples containing bisulfite-aldehyde adducts, forming a strong matrix, the SO_2 needs to be released by hydrolysis effectuated by highly concentrated strong acid or a strong base. Strong matrix effects can be handled by means of alkaline hydrolysis with 1 mol/L NaOH as described in the 'Swiss Book of Food Regulation' (SLMB) [4].

Experimental

A sample weight of potato powder m_{sample} = 10 g according to an expected concentration $c(SO_2)$ = 212 mg/kg is used (see Table 1).

Table 1: Optimal weights of potato powder m_{sample} depending on expected Total SO_2 concentrations $c(SO_2)$ assuming a result of 1 mgSO_2 per sample.

$c(SO_2)$ [mg/kg]	m_{sample} [g]
7 - 10	150 - 100
10 - 20	100 - 50
20 - 100	50 - 10
100 - 200	10 - 5
200 - 500	5 - 2
≥ 500	≤ 2

The sample is soaked in 20 mL ethanol 5 %v/v and hydrolyzed with 25 mL NaOH 1 mol/L. The sample mass is transferred into the sample tube and 15 mL of phosphoric acid 85 % is added. The sample is steam distilled into the specially designed BUCHI SO_2 absorption glass in which the separated SO_2 reacts with a defined volume of iodine standard solution. Subsequently the distillate is back-titrated with Na-thiosulfate standard solution using a titrator suitable to carry out redox titrations.

Results

The Total SO_2 content of the certified reference potato powder LGC7111 was determined by means of the described method. The results are given in Table 2 and in Figure 1. The range of standard deviations for the results of samples 1-8 is shown with the mean value M and compared to the result stated in the certificate for the certified reference material LGC7111.

Table 2: Comparison of results of Total SO_2 determinations of LGC7111 obtained by standard methods to $c(SO_2)$ results using the BUCHI SO_2 Method. $W(SO_2)$=weight of SO_2 per sample. Standard deviations are given in brackets and italics for the 20 results of (R) and 8 results of (M).

Sample	m_{sample} [g]	$W(SO_2)$ [mg]	$c(SO_2)$ [mgSO_2/L]
LGC7111 (R)	2		212 *(27)*
1.	10.0807	2.35	233
2.	10.0506	2.42	241
3.	10.0691	2.49	248
4.	10.0628	2.33	231
5.	10.0897	2.45	245
6.	9.9988	2.27	227
7.	10.0904	2.26	224
8.	10.0880	2.36	234
Mean 1-8 (M)			236 *(9)*

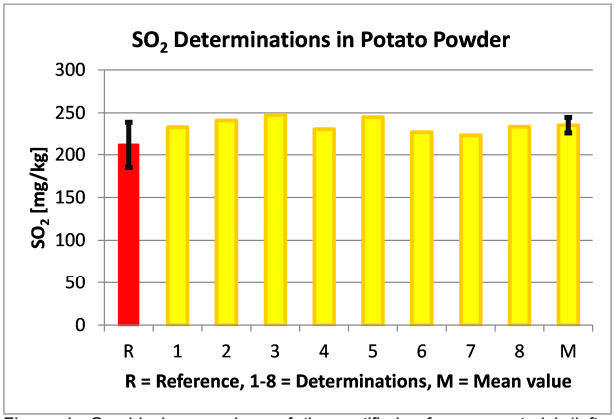

Figure 1: Graphical comparison of the certified reference material (left column in red) to the BUCHI SO2 Method (right column in yellow) for the samples numbered 1 to 8 and the mean value M. Sd given in Table 2.

Conclusion

The new BUCHI SO_2 Method for food can replace classical methods.

References

[1] AOAC Official Method 990.28 Sulfites in Food (1998)
[2] BUCHI Application Note 065/2011,Determination of Total SO_2 in Wine
[3] BUCHI Application Note 066/2011, Determination of Total SO_2 in Beer
[4] Swiss Book of Food Regulations, SLMB

1 Introduction

Classical methods for the determination of Total SO_2 in food are based on the optimized Monier-Williams Method [1]. In a specific apparatus acidified sample (e.g. by HCl) is entrained from the sample by means of nitrogen flow into H_2O_2 solution forming H_2SO_4. The sulphuric acid is titrated with NaOH standard solution and the SO_2 calculated.

