

WHITEPAPER

Increasing efficiency in food analysis: Alternative methods for SO₂ determination

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CONTENT

WHITEPAPER BY CG	2
HEALTH IS WEALTH	2
TIME IS MONEY	3
UPGRADING THE REFERENCE METHOD	4
SO ₂ DETERMINATION IN HIGH SPEED	5
NORMS AND REGULATIONS	6
MORE DETAILS ON THE ANALYSIS	8
OVERVIEW OF METHODS	10
SUMMARY	11
REFERENCES	11

WHITEPAPER BY CG

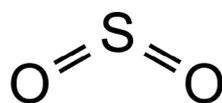
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HEALTH IS WEALTH

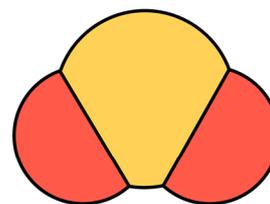
A healthy, but also sustainable diet has become the new top goal for most of society during the last couple of years, forcing the food industry to rethink and restructure.

Not only have modern consumers become more aware of nutritional information and ingredients of the food they consume. Regulations and norms by official institutions and authorities are also becoming more and more. This in turn presents food manufacturers with new challenges: Due to stricter regulations, products have to be analysed more detailed than ever before. Now, on the one hand there are standard values such as protein or fat content that need to be determined. But in addition to that, products must also be analysed for parameters such as preservatives and antioxidants.

In this white paper we will deal with the preservative sulphur dioxide (SO₂) and the determination of this substance in food. This is because SO₂ is used - usually in gaseous form or dissolved in water - in many everyday foods such as dried fruits, wines, potato dishes or seafood. SO₂ is so popular with manufacturers because it extends shelf life by inhibiting the growth of fungal and bacterial cultures. SO₂ also slows down the oxidation process when the product comes into contact with oxygen, which in turn delays the degradation of colourings, vitamins and flavours, so the food stays fresh longer.



Schwefeldioxid



Schwefeldioxid

Figure 1: Chemical representation of sulphur dioxide

But in addition to these classical antimicrobial properties, SO₂ also has a toxic effect, which is why there is a labelling obligation in the EU from a concentration of 10 mg/kg.

HIGHLIGHTS

„The optimised Monier-Williams method is established as the reference method for determining the SO₂ content in food.“

„SO₂ also has a toxic effect, which is why there is a labelling obligation in the EU from a concentration of 10 mg/kg.“

This means a balancing act for the food manufacturers, because on the one hand compliance with the prescribed limit values is necessary. On the other hand though, the SO₂ content of the product must be sufficient for the preservative to achieve its full effect. An analysis that is as accurate as possible and efficient at the same time is therefore of great importance, both for manufacturers and consumers.

TIME IS MONEY

Thus, a suitable reference method for determining the SO₂ concentration in food is of great importance. The optimised Monier-Williams method (oMW) is defined as this reference method in accordance with the Association of Official Analytical Collaboration (AOAC) 990.283 and DIN EN 1988-14 as well as §64 of the German Food and Feed Code (LFGB5).

Briefly outlined, the principle of the method is based on a boiling and distillation process with subsequent quantitative determination of the sulphur dioxide content. It should be noted that the recovery rate of SO₂ even with the optimised Monier-Williams method is >80 %. This means that fluctuating or deviating analytical results are not unusual and are also taken into account in the official norms and regulations. However, since this method is used by all laboratories and all determined values refer to this one method, it can be neglected that the recovery rate is not 100 %.

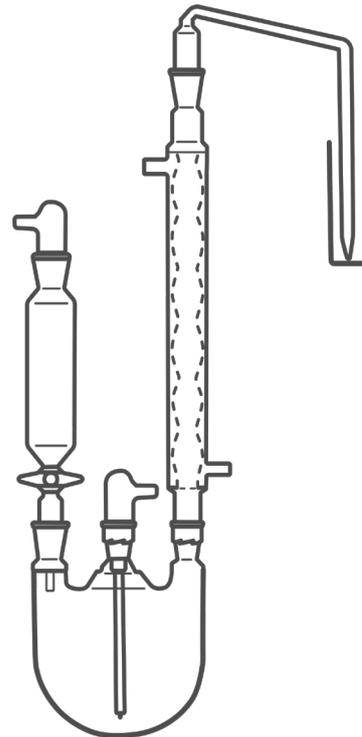


Figure 2: Apparatus for Monier-Williams method

HIGHLIGHTS

„Time, space and work effort required for the optimised Monier-Williams method is very high.“

„There is a great interest in alternative methods that produce equivalent results more efficiently.“

The time and effort required for the oMW method, however, is very high. The analysis takes over two hours per measurement, as all the work steps have to be carried out manually. In addition, only one sample can be measured per apparatus.

