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G.N. FLINT AND
S. PACKIRISAMY
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CONTACT DERMATITIS

Systemic nickel: the contribution made by stainless-steel cooking utensils

G. N. Flint[1] and S. Packirisamy[2]

[1]The Nickel Development Institute, The Holloway, Alvechurch, Birmingham B48 7QB, UK,
[2]Food Composition Group, Laboratory of the Government Chemist, Queens Road, Teddington, Middlesex TW11 OLY, UK

An extensive programme of cooking operations, using household recipes, has shown that, apart from aberrant values associated with new pans on first use, the contribution made by 19 Cr/9 Ni stainless-steel cooking utensils to nickel in the diet is negligible. The amount of nickel (0 to 8 μg) derived from the utensils in standard portions of various "aggressive" foodstuffs tested was less than that to be found occurring in 1 square of a bitter-sweet chocolate bar. New pans, if first used with acid fruits, can show a greater pick-up of nickel, which, in the worst case observed, amounted to approximately 1/5 of the normal daily intake for the average person (ca. 200 μg). This situation does not recur in subsequent usage, even after the pan has been cleaned by abrasion. A higher rate of nickel release was observed in new pans on first use from 4 manufacturers located in different countries and appears to be a general phenomenon. This could provide a possible explanation for the high pick-up of nickel by acid fruits reported in 1 instance in the literature.

Key words: stainless steel; cooking utensils; food; nickel; allergic contact dermatitis; diet. © Munksgaard, 1995.

A number of investigators (1–6) have shown that ingested nickel can cause exacerbation of hand eczema in patients who are already sensitized to nickel. Only a minority of nickel-sensitive patients react to oral doses below 1250 μg (as nickel) of nickel sulfate (7) and, indeed, in 1 investigation (8) it was found that doses lower than 5600 μg "failed to excite reactions more frequently than did a placebo in a double-blind study". In consequence, the practical significance of ingested nickel has been in doubt (9–11).

A diet with a low nickel content has been found to diminish the activity of hand eczema (2, 12–14) and special diets have been devised with the aim of alleviating this condition in nickel-sensitized patients. The diets included a recommendation to avoid acid fruits cooked in stainless-steel utensils.

In contrast, it has been found that oral exposure to nickel, prior to sensitization, results in a reduced frequency of nickel hypersensitivity. That conclusion was reached from a survey (15) of patients who had oral contact with nickel-releasing appliances (dental braces) at an early age prior to ear piercing, a common cause of nickel sensitization. The effectiveness of nickel ingestion as a means of

inducing tolerance to sensitization by nickel was subsequently established experimentally (16).

The average, human, daily intake of nickel is approximately 200 μg (12, 17–18) and, although the essentiality of nickel in the diet of animals such as sheep, goats, rats, chickens has been proven (19–21), as it also has in plants (22), the ubiquitous nature of nickel makes it difficult to establish its essentiality in the human diet. Nevertheless, Nielsen (23) has proposed a nickel dietary requirement for humans of 50 μg per day.

To date, opinion on nickel pick-up by foods cooked in stainless-steel utensils has been based on experiments conducted using acid solutions ostensibly simulating real foods. Generally, organic acid solutions have been used (acetic, citric, maleic, oxalic) at or near boiling point (24–29). However, it is well-known (30–33) that considerable variability in performance can be shown by stainless steels in such conditions, depending upon the transition from passive to active states during the test period. That transition is dependent primarily on the concentration of acid, the presence of chlorides and other contaminants, particularly those of an oxidizing or reducing character. The situation is well

exemplified by the results obtained in oxalic acid solutions: the nickel pick-up was below the limit of detection at pH 4 (28) and at a pH of about 2 (29), the nickel pick-up exceeded 3 mg/l. The significance of results in solutions simulating foods requires careful interpretation.

Tests involving real foods demand more exacting experimental techniques and consequently are much less numerous. One investigation (24) compared nickel contents of fruits cooked in enamel or stainless-steel utensils and found significant pick-up from the stainless steel. Conversely, a more recent investigation (34) of actual cooking operations using real foods found that the nickel and chromium contents of spinach, sauerkraut and rhubarb, cooked in 19 Cr/9 Ni stainless-steel saucepans (UNS* S30400), were within the normal range of values found in these foods in the raw state. These latter results are within expectation based on the extensive, satisfactory performance and retention of surface finish of S30400 stainless steel in food handling and preparation.

