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CONCENTRATION OF NICKEL IN EDIBLE FATS

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The concentration of nickel in various types of edible fat samples including vanaspati, domestic ghee, cooking oil, butter and margarine was determined by atomic absorption spectrophotometric technique after pre-concentration by solvent extraction using the APDC-MIBK system. Among all the varieties of edible fats analyzed, vanaspati samples were found to contain much higher amount of nickel with a significant variation indicating the lack of standardized industrial procedures for the addition and post hydrogenation removal of the catalyst used in the hydrogenation process. Cooking oils were found to have the lowest nickel contents. The results were compared with the reported values from the other countries. Daily intake of nickel through various types of edible fats was estimated for urban populations in the low, middle and high income groups.

Key words: Nickel, APDC, MIBK, Atomic absorption spectrophotometry, Edible fats.

Introduction

The essentiality of nickel metal in human body was first reported by Nielsen and Saubelich [1], however, its distribution in the body seems to be fairly uniform without any evidence for its accumulation in any significant extent in particular organs [2] except in the lungs [3]. It becomes toxic above a daily intake of 2-7 mg of nickel causing respiratory tract neoplasia, dermatitis and aczema [4].

Nickel like other elements finds its way to the human body through the food chain which could be contaminated during and after processing. The monitoring of nickel in food items is therefore, important in general and is of special significance where it is added artificially during processing such as the hydrogenation of vegetable oils during the production of vanaspati. It is, therefore, important to monitor the concentration of nickel in vanaspati and other edible fats in order to establish a base line and to estimate its daily intake through this source. Various methods of nickel extraction/ separation from edible fats and subsequently its determination with different analytical techniques have been reported by several authors [5-7].

In the present study, nickel content of various types of edible fats was determined by the destruction of organic matter followed by extraction of the nickel complex with ammonium pyrrolidine dithiocarbamate (APDC) into 4-methylpentane-2-one (MIBK) prior to its quantitation by flame atomic absorption spectrophotometry of the solvent extracts. The method was adopted since the recovery of nickel is quantitative [8] and is also recommended by the Analytical Methods Committee [9].

Experimental

Instrumentation. The absorption measurements were carried out with Hitachi Z-8000 polarized zeeman effect atomic absorption spectrophotometer coupled with a microprocessor and built in printer. The hollow cathode lamp used as Radiation source was from Westinghouse.

Reagents. Stock solution of nickel (1000 mg/l) was prepared by dissolving appropriate weight of specpure nickel metal in distilled nitric acid [10] and the solution was evaporated to near dryness. The desired volume was made with 0.02 N nitric acid solution. Fresh standard solutions for the construction of calibration curve were prepared by appropriate dilutions of the stock solution. Glassware was cleaned by overnight soaking in nitric acid (1+1) followed by multiple rinses with demineralized water. Analytical reagent grade sulphuric acid and 30% hydrogen peroxide were used as such without any pretreatment. One percent (w/v) ammonium pyrrolidine dithiocarbamate (Eastman 9279) solution was prepared in water. This solution was prepared daily and was filtered before use. MIBK was used after saturation with water.

Sampling. Samples of vanaspati, cooking oil, butter and margarine were randomly purchased from different shops of Rawalpindi and Islamabad during May to Sept. 1987. Domestic ghee (animal shortening) samples were prepared by inoculating freshly boiled buffalo milk with sour milk and when curding had taken place solid material was separated by churning the contents. This solid material was then melted and the organic layer was separated by decanting the upper aqueous layer. The organic layer was then allowed to cool and stored for analysis. Before analysis equal weights of the samples of the same brands were melted and stirred thoroughly with glass rod to produce homogenous and representative samples. Three samples of each brand of all types of edible fats were used. Plastic gloves were used during this treatment in order to avoid contamination through sweat which is rich in nickel [11]. After homogenization all the

samples were refrigerated in cleaned and dried glass bottles till required for analysis.

Instrumental conditions. Optimum measuring conditions for the determination of nickel with atomic absorption spectrophotometry were determined by the extraction of 2 ppm nickel solution with APDC in MIBK and aspirating this extract into the flame, with systematic alteration of fuel pressure and burner height. For optimization of instrumental conditions the criterion of maximum signal-to-noise ratio (S/N) was employed.

Procedure. About one gram of sample was taken in triplicate in 250 ml conical flasks along with 5 ml of concentrated sulphuric acid. The mixture was warmed, followed by dropwise addition of hydrogen peroxide till the mixture was clear. The contents of the flask was carefully heated till dense white fumes of sulphuric acid evolved. The digested solution was cooled, diluted to 70 ml and transfered into a separating funnel. After the addition of 2.0 ml of APDC solution, the contents were thoroughly mixed and allowed to stand for 5 min. The nickel complex was extracted in 10 ml of MIBK and aspirated in the flame. A blank solution as a zero reference was also prepared and treated similarly under identical conditions for each brand of the edible fat.

Standard solution of nickel (upto 3.0 ppm) with a blank were prepared and treated in a similar manner as described for the sample solution. A calibration curve was prepared from the absorbance values of the standard solution extracts. The absorption signals were evaluated by subtracting the mean value of the blank from the sample extracts.

Results and Discussions

Under the optimized instrumental conditions (Table 1) twenty five brands of edible fats including vanaspati, domestic ghee, cooking oil, butter and margarine were analyzed for their nickel contents by atomic absorption spectrophotometry. The results are summarized in Table 2 alongwith standard deviations.

In order to check the accuracy of the present method, NBS standard reference material Oyster Tissue (SRM-1566) was analyzed for its nickel content using the method described above. The concentration of nickel was found to be 1.19 ± 0.12 µg/gm which is in good agreement with the certified value of 1.03 ± 0.18 µg/gm.