The approach chosen for steam distillations using BUCHI distillers consists of four steps:

- Reaction of sample with suitable reagent to release SO_2 from matrix
- Use of steam as transport media to separate SO_2 from sample tube into receiving vessel
- Use of selective redox titration for determination of SO_2

A distillation method for SO_2 determinations in wine and beer, representing weak matrices, is reported in BUCHI Application Notes [2], [3]. In samples consisting of a stronger matrix, binding SO_2 in the form of bisulfite adducts as present in sugars and starch, the SO_2 needs to be released from the matrix by means of hydrolysis effectuated by strong acid or base. The choices of suitable strong acids are limited and phosphoric acid is the mineral acid of choice in steam distillations involving weak matrices. Handling strong matrix effects calls for basic hydrolysis as described in the 'Swiss Book of Food Regulation' (SLMB) [4].

2 Equipment

- Distillation Unit K-355 with SO_2 absorption glass (order number 043070)
- Metrohm Titrino 848 plus
- Pt-Titrode 6.0431.1002
- Bulb pipette 5 mL
- Glass beaker 500 mL

3 Chemicals and Materials

- NaOH, Sigma-Aldrich (30620)
- 1 mol/L NaOH prepared by dissolving 4 g NaOH pellets in 100 mL H_2O
- Ethanol, Brenntag Schweizerhall AG (13194-356)
- 5 % ethanol solution prepared by diluting 50 mL of ethanol to 1 L volume
- pH indicator paper Merck (1.10962.0003)
- Iodine solution 0.05 mol I_2/L, Riedel-de Haën (35090)
- Sodium thiosulfate 0.1 mol/L (Fixanal), Riedel-de Haën (38200)
- Sodium thiosulfate 0.01 mol/L by dilution of 0.1 mol/L thiosulfate
- Ortho-phosphoric acid (85%), Riedel-deHaën (30417)
- Sulfuric acid 0.5 mol/L, Riedel-deHaën (35354)

4 Samples

Certified potato powder reference material containing sulfur dioxide from LGC Standard LGC7111.

5 Procedure

5.1 Principle

The presented method is based on the chemical conversion of the sulfites into volatile sulfur dioxide which is separated from the sample matrix by steam distillation 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.

5.2 Reaction

Preparation

Alkaline hydrolysis of bisulfite adduct

The CH_2-S bond in the adduct is weakened by the two neighboring $\delta+$ partial charges and cleavage of the adducts into aldehyde hydrate and sulphite is eased according to chemical equation (1). The base catalysed hydrolysis is instantaneously fast if 1 mol/L NaOH is added to a HMS (formaldehyde-bisulfite adduct = sodium **h**ydroxy **m**ethyl **s**ulfonate). The cleavage of HMS is shown in equations (1) and (2) representing the typical process of releasing SO_2 from bisulfite adducts found in food. HMS is proposed as a model to judge the effectiveness of releasing SO_2 from strong matrices in food samples [1].

$$H\text{-}O^- + \underset{\text{Adduct}}{H\text{-}O\text{-}\overset{\delta+}{C}H_2\text{-}\overset{\delta+}{S}O_2\text{-}O^-} \rightleftharpoons \underset{\text{Hydrate}}{HO\text{-}CH_2\text{-}OH} + \underset{\text{Sulfite}}{SO_3^{2-}} \quad (1)$$

$$\underset{\text{Hydrate}}{H\text{-}O\text{-}CH_2\text{-}OH} + \underset{\text{Sulfite}}{SO_3^{2-}} \rightleftharpoons \underset{\text{Formaldehyde}}{CH_2O} + H\text{-}O^- + \underset{\text{Bisulfite}}{HSO_3^-} \quad (2)$$