This high effort is particularly problematic for laboratories with a high sample throughput. That is why there is great interest in alternative methods that produce equivalent results more efficiently.

But as much as the market strives for it, an analysis cannot always be easily modified or automated. Adapting a method or even creating a completely new method is a challenge in itself, as it requires intensive research and, above all, validation.

UPGRADING THE REFERENCE METHOD

The automation of a method is already a great help for laboratories, as it usually makes the work not only more efficient, but also safer for the laboratory staff.

The TURBOTHERM infrared digestion unit, for example, can be specially modified for SO₂ determination, making the analytical process much more automated. In addition to the heating coil, the modified apparatus consists of digestion tubes with nitrogen inlet and a neck for dropping funnels, spherical coolers and absorption tubes. In contrast to the oMW method, no support rods or holding clamps are used in this apparatus, which greatly reduces the space required in the laboratory. In addition, there are significantly fewer ground glass joints, which reduces the method's error rate.



Figure 3: Modified TURBOTHERM apparatus

From an analytical point of view, this method is strongly derived from the optimised Monier-Williams method and is therefore quite similar to it in terms of the analytical process. First, the digestion tubes and the absorption vessels are rinsed with water and certain solutions. Afterwards, the entire system is flushed with nitrogen for 15 minutes.

HIGHLIGHTS

„With VAPODEST 550, the SO₂ content of a sample can be determined in less than 10 minutes.“

Subsequently, the samples are kept in boiling for 1:45 hours, after which the absorption vessels are removed and the samples are transferred to erlenmeyer flasks. With the TURBOTHERM method, the titration is also carried out by a titrator. The calculation of the mass fraction of SO₂ is also performed analogously to the reference method.

In contrast to the oMW, the modified TURBOTHERM apparatus offers the great advantage that four samples can be determined simultaneously in one apparatus, whereas only one sample can be analysed at a time in an oMW apparatus. The space saved in the laboratory by using the TURBOTHERM is therefore enormous. The fact that the work steps are more automated saves the laboratory staff not only space, but also valuable time.

SO₂ DETERMINATION IN HIGH SPEED

While TURBOTHERM already offers clear advantages compared to the optimised Monier-Williams method in terms of space savings and degree of automation, VAPODEST 550 steam distillation unit goes one step further: with that system, SO₂ analysis can be carried out fully automated and in less than 10 minutes per sample.

With VAPODEST 550, the SO₂ content is determined by fully automated steam distillation and subsequent titration. For this purpose, addition of chemicals and receiver are already integrated in the system. Extraktion of sample and receiver as well as the titrator are also integrated features.

Before each use, the apparatus must be pre-heated by a blank distillation and the blank value of the receiver solution must be determined. The addition of water during distillation increases the pH value of the receiver solution. The pH value is then set as end point for titration of the samples.

The sample is placed in the digestion tube and distilled for six minutes. This is followed by automatic titration with natrium hydroxide solution (0.01 mol/l). The SO₂ content is calculated in the same way as in the reference method, but the blank value is not deducted.



Abbildung 4: VAPODEST 550 im Labor

„The higher the recovery rate of an analytical method, the better the analytical quality. “

NORMS AND REGULATIONS

Not only the food industry has to adhere to strict standards and regulations. Modern analytics must also meet the high demands of national and international norms and guidelines, such as those established by DIN, ISO or AOAC.

And of course, adapted analytical methods must also meet these requirements. Therefore, the C. Gerhardt methods with VAPODEST and TURBOTHERM have to be verified for their recovery rate before they can actually be used in laboratories.

The recovery rate serves as an indicator for the quality of analytical methods and is usually stated in percentage. It is determined by repeating the method many times with different sample matrices and quantities. The higher the recovery rate, the better the analytical quality of the method.

To determine the recovery rate of the adapted analytical methods for SO₂ determination with TURBOTHERM and VAPODEST, mainly commercial food samples such as meat, wine or mashed potatoes were determined. In addition, three quality control materials by FAPAS - i.e. tested and standardised sample material - were analysed.