In view of the concern of some dermatologists, and since contamination is of importance to the public, to processors of food and manufacturers of catering equipment, an investigation has been made of the pick-up of nickel from S30400 stainless-steel saucepans used in a variety of foods. Foods were chosen which, because of their acidity and/or chloride content, are likely to be aggressive to stainless steels.

Materials and Methods

The following determinations were made.

(a) The pick-up of nickel by rhubarb cooked in new S30400 stainless-steel pans. Tests were performed in triplicate and a sequence of 20 cooking operations was undertaken.

(b) The pick-up of nickel by rhubarb cooked in the above pans after completion of (a) followed by abrasion of the test surface using either plastic or wire-wool abrasives.

(c) The pick-up of nickel by apricots cooked in new S30400 stainless-steel pans. Tests were performed in duplicate and a sequence of 16 cooking operations was undertaken.

(d) The pick-up of nickel by apricots cooked in the above pans after completion of (c) followed by abrasion of the test surface using either plastic or wire-wool abrasives.

(e) The pick-up of nickel by other foodstuffs of an "aggressive" nature cooked in new S30400 stainless-steel pans. These tests were performed in

* Unified numbering system.

duplicate and sequences of 5 cooking operations were undertaken.

Materials

Care was taken, at all stages, to avoid contamination of the test samples. Where possible plastic utensils were used. Stainless-steel saucepans of 1.6 l capacity, 160 mm diameter and from the same manufacturer were purchased from a London store. Before and between testing, the pans were washed in demineralized water with gentle cleaning using a soft sponge and dried using tissues. A check analysis on one pan confirmed that it met the specification for S30400 stainless steel.

The foods listed overleaf were purchased in bulk and sampling techniques were performed to ensure minimum variation within each ingredient of the samples tested. Once prepared, all perishable ingredients were stored frozen, whilst the non-perishables were stored at room temperature: (a) rhubarb; (b) dried apricots; (c) ingredients for the preparation of lemon marmalade (p. 359, ref. (35)); (d) ingredients for the preparation of green tomato chutney (pp. 383, 384, ref. (36); (e) potatoes.

Demineralized water was used to wash all samples and distilled water was used for all cooking operations. All weighings of food items were carried out to an accuracy of ±1 g/1 ml).

Cooking procedures

A domestic cooker was used for all cooking operations.

Rhubarb. 250 g of sliced rhubarb and 30 ml of distilled water were placed in the pan, brought to the boil and simmered for 15 min. The surface area of the pan exposed to the mixture was 250 cm^2.

Apricots. 250 g of dried apricots were placed in 500 ml of distilled water and allowed to soak for 16 h in the pan. The soaked apricots and water were brought to the boil and simmered for 15 min. The surface area of the pan exposed to the mixture was 400 cm^2.

Lemon marmalade. The juice, peel, pips, flesh and pith of the lemons (450 g) were separated. The juice was refrigerated until required for use. The lemon peel was cut into strips and placed in the pan with 568 ml of distilled water and a nylon bag containing the pips, flesh and pith. The contents of the pan were allowed to soak overnight (16–18 h), following which the pan was heated strongly for 5 min. The pan was covered and simmered for 1 h. The nylon bag was removed prior to the addition of the refrigerated lemon juice and 450 g of sugar. The contents of the pan were stirred for 3

min with heating to dissolve the sugar prior to being heated strongly and brought to the boil with stirring (3 min). The heat was reduced and the contents of the pan were allowed to gently boil without stirring for 4 min (p. 359, ref. (35)). The surface area of the pan exposed to the mixture was 490 cm².

Green tomato chutney. The prepared fruit and vegetables were placed in the pan with sultanas, sugar, salt and pepper. 250 ml of malt vinegar was added and the pan was gently heated for 3 min to dissolve the sugar. Grated ginger and mustard seeds were placed in a nylon bag and put into the pan. The pan was covered and the contents were gently simmered for 2 h (pp. 383, 384, ref. (36), ¼ of the recipe weight was used). The surface area of the pan exposed to the mixture was 440 cm².