Distillation

Formation of sulfur dioxide

SO_2 can not be distilled out of a basic sample and acidification is needed to shift the chemical equilibrium towards the formation of SO_2 in the distillation step according to the chemical equations (3) and (4). Phosporic acid is perferably used because other strong mineral acids like hydrochloric and sulfuric acid have undesired disadvantages. Hydrochloric acid acts corrosive on rubber and steel parts of the analysis equipment. Sulfuric acid contains small amounts of SO_2 which makes its use inappropriate especially at low SO_2 concentrations. In addition sulfuric acid acts as an oxidizer producing SO_2 in the presence of carbohydrates found almost always in food materials.

$$\underset{\text{Bisulfite}}{HSO_3^-} + \underset{\text{Acid}}{H_3O^+} \rightleftharpoons \underset{\text{Sulfurous acid}}{H_2SO_3} + H_2O \quad (3)$$

$$H_2SO_3 \rightleftharpoons \underset{\text{Sulfur dioxide}}{SO_2} + H_2O \quad (4)$$

Iodometric Titration

Reaction of SO_2 with I_2

In the receiving vessel the distilled SO_2 reacts with the submitted iodine standard solution in a redox-reaction according to equation (5).

$$SO_2 + I_2 + 4\,H_2O \rightleftharpoons 2\,HI + SO_4^{2-} + 2\,H_3O^+ \quad (5)$$

Back-titration of excess I_2 with thiosulfate standard solution

After completion of the distillation the residual iodine is determined by means of a redox-titration using sodium thiosulfate standard solution according to equation (6).

$$I_2 + 2\,S_2O_3^{2-} \rightleftharpoons 2I^- + S_4O_6^{2-} \quad (6)$$

5.3 Optimal Sample Amount

For a successful determination the amount of SO_2 present in the sample must be higher than the limit of quantification (LOQ) for the applied method. Previous studies of steam distillations of sulfite standard solutions have shown an LOQ = 0.85 mgSO_2 per sample [5]. In Table 1 the minimum sample weights m_{sample} needed for SO_2 determinations are correlated with ranges of concentrations c(SO_2). The ranges were established by calculations assuming an SO_2 content of 1 mg in the sample, a value slightly higher and close to the experimental LOQ. If 2 mgSO_2 is supposed to be present in the sample the optimal combination of c(SO_2) with m_{sample} can be obtained by doubling m_{sample}.

Table 1: Optimal weights of potato powder m_{sample} depending on expected Total SO_2 concentrations c(SO_2) assuming a result of 1 mgSO_2 per sample.

c(SO_2) [mg/kg]	m_{sample} [g]
7 - 10	150 - 100
10 - 20	100 - 50
20 - 100	50 - 10
100 - 200	10 - 5
200 - 500	5 - 2
$\geq$ 500	$\leq$ 2

5.4 Distillation

Sample Preparation

In order to be at a safe distance above the limit of quantification 10 g sample was weighed into 100 mL glass beakers and soaked with 20 mL of 5 % ethanol solution. 25 mL of 1 mol/L NaOH solution was added to the samples and the mixtures thoroughly stirred with a glass rod which was carefully rinsed with distilled water after use transferring all adhering sample material back into the beaker. When adding 15 mL of 85 % phosphoric acid a pH of <2 was measured by means of pH paper.

Preparation of Receiver

The SO_2 absorption glass is shown in Figure 1 and consists of a 1st receiver on the left directly connected to the cooler outlet. In the 1st receiver 5 mL of 0.05 mol/L iodine standard solution is added together with 30 mL of distilled water. The 1st receiver is connected to the 2nd receiver containing 30 mL of ethanol. The ethanol absorbs iodine vapors reducing losses by evaporation of iodine during distillation.

Blank

- Preheat the K-355 for 5 minutes
- Transfer 20 mL of 5% ethanol, 25 mL of 1 mol/L NaOH and 15 mL of 85 % H_2PO_4 and 10 mL distilled water into the sample tube and mount the tube to the K-355.
- Use the BÜCHI SO_2 absorption glass. By means of a bulb pipette transfer 5 mL of 0.05 mol/L iodine standard solution into the 1st receiver
- Add 30 mL of water to the 1st receiver vessel and 30 mL of ethanol to the 2nd one. Close absorption glass with the connecting piece and mount it to the K-355.
- Distill for 6:55 minutes applying a steam power of 100%[1].
- Carry out 2-4 reproducible blank determinations.