The sample preparation depended, as elsewhere in analytics, on the respective consistency and composition of the sample matrix. In this case, the samples were crushed and homogenised if necessary. The samples were transferred into the digestion tube either via weighing paper or a pipette. In the case of VAPODEST 550, the samples were partly slurried in distilled water before analysis in order to prevent the formation of clumps during the analysis.

However, before „normal“ samples were analysed, a six-fold determination of a hydroxymethanesulphonate solution (HMS solution) containing 100 mg SO₂ per kilogram was first carried out using all three methods. Since the SO₂ content of this solution is already specified, it is considered the standard for the analytical results.

In this case, three working ranges each with the absolute values 1 g, 5 g and 10 g were selected and then determined:

HIGHLIGHTS

Recovery rates:

oMW	80,0 %
TURBOTHERM	88,5 %
VAPODEST	94,4 %

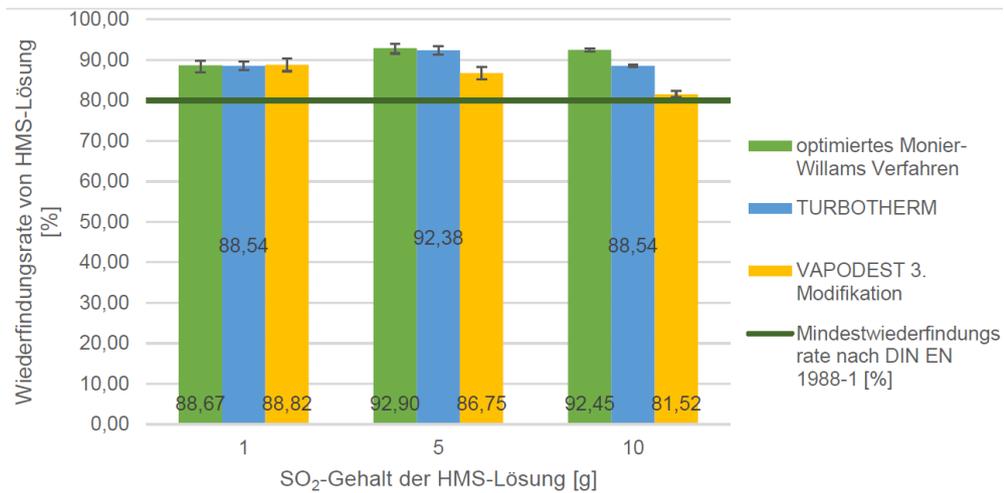


Figure 5: Comparison of the recovery rates in % of the standard HMS and with different SO₂ levels of the different methods.

The subsequently determined recovery rate for TURBOTHERM was 88.5 % ± 1.1 %. This rate is thus above the limit value of 80 % specified in AOAC 990.28 and DIN EN 1988-1 and is therefore more than acceptable.

With VAPODEST, too, the analysis procedure was first carried out with a solution, in this case a sodium disulphite solution, containing 100 ppm SO₂. A recovery rate of 94.4 % ± 1.7 % was achieved. The rate is therefore again above the limit value according to AOAC 990.28 and DIN EN 1988-1.

However, if the determination of the HMS solution was carried out during the analysis procedure with VAPODEST, as with TURBOTHERM, the recovery rate was only 49.5 %. The reason for this low recovery are the different analysis conditions to the reference method according to Monier-Williams. While the TURBOTHERM method is analytically very similar to the optimised Monier-Williams method, the VAPODEST method differs significantly.

The decisive differences here are the short analysis time and the use of phosphoric acid, which has a higher pKs value than the hydrochloric acid used in Monier-Williams and TURBOTHERM. These differences mean that HMS is not ideal as a standard for VAPODEST because the acid strength of the phosphoric acid is not sufficient for the analysis.

And although sodium disulphite is normally not recommended as a standard as it is volatile, the results obtained with VAPODEST show that a very good recovery can be obtained with a freshly prepared solution. Therefore, sodium disulphite is recommended as the standard for VAPODEST.

HIGHLIGHTS

„It is even likely that the contents determined with TURBOTHERM and VAPODEST are closer to the true value than the contents determined with the optimised Monier-Williams method.“

MORE DETAILS ON THE ANALYSIS

For the comparison of the three methods, the different samples were analysed with each of the methods multiple times. With the optimised Monier-Williams method, with the TURBOTHERM method and for VAPODEST with the alkalimetric method. If the content determined with VAPODEST alkalimetric method was unusual, the sample was additionally determined iodometrically.