Potatoes. 3 potatoes (approximately 470 g) were peeled, rinsed with demineralized water, dried with tissues and cut into 30–40 g cubes. 400 g of these potato cubes, 2 g of salt and 400 ml of distilled water were placed in the pan, brought to the boil and simmered for 20 min. Salt was added before the water as this gives maximum possibility for the attack on the stainless steel. The surface area of the pan exposed to the solution was 390 cm².

Once cooked, all samples were transferred to plastic boxes for cooling prior to the measurement of pH, weighing and homogenization in a stainless-steel-bladed blender. All cooked samples were stored frozen until required for analysis. Except in the case of potatoes, the analyses were performed on the homogenized liquid plus solid material. For potatoes, analyses were performed separately on

Table 1. Naturally occurring nickel content and acidity of foods tested

Foodstuff	Mean nickel content (μg/kg)	pH raw. or cooked in glass pans	pH after cooking
rhubarb	40±10	3.5 (n=10)	3.5 (n=60)
apricots	120±10	3.7 (n=10)	3.6 (n=36)
lemon marmalade	80±20	[a]2.6 (n=5)	2.8 (n=10)
green tomato chutney	30±10	[a]3.3 (n=5)	3.5 (n=10)
potatoes	10±10	[a]5.8 W (n=5)	5.8 W (n=10)
		[a]5.8 P (n=5)	5.9 P (n=6)

n: no. samples analysed for pH.
[a] pH was measured in samples that had been cooked in glass pans.
W: pH of boiled water used for boiling the potatoes.
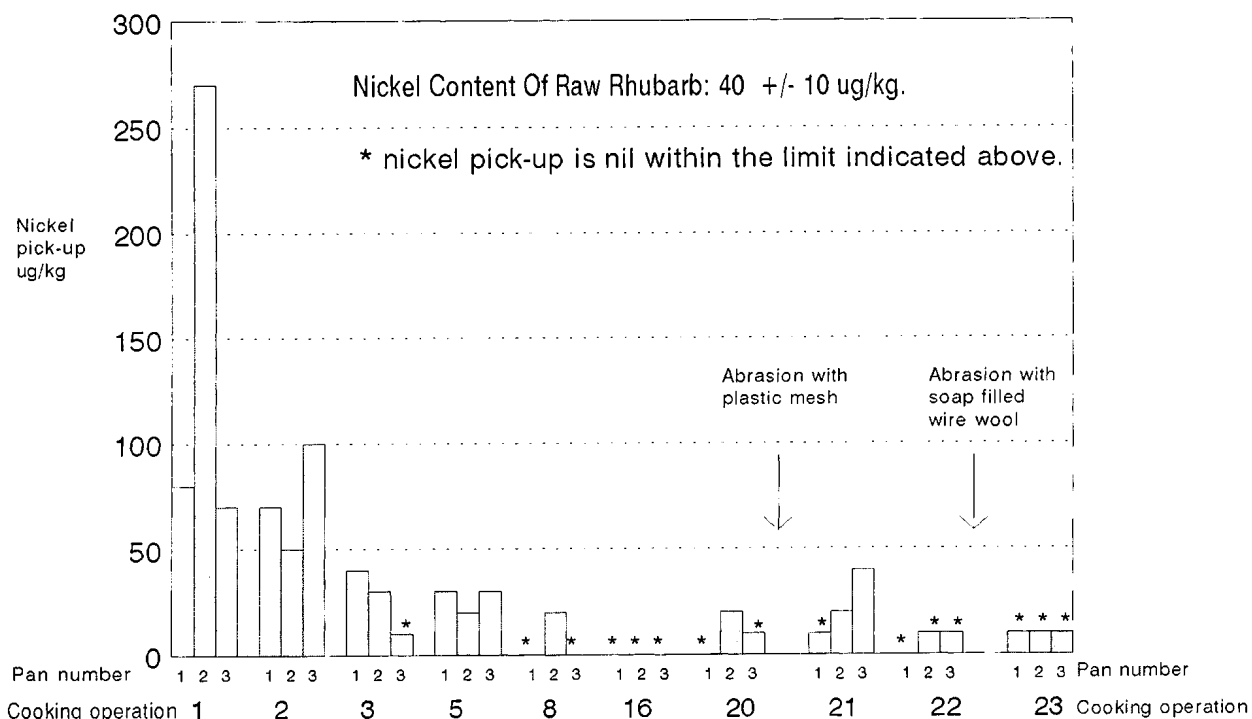P: pH of boiled potatoes after homogenization.