[1] The distillation time may vary. Use time needed to fill up absorption vessel to the neck.

Table 2: Parameters for the SO_2 distillation of potato powder.

Parameter	Value
Sample amount	10 g
Size of sample tube	500 mL
5 % ethanol	20 mL
1 mol/L NaOH	25 mL
85 % H_2PO_4	15 mL
Distillation time	6:55 min
Steam power	100 %
0.05 mol/L iodine solution in1st receiver	5 mL
Water in 1st receiver	30 mL
Ethanol in 2nd receiver	30 mL

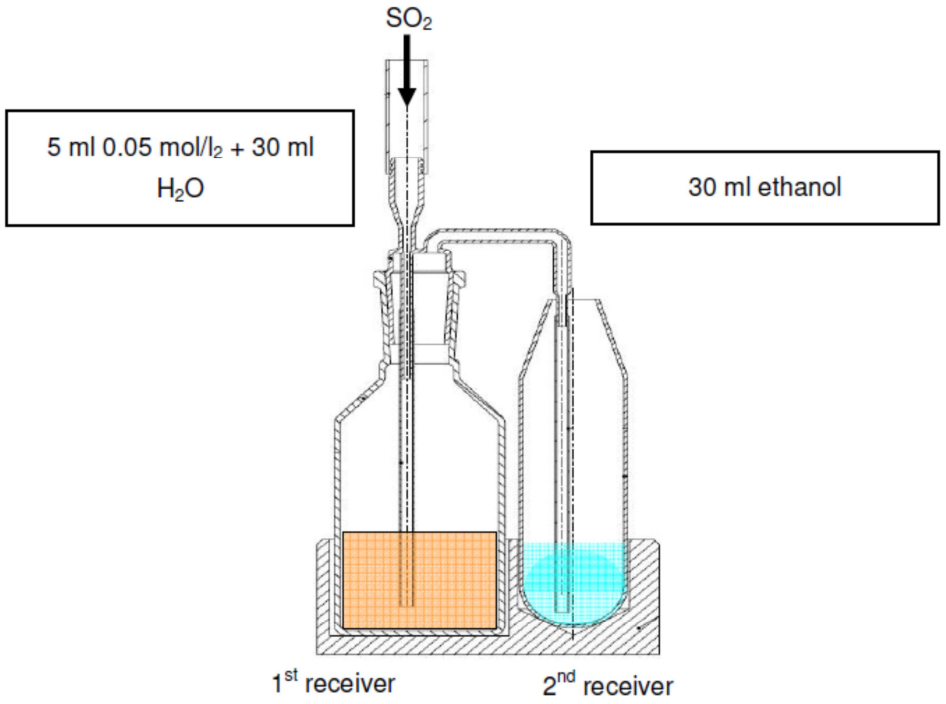

Figure 1: BUCHI absorption glass for collecting SO_2 in aqueous iodine solution

Sample

- Preheat the K-355 for 5 minutes
- Transfer all sample from glass beaker into the sample tube. Rinse carefully with small volumes of distilled water avoiding any loss of sample.
- Use the BÜCHI SO_2 absorption glass. Pipet 5 mL of 0.05 mol/L iodine standard solution into the 1st receiver and 30 mL of ethanol to the 2nd one.
- Add 30 mL of water to the 1st receiver vessel
- Distill for 6:55 minutes applying a steam power of 100%.

5.5 Titration

The titrations were carried out with a titrator capable of recording and evaluating the end-point from the titration curve. The Pt-Titrode was defined as given in the titrator handbook. Start and stop criteria for the titrations were selected for every experiment in accordance to the expected titrant consumptions. To be sure that the correct end point was not missed, 3 end points were allowed. After every titration the titration

curve was checked and the end points evaluated. The positions of the selected end points were chosen in a reproducible manner for the blanks and the samples. A stirrer was used to mix titrant and sample quickly for appropriate measurement of the redox potentials.

