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SULPHUR DIOXIDE: COMPARATIVE STUDY OF THREE ANALYTICAL METHODS AND DETERMINATION IN MALAYSIAN FOODS

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BY

NIK SHABNAM BINTI NIK MOHD. SALLEH

Thesis Submitted in Fulfilment of the Requirements for the Degree of Master of Science in the Faculty of Food Science and Biotechnology Universiti Putra Malaysia.

June 1998

Dedicated to my husband, Ahmad Faisal Zakaria

children, Sarah and Sariha

parents, Allahyarham Nik Mohd. Salleh Nik Mat
Nik Latifah Nik Jaafar

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The study was conducted in four phases. In the first phase, three methods of analysis were studied on eight different types of foods. The methods were (i) the Shipton's modification of the Monier-Williams' method or the Shipton method, (ii) the modified Rankine method, and (iii) the Iodine distillation method. The eight types of foods were meehoon, orange cordial, mashed potato (granule), pickled nutmeg, strawberry jam, mayonnaise, orange juice and wine. Comparative studies showed that the Iodine distillation method gave the highest mean values followed by the Shipton and modified Rankine methods, and this was true for seven out of the eight types of food studied. Recovery studies showed that the Shipton method was reliable for foods with sulphur dioxide content of more than 50 ppm, namely meehoon, cordial, mashed potato(granule) and pickled nutmeg.

The second phase focussed on the study of methods for foods with less than 50 ppm, that is strawberry jam, mayonnaise, orange juice and wine. The methods were (i) the Shipton method, and (ii) the Wedzicha method. Comparative studies showed that results obtained by the Shipton method were higher than those obtained by the Wedzicha method, and this was true for all the foods studied. From the recovery studies, it was found that the Wedzicha method was the method of choice for foods with less than 50 ppm of sulphur dioxide although it is also reliable for foods which contain more than 50 ppm sulphur dioxide.

The correlation between the Shipton and Wedzicha methods were studied in the third phase of the study. It was observed that the methods showed good correlation for foods with sulphur dioxide content of more than 200 ppm, moderate correlation for food with sulphur dioxide content of between 50 - 200 ppm and bad correlation for food with sulphur content of less than 50 ppm.

The prevalence of sulphur dioxide in eighty-six types of foods were studied in the last phase. It was found that 30.23 % of the foods contravene the Food Regulations 1985 in the sulphur dioxide content. The estimate of the Daily Dietary Intake (DDI) was calculated and it was much lower than the Acceptable Daily Intake (ADI) for sulphur dioxide.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi syarat keperluan untuk Ijazah Sarjana.

SULFUR DIOKSIDA :
KAJIAN PERBANDINGAN TIGA KAEDAH ANALISIS DAN PENENTUAN DALAM MAKANAN DI MALAYSIA

oleh

NIK SHABNAM BT. NIK MOHD. SALLEH

Jun 1998

Pengerusi : Dr. Sharifah Kharidah Syed Muhammad

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Kajian ini telah dilaksanakan di dalam empat fasa. Di dalam fasa pertama, tiga kaedah analisis telah dikaji keatas lapan jenis makanan. Kaedah-kaedah tersebut ialah (i) kaedah Monier-Williams' yang telah diubahsuai oleh Shipton atau kaedah Shipton, (ii) kaedah Rankine yang telah diubahsuai, dan (iii) kaedah penyulingan iodin. Lapan jenis makanan yang dikaji ialah meehoon, kordial oren, ubi kentang lecek (serbuk), buah pala jeruk, jem strawberi, mayonis, jus oren dan wain. Kajian perbandingan menunjukkan bahawa kaedah penyulingan iodin memberikan nilai min yang paling tinggi diikuti dengan kaedah Shipton dan kaedah Rankine yang telah diubahsuai, dan ini adalah benar bagi tujuh dari lapan jenis makanan yang dikaji. Kajian "recovery" menunjukkan bahawa kaedah Shipton adalah kaedah yang boleh dipakai untuk makanan yang mempunyai kandungan sulfur dioksida melebihi 50 bsj, iaitu meehoon, kordial oren, buah pala jeruk dan ubi kentang lecek (serbuk).