Fig. 1. Pick-up of nickel by rhubarb cooked in new S30400 stainless-steel saucepans.
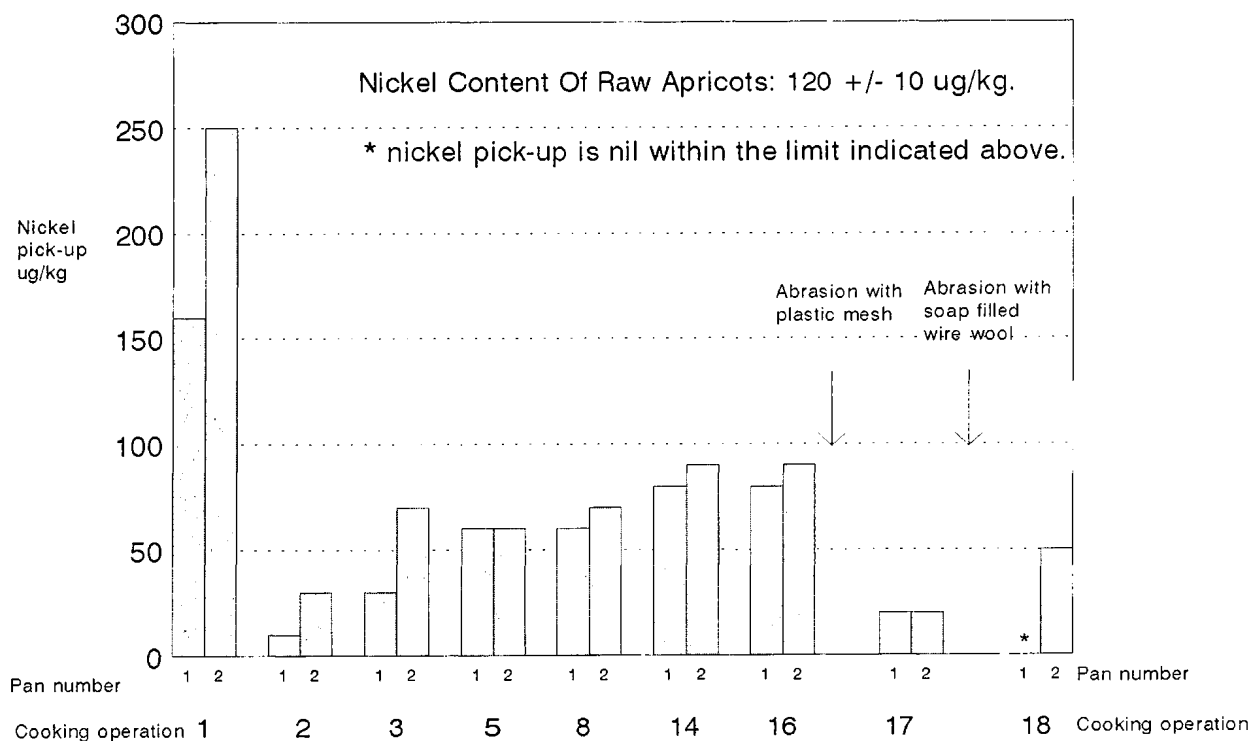
Fig. 2. Pick-up of nickel by apricots cooked in new S30400 stainless-steel saucepans.

the solid homogenized potato and on the water used to boil the potatoes.

Field blanks were performed to assess if there had been any contamination during sample homogenization. Blank wheat starch solutions were taken through the blender both before and after the homogenisation of test samples. The starch solutions were analysed for nickel.

Determination of nickel

All samples were wet oxidized using a combination of concentrated acids (37) prior to the determination of nickel by atomic absorption spectrometry. The instrument used was a Perkin Elmer 2100 with a heated graphite analyser (HGA700). Measurement of nickel was performed at a wavelength of 231.7 nm. National Institute of Standards and Technology (NIST) certified reference materials were run with every assay to check the accuracy of the analysis. Also, with every assay, reagent blanks were taken through the analytical procedure to check for contamination during the measurement stage. The limit of determination of the analytical method, calculated on 3 standard deviations (~99% confidence limit) of the mean of the reagent blank responses from successive assays, was calculated to be 10 μg/kg for nickel.

