Boric Acid and its Determination in Foods

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ABSTRACT

The first part of the paper discusses the properties of boric acid, its uses and abuses, dietary sources, daily dietary intake (DDI), body burden and physiology of boric acid. The effects of high intakes of boric acid on human and some poisoning cases are briefly described. The second part of the paper presents results of an evaluation of three methods of analysis of boric acid in foods. These methods are titrimetric method using mannitol and two colorimetric procedures based on reactions with carminic acid or curcumin. All the three procedures were carried out on four selected foods namely agar-agar strips, pickled mango, noodles and prawns for repeatability, sensitivity and recovery determinations. The accuracy of the methods was studied using an NBS Standard Reference Material. Various parameters studied have shown that the curcumin method is the most reliable and hence would be the method of choice for boric acid determination in foods.

INTRODUCTION

In the past, boric acid was considered to be a relatively benign and non-toxic substance. Not only was boric acid widely used by the medical profession in the form of ointments and irrigating solutions, the compound also became a common item in household medicine cabinets and nurseries. Boric acid and borates are now known to be toxic to all cells. It is deleterious to health and its use should be avoided. Death has occurred from less than 5 g in infants and from 5 to 20 g in adults. Chronic use may cause borism (dry skin, eruptions, gastric disturbances (Browning, 1969).

Boric acid has been declared unsafe by an FAO/WHO Expert Committee especially as a food preservative in view of its cumulative nature and its possible use to mask incipient putrefaction (Davidson,Passmore,Brock & Truswell, 1975 and Egan,Kirk & Sawyer, 1981). In the United Kingdom, boric acid was prohibited to be used as a preservative in 1925 (Egan et al., 1981). The Ministry of Health, Thailand officially banned borax as a food additive in 1974 (Monsereenusorn, 1982). Many other countries, including Malaysia, also prohibit the use of boric acid and borax for the preservation of foods. However, boric acid is still being illegally used as a food preservative in the country. In order to facilitate the effective surveillance of the abuse of boric acid, reliable methods for its determination should be established. A detailed study of the subject was thus undertaken. A comparative study of three methods of determination was undertaken to identify a suitable analytical

method, which was then applied to the determination of boric acid in a wide variety of foods. Boric Acid, Its Uses and Abuses

Boric acid is a colourless, odourless compound commercially available as crystals, granules and as a white powder. It is soluble to the extent of five percent in water at 68°F or 20°C. It is usually prepared by reaction of sulphuric acid on borax which is highly soluble in water.

Boric acid is used industrially as compound in nuclear reactors, semiconductors, catalyst in organic chemistry, for protection of μg and other metals from oxidation, in metallurgy, in soldering, preservative of wood, in fireproofing, skin curing, manufacture of glass, glazes, and enamels, in printing, dyeing, and in photography (Russin and Minkina, 1977 and Berman, 1980). Most commonly boric acid is used as an antiseptic, a local astringent, a food preservative and to make talcum powder flow freely.

Boron, the element in boric acid, is essential to plants, but not to animals and humans (Christian and Feldman, 1970 and Berman, 1980). The soil content of boric acid usually averages 172 μg/g (23 to 515 μg/g). Boric acid μg/g concentrations are normally higher in plants than in animal tissues. Dietary intake of boric acid thus depends on the quanti ty of vegetables and fruits or animal products con sumed. An average daily dietary intake (DDI) of 6 (2 to 16) mg boric acid is considered as representative (Berman, 1980 and Hamilton, 1980). DDI as high as 57 to 114 mg has been reported, possibly due to the consumption of vegetable or food preserved with boric acid (ICRP, 1975).

Toxicity of Boric Acid

The average concentration of boric acid in the blood is 0.14 g per 100 ml of blood with a range of 0.00 to 0.72 (Valdes-Dapena and Arey, 1962). The body burden of boric acid is estimated to be about 114 μg or equiva lent to 20 μg boron (Christian and Feldman, 1970). The minimal lethal dose of boric acid for man is not known but the often quoted 'fatal oral dose for man' is 27.6 g of boric acid (Valdes-Dapena and Arey, 1962). Boric acid in food is rapidly and almost completely absorbed. They may be absorbed via the mucous membranes and injured skin (Russin and Minkina, 1977 and Berman, 1980). Tissue levels are raised after ingestion of excess boric acid, the highest concentrations being found in the brain (Christian and Feldman, 1970, Russin and Minkina, 1977 and Berman, 1980).