Fasa kedua menumpukan perhatian kepada kaedah-kaedah untuk makanan yang mempunyai kandungan sulfur dioksida kurang daripada 50 bsj, iaitu jem strawberi, mayonis, jus oren dan wain. Kaedah-kaedah tersebut ialah (i) kaedah Shipton, dan (ii) kaedah Wedzicha. Kajian perbandingan menunjukkan bahawa keputusan yang diperolehi dari kaedah Shipton adalah lebih tinggi dari kaedah Wedzicha, dan ini adalah benar bagi semua jenis makanan yang dikaji. Daripada kajian "recovery", adalah didapati bahawa kaedah Wedzicha adalah kaedah yang boleh dipakai untuk makanan yang mempunyai kandungan sulfur dioksida kurang daripada 50 bsj, walaupun ia boleh juga diterima bagi makanan yang mengandungi lebih dari 50 bsj sulfur dioksida.

Korrelasi di antara kaedah-kaedah Shipton dan Wedzicha telah dikaji di fasa ketiga kajian ini. Adalah didapati bahawa kedua-dua kaedah menunjukkan korrelasi yang baik untuk makanan yang mempunyai kandungan sulfur dioksida melebihi 200 bsj, korrelasi sederhana untuk makanan yang mempunyai kandungan sulfur dioksida di antara 50- 200 ppm dan korrelasi yang lemah bagi makanan yang mempunyai sulfur dioksida kurang daripada 50 bsj.

Kehadiran sulfur dioksida di dalam lapan-puluh enam jenis makanan telah dikaji di fasa akhir. Sebanyak 30.23 % daripada makanan tersebut didapati melanggar Peraturan-Peraturan Makanan 1985 dalam kandungan sulfur dioksida. Anggaran pengambilan diet harian sulfur dioksida telah dikira dan didapati lebih rendah daripada pengambilan harian yang boleh diterima.

CHAPTER I

GENERAL INTRODUCTION

Sulphur dioxide is the most commonly used food preservative. It belongs to the group of food additives known as sulphiting agents which can be defined as ionic species that form sulphur dioxide. Sulphur dioxide is present in foods as a result of the addition of salts of sulphites, bisulphites or metabisulphites.

Sulphur dioxide is permitted in a broad range of foods and beverages including pickled fruits, dried fruits, soft drinks, fruit juices, jelly and sauces. Sulphur dioxide is essential in the preservation of these foods because it increases storage life, preserves colour and flavour and aids in the retention of ascorbic acid and carotene. Maximum permitted levels of sulphur dioxide in foods are stipulated in the Malaysian Food Regulations 1985. The maxima stated in the regulations relate to the total amount present calculated as sulphur dioxide weight by weight. Where a limit is not specified for sulphur dioxide in the regulations, it is not permitted to be added to that food.

Although sulphur dioxide has been recognised as a safe food additive, its safety as a food ingredient needs to be studied in the local context. Whether or not a particular dietary component or food ingredient poses a hazard to human health depends on a combination of factors which include:

(i) the concentration of the food component in foods;

(ii) the amount of the foods consumed;

(iii) individual susceptibility to the substance; and

(iv) any interactions between the substance and other dietary components that could modify its toxicity.

Thus, a particular food ingredient will only become hazardous if it can exert its harmful effect under the circumstances of exposure to it.

The concentration of the sulphur dioxide in foods is regulated by the food legislations to ensure that the public is protected against health hazards and fraud in the preparation, sale and use of food. The Malaysian Food Act 1983 and the Food Regulations 1985 were adopted from the food laws of several developed countries. This is acceptable as international differences in food legislations will form a significant barrier to trade between countries. However, the concentration of sulphur dioxide recommended may be suitable in those developed countries from where the regulations were adopted. It has not taken into consideration factors such as socio-economic status, climate, food consumption habits and types of foods consumed. The records of the monitoring activity on the use of sulphur dioxide in foods by the