Calculation of pick-up

It was necessary to obtain reliable figures for the nickel content of each food, to determine whether any pick-up had occurred during the cooking operation. For rhubarb and apricots, 10 raw samples were selected at random and analysed. For lemon marmalade, green tomato chutney and potatoes, 5 samples of ingredients were selected at random and cooked in glass pans.

The mean nickel contents were calculated for each food and used as the base levels for calculation of pick-up values (Table 1), i.e., the "true" nickel pick-up could vary within ±10 μg/kg for all foods tested, except lemon marmalade which could vary within ±20 μg/kg of the calculated value, depending on whether the test sample had a higher or lower nickel content than the mean.

Results

The field blank studies demonstrated that no detectable contamination of the test samples occurred during sample homogenization. The levels of nickel in uncooked rhubarb and apricots and glass pan cooked lemon marmalade, green tomato chutney and potatoes are given in Table 1. All values fall within or are close to the range of nickel contents of these foods reported in the literature
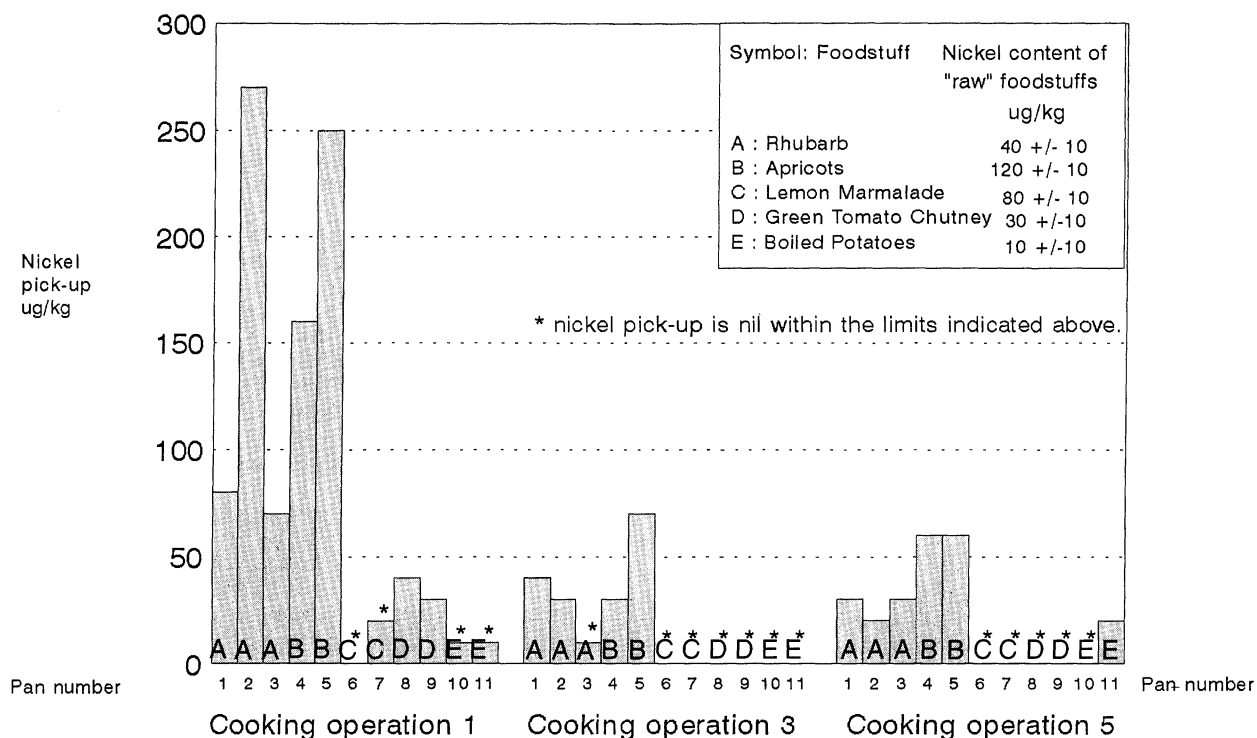
Fig. 3. Pick-up of nickel by various foodstuffs cooked in new S30400 stainless-steel saucepans.