Boric acid in relatively high doses provoke intoxication including gastrointestinal nausea, vomiting, diarrhoea, skin and mucous membrane lesion (Michaux,Boiteau & Tblot, 1971), depressant action on brain with a blocking of the formation of glutamine from glucose and impairment of ammonia metabolism (de Bruin, 1976), testicular lesion (Lee,Sherin & Dixon, 1978), fall in albumin/globulin ratio with a rise of globulin components (de Bruin, 1976 and Russin and Minkina, 1977) and marked increase in urinary excretion of riboflavin (Pinto,Huang,McConnell & Rivein, 1978).

The literature of boric acid poisoning may be divided into two categories; instances of poisoning due to absorption of boric acid from wounds and burns and cases of poisoning due to oral ingestion of boron. The many cases of serious boric acid poisoning have focus attention on the toxic potentialities of the compound. Valdes-Dapena and Arey (1962) reported three cases and reviewed the literature on prior instances of boric acid poisoning; the authors cited 172 cases, of which 89 were fatal.

Comparative study of three methods of analysis of boric acid

Materials

Four types of foods, from four different food groups, namely wet noodle, agar-agar strips, pickled mango and prawns (fresh) were selected for the study. These foods were selected because they were thought to contain considerable amounts of boric acid, either intentionally added or naturally occurring. All the four food samples were made homogeneous by separately introducing them into the blender. Several test portions of the homogenised food samples were then taken for analysis.

Borosilicate glassware and containers were not used in the study to avoid boron contamination. Water used for sample preparation and dilution of standard and test solutions was double-distilled and deionised.

Methods

A review of the literature showed that three methods have been commonly used for the determination of boric acid in foods. These are the titrimetric method using mannitol, and colorimetric procedures based on reactions with carminic acid or curcumin. These methods have been selected for study and characterization of their accuracy, repeatability, sensitivity and recovery.

Titrimetric method

The titrimetric method used in this study followed closely that specified by the Association of Official Analytical Chemists (AOAC) Official Methods of Analysis (Williams, 1984). In this method, neutralised mannitol is used to convert boric acid present in the food sample into a relatively strong monobasic acid which will be titrated with sodium hydroxide.

Carminic acid-spectrophotometric method

Carminic acid changes colour from red to blue in the presence of boric acid in concentrated sulphuric acid (H_2SO_4). This reaction has been made use of for the determination of boron in water, soil extracts and plant materials (Hatcher and Wilcox, 1950; Callicoat and Wolszon, 1959; Fries and Getrost, 1977). The methods described in these publications have been adapted for use in this study.

Curcumin-spectrophotometric method

This method is based on the formation of a coloured product upon reaction of boric acid with curcumin in the presence of an acetic acid - sulphuric acid mixture. After extracting this coloured complex into ethanol, the intensity was measured in a spectrophotometer at 555 nm (Kuemmel and Mellon, 1957; Williams, 1984). This method has been said to give a detection limit of 1 μg/kg (Egan et al., 1981). The procedure adopted in this study is based essentially on that given in the AOAC (Williams, 1984), with some minor changes.

Comparative study

For each of the four foods selected, 15-20 analysis were carried out using each of the three methods. Mean values and standard deviations of the three methods were then compared. For comparisons of the accuracy of each of the three methods, the level of boric acid in NBS Standard Reference Material Tomato leaves 1573 was determined. Recovery of boric acid from the food samples after spiking with various concentrations of boric acid standards was determined. The concentrations of boric acid added were 172, 343, 515 and 686 μg corresponding to 30, 60, 90 and 120 μg boron.

Statistical Analysis

To determine the statistical differences in the means of boric acid content of all the four foods and percent recoveries as obtained by the three methods, the one-way analysis of variance and student's t-test were performed (Wernimont, 1985).

RESULTS AND DISCUSSION

Mean Values and Variability of Methods

Table 1 shows the mean concentrations of boric acid as obtained from three different methods of determination, carried out on agar-agar strips, mango (pickled), noodle (wet) and prawns. One way analysis of variance showed that for all the four foodstuffs, there was a statistically significant difference between the mean values obtained for the three techniques ($p<0.001$).

Using Student's t-test, it was observed that mean values obtained by the curcumin method were significantly higher than that given by the carminic acid method ($p<0.001$) for all the four foods studied. Comparing values given by the titrimetric and curcumin methods, it was observed that a statistically significant difference was obtained only for agar-agar strips ($p<0.001$) and prawns ($p<0.001$). Finally, when comparing the titrimetric and carminic acid methods, it was obtained that the former gave higher mean values, although a statistically significant difference ($p<0.001$) was obtained only for noodle, agar-agar strips and mango.