Table 3: Titration parameters for the SO_2 determination for blank and potato powder sample.

Parameter	Value
Type	Redox back-titration of I_2 by $Na_2S_2O_3$
Start volume	30 mL[2]
Stop volume	53 mL
Stop EP	3
Nominal concentration $c(I_2)$	0.05 mol/L
Titration sample	SO_2 in distillate reacted with 5 mL I_2 solution
Titrant c^T (see Table 4)	0.01 mol/L $Na_2S_2O_3$

Blank and Sample

Carry out two to four reproducible blank and sample distillations and:

- Combine the two iodine solutions of the 1st and 2nd receiver in a 400 mL glass beaker.
- Carefully rinse the connecting glass piece and the emptied receiver vessels with distilled water.
- Acidify combined iodine solution with 2 mL of 0.5 mol/L H_2SO_4.
- Use a freshly prepared sodium thiosulfate standard solution.
- Titrate with 0.01 mol/L sodium thiosulfate standard solution.
- Evaluate end point as given in the general remarks of chapter 5.5.

6 Calculations

Based on equation (7) the absolute amount of SO_2 in the sample is calculated and equation (8) produces the SO_2 concentration of the sample.

$$W(SO_2)_{sample} = \frac{(V^T_{blank} - V^T_{sample}) \bullet c^T \bullet M(SO_2)}{z} \quad (7)$$

$$c(SO_2)_{sample} = \frac{W(SO_2)_{sample} \bullet 1000}{m_{sample}} \quad (8)$$

Table 4: Explanation of symbols used in equations, tables and figures

Legend	Text	Unit
$W(SO_2)_{sample}$	Determined weight of SO_2	$mgSO_2$
V^T_{blank}	Consumption of thiosulfate solution for blank	mL
V^T_{sample}	Consumption of thiosulfate solution for sample	mL
c^T	Concentration of 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 sample (by BUCHI SO_2 Method)	$mgSO_2/kg$
$W(SO_2)$	Weight of SO_2 in sample	mg
m_{sample}	Sample weight	g

[2] Start and stop volumes may vary according to expected titrant consumptions

BUCHI offers an Excel template for the calculations for the redox back-titration of iodine with thiosulfate[3].

7 Results

The nominal concentration of the iodine standard solution $c(I_2)$ was 0.05 mol/L. In the back-titration the concentration $c(I_2)$ and the volume of iodine standard solution $V(I_2)$ are cancelled out and do not appear in the equations. The condition for back-titration however is that the $c^T * V^T_{sample} < c(I_2) * V(I_2)$ (see Table 4).

The results of the SO_2 determinations are based on equations (7) and (8) and the weight of SO_2 in the samples 1 to 8 $W(SO_2)$ and the concentration of SO_2 $c(SO_2)$ were calculated as shown in Table 5.

The expected result reported by the supplier of the certified potato powder reference material, LGC, is 212 (27) mgSO_2/kg with 2 g of sample determined at 20 laboratories. The results given in Table 5 and the expected result from the Statement of measurement by LGC are graphically shown in Figure 2.

Table 5: Determination of sulfur dioxide by backtitration of 0.05 mol/l iodine solution with 0.01 mol/l sodiumthiosulfate standard solution.

No.	m_{sample} [g]	$V(Na_2S_2O_3)_{blank}$ [mL]	$V(Na_2S_2O_3)_{sample}$ [mL]	$W(SO_2)$ [mg]	$c(SO_2)$ [mg/kg]
Blank 1		47.661			
Blank 2		47.665			
Blank 3		47.510			
Blank 4		47.453			
Blank 5		47.698			
Mean		47.597			
sd		0.108			
rsd		0.23 %			
Sample 1	10.0807		40.255	2.35	233.3
Sample 2	10.0506		40.030	2.42	241.2
Sample 3	10.0691		39.815	2.49	247.6
Sample 4	10.0628		40.338	2.33	231.1
Sample 5	10.0897		30.942	2.45	244.9
Sample 6	9.9988		40.499	2.27	227.4
Sample 7	10.0904		40.548	2.26	223.8
Sample 8	10.0880		40.236	2.36	233.7
Mean					235.6
sd					9.1
rsd					3.8%

[3] Available on request from your local BUCHI representative or BUCHI Labortechnik AG, 9230 Flawil, Switzerland.