Ministry of Health, Malaysia have shown that the contravention in the use of sulphur dioxide is most common in foods such as pickled fruits and noodles. The contravening levels detected could be the actual concentration of sulphur dioxide in those foods or the concentrations which were underestimated or overestimated depending on the method of analysis used by the Department of Chemistry, Malaysia. For foods that do not have standard methods for analysis, an evaluation of the methods that are available in the literature for application to those foods should be performed. The method of sulphur dioxide determination involves the liberation and detection of the liberated sulphur dioxide. Comparative studies that have been carried out on the liberation and detection procedures are few and are not thorough in that they only consider a small number of procedures or food samples. Thus, the first aim of this study is to evaluate analytical methods for the determination of sulphur dioxide in local foods. The selected method or methods is or are then used to determine the concentration or prevalence of sulphur dioxide in our foods. This is the second aim of this thesis and the data obtained would subsequently assist in the estimation of the daily dietary intake of sulphur dioxide for Malaysians.

Limiting the concentration of a food component by food legislation only partly controls the hazard that might be associated with it. Generally, for individuals who consume much higher than the average amounts of a particular food, such measures would only provide limited protection. Sulphur dioxide has not been known to affect people at the levels permitted to be added to food. However, it can cause allergic

responses in some people such as asthmatics even at or below permitted levels. Results of studies conducted in the United States showed that not all asthmatics will show a reaction after ingestion of sulphited foods at permitted levels. The likelihood of a reaction however, is dependent not only on the level but also on the nature of the food, its acidity and the sensitivity of the consumer.

The eating habits of people from different countries differ, that is, some have the tendency of eating certain foods more than others. As such, the upper limit for the concentration of sulphur dioxide can only be specified for particular foods when the amounts of the particular foods consumed by the individuals are known. Some of the foods which contain sulphur dioxide and which are common in the Malaysian diet are noodles, pickled fruits and vegetables, dried fruits, jams, fruit juices, cordials and carbonated drinks. With these in mind, the third aim of this thesis is therefore, as mentioned earlier to estimate the daily dietary intake of sulphur dioxide for Malaysians. The findings would be useful in:

(i) ascertaining whether the consumers are at risk or not by eating the food containing sulphur dioxide by comparing the Daily Dietary Intake (DDI) with the Acceptable Daily Intake (ADI),

(ii) determining whether there is a relationship between any observed health effects and the intake of sulphur dioxide, and

(iii) providing indications as to whether the existing regulatory limits for sulphur dioxide in foods should be reviewed.

In summary, the specific objectives of this thesis are as follows:

(i) to conduct a comparative study of several methods for the determination of sulphur dioxide in foods and to identify the most accurate, reliable and economical method;

(ii) to determine the concentration or prevalence of sulphur dioxide in a variety of local foods; and

(iii) to estimate the daily dietary intake (DDI) of sulphur dioxide and to determine whether the daily dietary intake of sulphur dioxide exceed the Acceptable Dietary Intake (ADI) as set by the Codex Alimentarius Commission (CAC) and the Food and Agriculture Organisation (FAO)/ World Health Organisation (WHO) Committee on Food Additives and subsequently constituting a health risk to the consumers.

CHAPTER II

LITERATURE REVIEW

This chapter discusses the properties of sulphur dioxide, its uses and effects in foods, safety for use, toxicology, controversy over its use and regulatory status. The quantification of sulphur dioxide is also discussed in great detail.

Sulphur dioxide (SO_2) has long been known for its purifying ability. Sulphur dioxide, made on the spot by burning sulphur has been used since the time of Homer for fumigating houses and is supposed to have been used by the Romans and Egyptians for sanitizing wine vessels. Its use as a food preservative is more recent since the earliest reference that could be found in the literature was a suggestion in the seventeenth century, that casks should be filled with cider whilst they still contained sulphur dioxide, produced by burning sulphur in them (Roberts and McWeeny; 1972), this was a logical extension of its already known antiseptic properties (Roberts and McWeeny, 1972).

Sulphur dioxide was probably first used for the preservation of fruits and vegetables and their products, but the absence of toxic hazards associated with its use (Roberts and McWeeny, 1972) has led to its widespread use in the food