From the graphical presentation of coefficient of variation (CV) values in Figure 1, it can be clearly seen that curcumin method gave the least variation within method, while carminic acid method gave intermediate CV values.

Titrimetric method was found to give large CV values, especially for prawns.

Validation of methods

The accuracy determination of each analytical method was carried out using an NBS Standard Reference Material Tomato leaves 1573 with boric acid content of 172 $\mu g\ g^{-1}$. Boric acid values in the NBS Standard Reference Material obtained by the curcumin method vary from 126 to 194 $\mu g\ g^{-1}$ with a mean and standard deviation of 166 37 while those obtained by the carminic acid vary from 103 to 160 $\mu g\ g^{-1}$ with a mean and standard deviation of 141 µg 34. The curcumin and the carminic acid methods show %CV of 22 and 24 respectively. On the other hand, the titri metric method could not detect the low content of boric acid in the Standard Refer ence Material.

Recovery values

Mean percent recovery values of boric acid by the titrimetric, curcumin and carminic acid methods after spiking foods with various con centrations of boric acid standards are as shown in Table 2. At 172 µg level of boric acid addition, all the three methods showed good mean recovery values with CV% 10 only on wet noodle sample. At 343 µg level of boric acid addition, curcumin method showed the least variation in the mean percent recovery values (CV% 10) for all the four foods analyzed. Both titrimetric and curcumin methods gave good mean recovery values and CV% 10 on three foods namely wet noodle, agar-agar strips and pickled mango at 515 µg level of boric acid addition. At 686 µg level of boric acid addition, only the curcumin method gave good mean percent recovery values and CV% 10 for all the four foods ana lyzed. It can be seen that at all levels of boric acid addition, the mean percent recovery values obtained by curcumin method were found to lie very closely to 100% for all the foods analyzed.

CONCLUSIONS

Both titrimetric and curcumin methods did not show statistically significant differences in mean values. Lower mean values were given by carminic acid method. Among the three analytical methods, curcumin method was found to show the least variation in mean boric acid content as well as mean percent recovery values for the four types of food analyzed.

Curcumin and titrimetric methods appear to give good results for several of the parameters studied. However, from the practical point of view, the curcumin method is preferred. An amount of 0.5 g of food sample was sufficient for the curcumin method to give good reproducibility and recovery values. At least ten times this amount was needed for the titrimetric method. The determination using curcumin method could be accomplished within a shorter period of time (only three days) while that of titrimetric, doubled the time.

The findings mentioned above showed that curcumin method was found to be the most reliable and hence be the method of choice for boric acid determination in most local foods.

The method has been employed for the second phase of the project, that is, to study the prevalence of contamination of boric acid in various locally available foods. A total of 300 washed and unwashed food samples from nine food groups, including cooked and processed foods, had been analyzed for boric acid content. The results of which will be published later.

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Table 1: Boric Acid Content in Four Selected Foods as Obtained by Three Different Methods

	Titrimetric	Curcumin	Carminic
Agar-agar strips			
Mean, $\mu g\ g^{-1}$	1169	918	788
SD	114	60	72
n	16	16	16
CV, %	10	7	9
Mango, pickled			
Mean, $\mu g\ g^{-1}$	829	819	590
SD	47	21	70
n	15	16	16
CV, %	6	3	12
Noodle, wet			
Mean, $\mu g\ g^{-1}$	547	532	412
SD	62	32	41
n	20	20	20
CV, %	11	6	10
Prawns, fresh			
Mean, $\mu g\ g^{-1}$	313	347	287
SD	60	23	29
n	16	14	16
CV, %	19	7	10

Table 2: Percent Recovery of Boric Acid by Three Methods of Determination after Spiking Foods with Various Levels of Boric Acid[1]