The concentration of nickel found in different brands of vanaspati samples (V_1-V_{16}) ranges from 100-3980 (Median 450, average 1139 ng/gm). The nickel contents of samples V_1 V_2, V_5,V_9 and V_{12} were found to be significantly higher than the rest of the samples. These higher levels of nickel could be attributed to inefficient post-hydrogenation removal of catalytic nickel from the samples. This was confirmed by determining the nickel contents of samples from different stages of an industrial hydrogenation process. The concentrations of nickel in the original oil sample before hydrogenation, unrefined hydrogenated product and final product were 0.20, 1.33 and 0.72 µg/gm respectively. This indicates that only 46% nickel was removed during the post hydrogenation refining process. The results in Table 2 also reflect that in some industrial plants the procedures for the addition of nickel as a

TABLE 1. OPTIMUM WORKING CONDITIONS FOR ATOMIC ABSORPTION SPECTROPHOTOMETRIC MEASUREMENTS OF NICKEL.

Wavelength	:	232.0 nm
Lamp current	:	12.5 mA
Width of slit	:	0.2 nm
Burner height	:	10.0 mm
Burner path length	:	100.0 mm
Acetylene flow rate	:	2.2 l/min
Air flow rate	:	9.5 l/min
Scale expansion	:	x 1

TABLE 2. CONCENTRATION OF NICKEL IN DIFFERENT TYPES OF EDIBLE FATS.

Sample code	Conc. of nickel (ng/gm)	Sample code	Conc. of nickel (ng/gm)
A. Vanaspati			
V_1	3270 ± 210	V_9	1800 ± 70
V_2	3980 ± 240	V_{10}	450 ± 10
V_3	120 ± 10	V_{11}	720 ± 60
V_4	130 ± 20	V_{12}	2310 ±110
V_5	3170 ± 340	V_{13}	380 ± 10
V_6	720 ± 60	V_{14}	210 ± 10
V_7	130 ± 10	V_{15}	450 ± 20
V_8	100 ± 10	V_{16}	280 ± 30
B. Other types of fats			
G	112 ± 20	B_1	33 ± 5
C_1	21 ± 1	B_2	42 ± 2
C_2	45 ± 4	B_3	247 ± 25
C_3	140 ± 16	M	183 ± 53
C_4	59 ± 4	–	– –

TABLE 3. ESTIMATED DAILY INTAKE OF NICKEL THROUGH EDIBLE FATS.

Type of fat sample	Intake of nickel (µg)		
	A	B	C
Vanaspati	3-119	4-179	7-279
Domestic ghee	3	5	8
Cooking oil	2	3	5
Butter	–	2	3
Margarine	–	3	5

A = Low income group, B= Middle income group, C = High income group.

catalyst and subsequently its removal after hydrogenation are not standardized since significantly higher amounts of nickel were found in their final products. Therefore, a stick quality control system should be introduced in such industries.

The average concentration of nickel in the domestic ghee samples (G) was found to be 112± 20 µg/gm. The average concentration of nickel in two brands of cooking oil samples (C_1 and C_2) was 33 ng/gm which is almost equal to the lowest reported value for nickel in the cooking oil samples of USA (29-207 ng/gm) [12]. The concentration of nickel in sunflower oil (C_3) and corn oil (C_4) were 140±16 and 59 ±4 ng/gm respectively. The data show that the average concentration of nickel in cooking oil samples is about one half than that of corn oil samples where as that of sunflower oil samples is about two times higher than the value of corn oil samples.

The concentration of nickel in three brands of butter (B_1-B_3) ranges from 33-247 (average 107) ng/gm. Perusal of Table 2 shows that the concentration of nickel in the salted butter (B_9) is about seven times higher than the average value of rest of the butter samples (37 ng/gm). The higher amount of nickel in this sample could probably be due to the contamination during salting process. The average concentration of nickel in margarine samples (M) was found to be 183 ±53 ng/gm, which is similar to the reported values from Finland (<200 ng/gm) [13] and Poland (60-185 ng/gm) [14] and greater than USA (34-70 ng/gm) [12] and Japan (0-51 ng/gm) [15], but lower than Netherlands (> 1000 ng/gm) [16].

The daily intake of nickel through edible fats was estimated for low middle and high income group populations of Islamabad on the basis of 30, 45 and 70 gms consumption of edible fats per person per day respectively. Since butter and margarine are generally not used by people of low income, the daily intake of nickel from these fats was only calculated for the people of middle and high income groups on the basis of 15 and 25 gms consumption respectively. The intake amounts of edible fats were based on the survey of at least one hundred persons of each category. The results are tabulated in Table 3. The average concentration of nickel in each type of edible fats was used for such calculations except for vanaspati where the maximum and minimum values have been quoted due to large variations in the concentration of nickel in different brands of vanaspati. The screening of data shows that the estimated intake of nickel through vanaspati is significantly higher as compared to other types of fats studied during the present work, therefore, it is advisable to avoid the prolonged use of vanaspati brands with higher nickel contents or use cooking oil preferably.

Conclusion

The data on the concentration of nickel in edible fats will help to establish base line levels for this area and to monitor the degree of contamination. Of the various types of fats analyzed vanaspati was found to contain the highest and cooking oil the lowest amount of nickel. Since it is difficult to change the food habits of people quickly, it will be advisable to use different brands of vanaspati or other types of edible fats, to avoid the risk of nickel toxicity by using the same brand of vanaspati which may contain high nickel contents. Large variations of nickel concentration in different brands of vanaspati indicates inadequate nickel removal system and lack of quality control in some production units.

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