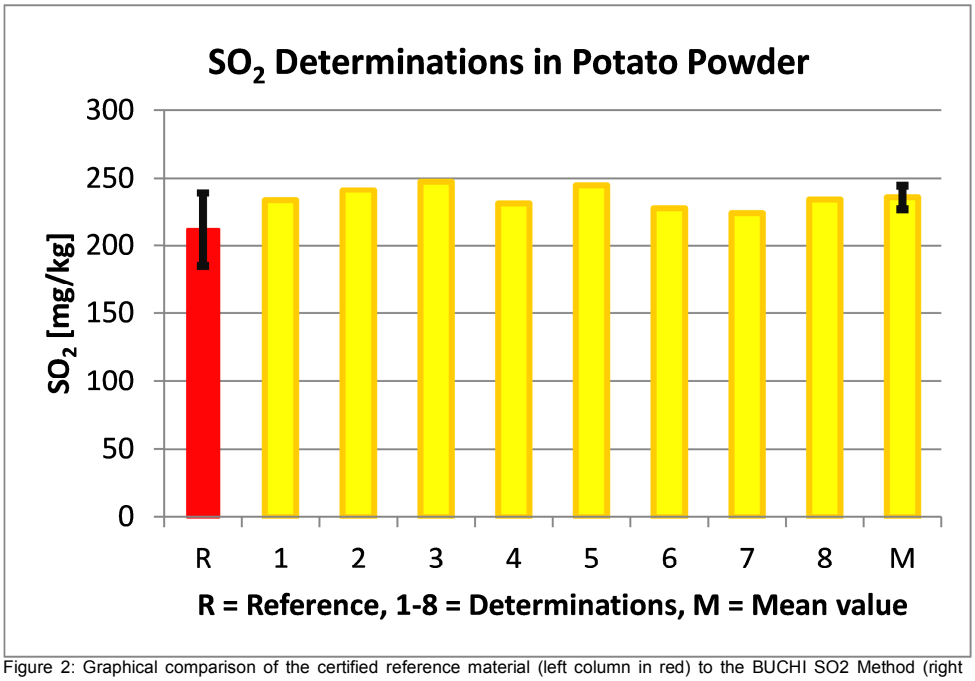

Figure 2: Graphical comparison of the certified reference material (left column in red) to the BUCHI SO2 Method (right column in yellow) for the samples numbered 1 to 8 and the mean value M. Sd given in Table 5.

8 Comparison to Standard Method

The U.S. Food and Drug Administration (FDA) established that the *Optimized Monier-Williams* method (AOAC 990.28) is to be used as a standard method for official samples [1].

Table 6: Comparison to the standard method AOAC 990.28

Criteria	This application note	Standard method	Reason, influence
Release of SO_2	Hydrolysis of bisulfite adducts by means of 1 mol/L NaOH solution and acidification by H_3PO_4	1N HCl	Avoid corrosion by HCl, improved separation of SO_2 from matrix
Carrier gas	Steam	Nitrogen stream	No influence
Titration	Redox	Acid-base	Avoid interference with acids

9 Conclusion

The results of the SO_2 determinations by means of the presented new BUCHI SO_2 Method for food are well in line with the expected values found for the certified potato powder reference material. The BUCHI steam distillation has proven to be a valid method to replace the inconvenient classical distillation using nitrogen flow and custom made glassware.

10 References

[1] AOAC Official Method 990.28 Sulfites in Food (1998)

[2] BUCHI Application Note 065/2011,Determination of Total SO_2 in Wine

[3] BUCHI Application Note 066/2011, Determination of Total SO_2 in Beer

[4] Schweizerisches Lebensmittelbuch SLMB (Swiss Book of Food Regulations), 30A Wein aus Trauben, Untersuchungsmethode 11.3

[5] BUCHI Application Note No. K-355_011 V.1.1 (2008), Limit of Quantification and Recovery Rates

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