Boric acid Levels[2] (μg)	Titrimetric Mean±SD	CV%	Curcumin Mean±SD	CV%	Carminic Mean±SD	CV%
Agar-agar strips						
172	92±62	62	84±13	15	77±16	21
343	74±15	20	98± 3	3	88±18	21
515	85± 5	6	100± 3	3	86± 8	10
686	87± 5	5	98± 3	3	80±15	19
Mango, pickled						
172	97±18	19	99±10	10	100±18	18
343	97± 6	6	108± 2	2	94± 5	5
515	97± 6	7	99± 3	3	89±19	21
686	100± 5	5	106± 3	2	87±12	14
Noodle, wet						
172	99± 7	7	101± 4	4	93±23	25
343	85±13	15	97± 2	3	85±21	25
515	92± 3	3	103± 7	7	87±21	24
686	85± 4	4	104± 1	1	85±18	21
Prawns, fresh						
172	79±17	21	105± 9	8	88±13	15
343	78± 6	7	99± 5	5	77± 7	10
515	99± 9	9	100± 8	8	81± 8	10
686	88± 5	5	99± 2	2	75± 8	11

[1] each value is the mean of 4 determinations

[2] for the titrimetric method, the concentrations of boric acid used for spiking were ten times those listed

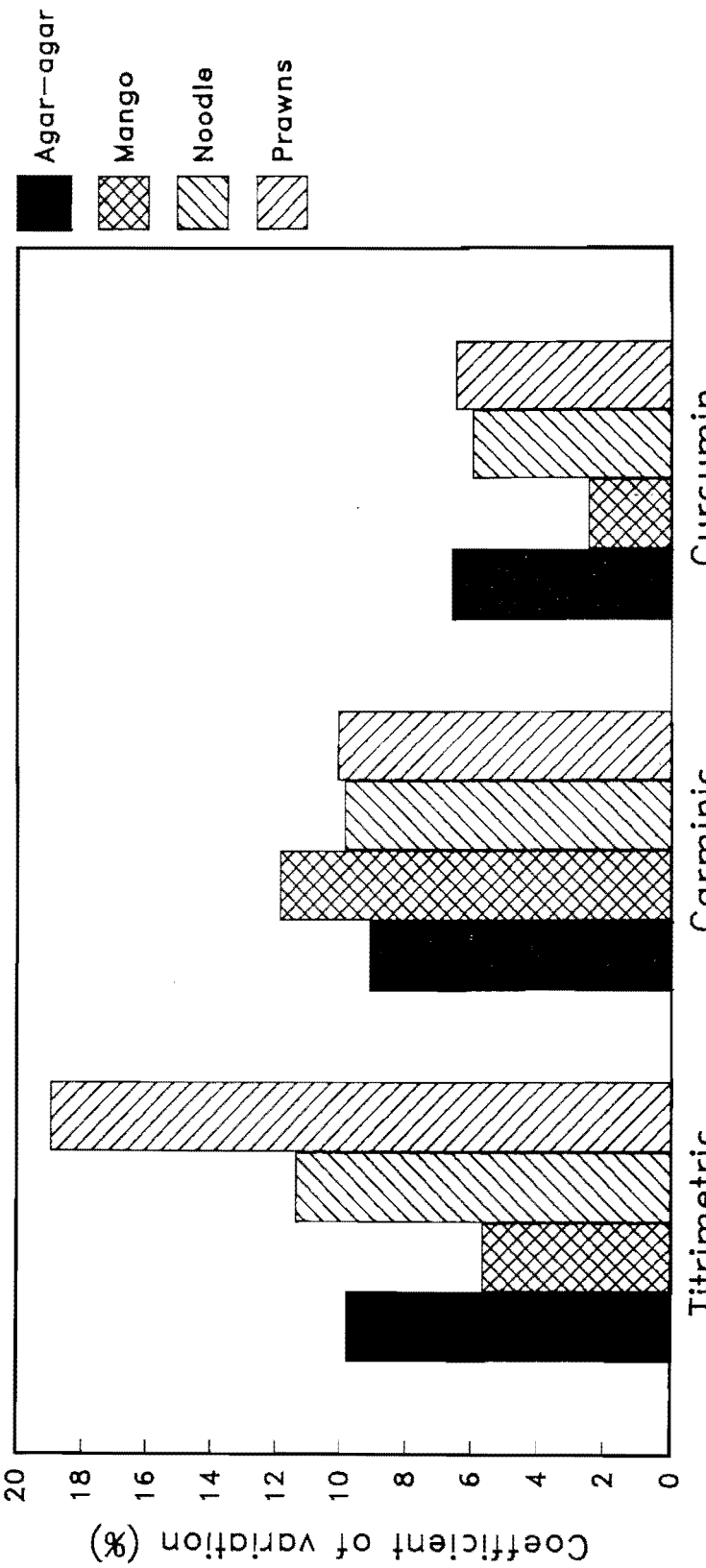

Figure 1. Coefficient of Variation values as obtained by the Three Methods

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