The analytical results seen below in table 1 were formed by the mean value of all the determinations. For the methods with VAPODEST and TURBOTHERM, the percentage deviation of the results from the optimised Monier-Williams method was then calculated. This deviation is also called bias.

Table 1: Comparison of the TURBOTHERM and VAPODEST methods with the optimised Monier-Williams method as reference method. In each case, indication of the percentage deviation of the result - bias.

Sample	Reference method	TURBOTHERM		VAPODEST alkalimetric		VAPODEST iodometric	
	Content [mg/kg]	Content [mg/kg]	Bias	Content [mg/kg]	Bias	Content [mg/kg]	Bias
Prawns	17,7	19,6	9,6 %	19,2	7,8 %	-	-
Mashed potatoes	25,5	27,6	7,5 %	86,2	70,5 %	27,5	7,3 %
Wine (ring test sample)	100,8	101,7	0,8 %	136,6	26,2 %	99,8	1,0 %
Wine (CG sample)	150,3	153,3	2,0 %	172,8	13,0 %	154,8	2,9 %
Meat	452,0	463,8	2,5 %	477,1	5,3 %	-	-
Horseradish	708,1	716,8	1,2 %	916,9	22,8 %	713,2	0,7 %
Potato dumpling mix	1441,4	1499,9	3,9 %	1503,0	4,1 %	-	-
Dried apricots	2307,0	2285,5	-0,9 %	2152,3	-7,2 %	-	-

Table 1 shows that the bias between TURBOTHERM and the optimised Monier-Williams method is between -0.9 % and 9.6 %. It is interesting that the higher deviations in results are related to the samples with the lowest sulphur dioxide contents, namely the shrimps and the mashed potatoes.

In the alkalimetric method with VAPODEST, the bias is clearly above 10 % in four samples. All these samples contain other volatile components, such as volatile acids, which are also determined after distillation, resulting in overdetermination. It can therefore be concluded that the VAPODEST method is not suitable for samples that contain volatile components.

HIGHLIGHTS

„In conclusion, the **TURBOTHERM** provides equivalent results to the reference method. The **TURBOTHERM** results even reflect the SO_2 content somewhat more accurately.“

For the other samples, the bias between VAPODEST and the optimised Monier-Williams method is between -7.2 % and 7.8 %. The samples with unusual results while analysed with the alkalimetric titration were also analysed iodometrically. With the iodometric analysis, the bias was between 0.7 % and 7.3 % - even better than with TURBOTHERM, since the other volatile components of a sample are not measured with the iodometric method.

In general, the contents determined with TURBOTHERM and VAPODEST are higher than those of the reference method. However, this is not a bad sign. On the contrary: it is even likely that the contents determined with TURBOTHERM and VAPODEST are closer to the true value than the contents determined with the optimised Monier-Williams method. This is because although the optimised Monier-Williams method is the reference method, the recovery rate of the method is >80 %.

In order to determine the accuracy of the results obtained with VAPODEST and TURBOTHERM, the z-scores of the FAPAS reference material, i.e. the three quality control samples, were determined. The samples were meat, wine and dried apricots.

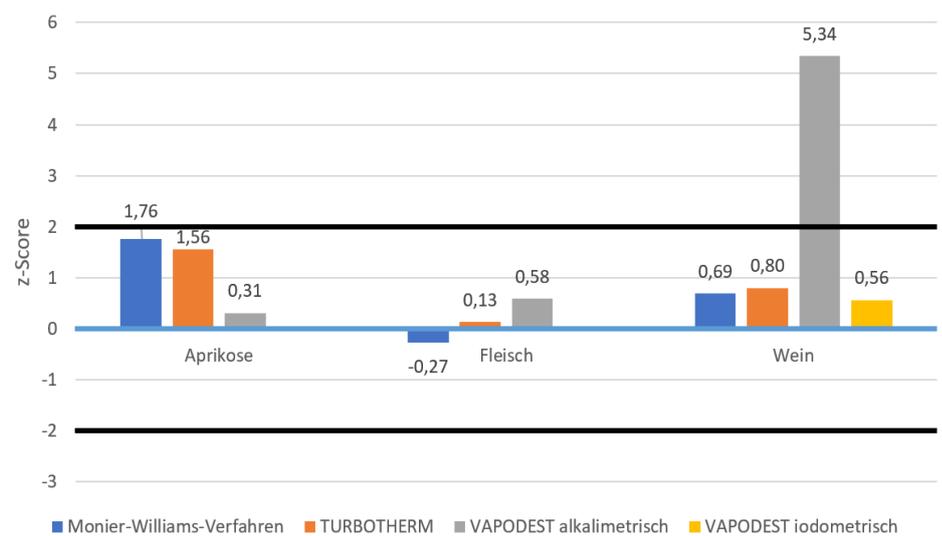


Figure 6: z-score of the determined SO_2 contents in FAPAS samples with the different methods.