(17, 18). The pH values of both cooked (in S30400 stainless-steel saucepans) and uncooked foods are also given in Table 1.

The pick-up of nickel by rhubarb cooked in the S30400 pans in the initial sequence of 20 cooking operations is shown in Fig. 1. It is evident that new pans can release some nickel but that after 2 operations, the pick-up is effectively nil, bearing in mind the variation of ±10 µg/kg that could occur in the test samples of uncooked rhubarb. New pans, when first used for the stewing of apricots, also released some nickel (Fig. 2), but in contrast to rhubarb, some pick-up of nickel remained meas-

urable even on continued use. After abrasion of the pan surface, the pick-up remained generally nil within the specified limits for rhubarb, but a general reduction in pick-up was observed with apricots. In the preparation of lemon marmalade and green tomato chutney, the pick-up of nickel was at or below the mean nickel base levels of lemon marmalade and green tomato chutney cooked in glass pans (80 µg/kg and 30 µg/kg respectively), even in the new pans on first use, a somewhat surprising observation in view of their greater acidity when compared with that of rhubarb or apricots. In one case, some slight pick-up was detected in

Table 2. Pick-up of nickel by standard food portions arising from the use of new stainless-steel saucepans[a]

| | Standard portion (33) (g) | Mean base levels of nickel (µg)[b] | Pick-up of nickel/micrograms[a] | | | | | |
| | | | 1st cooking operation | | | 5th cooking operation | | |
Foodstuff			pan 1	pan 2	pan 3	pan 1	pan 2	pan 3
rhubarb	140	6	11	38	10	4	3	4
apricots	140	17	22	35	–	8	8	–
lemon marmalade	25	2	nil	1	–	nil	nil	–
green tomato chutney	30	1	1	1	–	nil	nil	–
potatoes	220	2	2	2[c]	–	nil	4	–

[a] Results expressed as µg nickel pick-up per standard portion of cooked food. [b] Per standard portion of foodstuff. [c] The water after boiling contained 110 ug Ni/l.
Nil pick-up values were at or below the mean base levels of nickel.
"Normal" nickel content of the daily diet is within the range of 150–250 µg (12, 16–17).

the salt water used to boil potatoes though this was not observed in the potatoes (Fig. 3).

The effects of abrading the surface of the pans are shown in Figs. 1 and 2. Clearly, abrasion had no adverse effects.

Discussion

The results show that apart from the aberrant values associated with new pans on first use, the contribution made by stainless-steel cooking utensils to nickel in the diet is very small and within the normal day-to-day variation of nickel intake. This is particularly evident in Table 2, which shows the nickel addition to standard portions (38) of various cooked foods arising from the S30400 stainless-steel saucepans. The amount of nickel picked up in a standard portion of foodstuff from pans that had been used for cooking for 5 or more occasions, was less than that occurring in a small 5 g square of a bitter-sweet chocolate bar (2.6 µg/g) (39).

Even with new pans on first use for the stewing of rhubarb (a non-recurring situation and the worst case observed), the nickel addition to the diet was not significant (0.27 µg/g of rhubarb).

The greater rate of nickel release from new pans on 1st use with acid fruits has been observed on pans from 3 other manufacturers located in 3 different countries, each using S30400 from different sources. This is evidently a real effect and is receiving detailed study to be reported in a later publication. It appears probable that the initial higher rate of nickel release is associated with the production process, since creation of a fresh surface by abrasion of a used pan had little if any effect on the pick-up of nickel by stewed rhubarb or apricots.

This initial "high" rate of nickel release from new pans on first use could explain, at least partly, the high rates of nickel pick-up by acid fruits observed by Brun (24). In the latter case, the poorer heat transfer characteristics of stainless-steel saucepans made 15 years ago may also have contributed to the observed nickel release.

It may be concluded that there is no advantage to be gained by nickel-sensitized persons who suffer from hand eczema, in avoiding the use of stainless-steel utensils, even for the cooking of acid fruits.

Acknowledgements

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Address:

G. N. Flint
The Nickel Development Institute
The Holloway
Alvechurch
Birmingham B48 7QB
UK