The z-score is used to standardise the measurement deviation by nominal value and standard deviation. With a z-score between -2 and +2, the value lies within the 95 % scatter range and is thus acceptable.

The z-score for the alkalimetric determination of wine with VAPODEST is 5.34, which is clearly above the limit value. This indicates that the result is incorrect and that the VAPODEST method is not suitable for this sample.

All other z-scores are within the tolerance range and can be accepted as correct. The various methods for SO_2 determination, i.e. both the TURBOTHERM method and the alkalimetric VAPODEST method, are suitable for these samples.

HIGHLIGHTS

„Since the VAPODEST method is analytically very different from the reference and the TURBOTHERM method, samples with other volatile acids may lead to false results.“

In summary, it can be said that TURBOTHERM provides equivalent results to the reference method, which even reflect the SO₂ content somewhat more accurately. Since the method is strongly oriented towards the optimised Monier-Williams method, this was to be expected.

VAPODEST enables a very rapid and automated determination of sulphur dioxide through steam distillation. However, since the analytical method differs greatly from the reference method, the appropriate method must be selected in advance depending on the sample, since samples with other volatile acids can lead to incorrect results.

OVERVIEW OF METHODS

The three methods can therefore all be used in the laboratory, but they differ from each other in various ways.

Table 2: Comparing the methods

Method	Time	Number of samples	State of automation	Recovery rate	Sample type
Monier-Williams	2 h	1	manual	80 %	all
TURBOTHERM	2 h	4	partly automated	88.5 %	all
VAPODEST	6 min	1	fully automated	94.4 % / 49.5 %	limited

The biggest difference is the degree of automation of the equipment. While the optimised Monier-Williams method has to be carried out completely manually, the process with the TURBOTHERM apparatus involves far fewer manual steps, as the boiling process is completely controlled by the apparatus. Not to mention the fact that the TURBOTHERM apparatus is much easier and safer to handle, both during set-up and operation.

In addition, a TURBOTHERM, in which four samples can be analysed simultaneously, takes up just as much space as the apparatus for the optimised Monier-Williams method, in which, however, only one sample can be analysed at a time.

With VAPODEST, the workflow is fully automated, as in addition to the boiling process, the system also controls the additives and titration. When using a VAPODEST with an automatic sample changer (VAPODEST 550 C), even the sample transfer is automated. The space requirement is also lower with VAPODEST, as the system is considerably more compact than the apparatus of the reference method. When using the VAPODEST 550 C with autosampler, the space requirement is naturally greater.

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The automation of the analytical process also makes it safer for laboratory staff to work with, as contact with the chemicals used in the analysis is avoided. Another advantage of the TURBOTHERM and VAPODEST methods.

In addition, the automation of the reference method saves time for the laboratory staff. With TURBOTHERM, this time saving is due to the fact that four samples can be analysed simultaneously in the apparatus, which results in a significant saving of space.

In the case of VAPODEST, the time saving is again due to the different analytical conditions and is significantly greater with a reduction from 120 to less than 10 minutes.

However, the VAPODEST method also entails losses, as the analysis of samples with volatile components results in overdetermination and is consequently not suitable for this type of sample. While all sample types can be analysed with the optimised Monier-Williams and TURBOTHERM methods, the sample spectrum is more limited with VAPODEST.

SUMMARY

In conclusion, the VAPODEST method for SO₂ determination can only be used as an alternative method to oMW for sample matrices without volatile acids. However, if such non-volatile samples are involved, the recovery rate is reliable and the handling in everyday laboratory work is clearly more efficient and safer for the operator than the reference method.

The TURBOTHERM method for SO₂ determination, on the other hand, can be used as an alternative method to the oMW for all sample matrices. Due to its analytical similarity to the reference method, it offers a reliable recovery rate and also saves the operator a lot of space in the laboratory.