

Contribution to chromium and nickel enrichment during cooking of foods in stainless steel utensils

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Nickel ingestion can cause exacerbation of dermatitis in patients who are already nickel-sensitive; Chromium (Cr VI) is the 2nd allergen, after nickel. However, stainless steel is widely used in home cookware. In this study, we determined nickel and chromium levels by atomic absorption spectrometry in 11 habitual menus cooked in different grades of stainless steel utensils. We noted a great difference in nickel and chromium intake depending on the menu, and a significant difference between the glass and stainless steel saucepans, but this was very low compared with the levels of nickel and chromium contained in the menus; mean intakes of these elements were under the tolerable daily intake (TDI) recommended by the World Health Organization. Hence, there is no advantage for nickel-sensitive patients in switching to materials other than stainless steel, provided that this is of good quality.

Key words: stainless steel; cooking utensils; home-cooked meals; nickel; chromium; allergic contact dermatitis; prevention. © Munksgaard, 1998.

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Chromium (Cr) in the form of Cr (III) or Cr (VI) is an essential element required for normal carbohydrate and lipid metabolism. Studies on patients under total parenteral nutrition have indicated that a lack of chromium may cause disturbances in glucose metabolism (1).

Yet, with the development of numerous industrial applications for this metal, adverse effects of chromium compounds on human health have been discovered. Chromium as a pure metal has no adverse effect. Little toxic effect is attributed to trivalent chromium even when present in very large amounts. Both acute and chronic toxicity of chromium are mainly caused by hexavalent compounds (2). The most important toxic effects, after contact, inhalation or ingestion of hexavalent chro-

mium compounds, are the following: dermatitis, allergic and eczematous skin reaction. Chromium (VI) is the 2nd allergen, after nickel.

Nickel (Ni) allergy is the most common form of cutaneous hypersensitivity and a number of investigators (3, 4) have shown that ingested nickel can cause aggravation of hand eczema in nickel-sensitive patients; in Europe, 20% of women and 2 to 4% of men are nickel-sensitized patients. A diet with a low nickel content has been found to diminish the activity of hand eczema (5).

In patients suffering from a high degree of hypersensitivity to nickel and chromium, it has been recommended that they should avoid eating nickel and chromium-rich food and cooking in stainless steel utensils. 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 (6, 7). The aim of our study was to monitor exposure to nickel and chromium in 11 habitual menus cooked in stainless steel utensils in comparison with these same menus cooked in glass pans.

Materials and Methods

The described analyses were made on 11 habitual menus chosen among hospital cafeteria menus (2×5 days with a 2-week interval for a good representation of menu variability) and cooked in different pans:

- diet 1: boiled potatoes+fried hamburger
- diet 2: creole rice+breadcrumb-coated fish
- diet 3: pasta+sausages
- diet 4: runner beans+chicken escalope
- diet 5: peas+fillet of fish
- diet 6: creole rice+fried veal
- diet 7: runner beans+fillet of fish
- diet 8: pasta+sausages
- diet 9: carrots in butter+fried hamburger
- diet 10: chicory+chipolatas
- diet 11: broccoli+chicken escalope

Materials

The stainless steel utensils were obtained as listed in Table 1; both models were manufactured by the same company (Ugine). A nickel-chromium free glass pan (Corning) was used as a negative control. 3 stainless steel pans were used: 2 of them (1 in Uginox F17MNb: grade 1.4526 (AISI 436) and 1 in Uginox 18-9E: grade 1.4301 (AISI 304)) were cleaned with an aqueous solution of acetic acid (concentration: 3% in weight); the 3rd one (Uginox 18-9E: grade 1.4301 (AISI 304)) provided from the same batch as previously was hand-polished in water with SiC paper, grain 240, instead of being washed in acetic acid.

Care was taken at all stages of the determinations to avoid contamination of the test samples. When possible, plastic utensils were used. Prior to and after testing, the pans were washed gently in tap water using a soft sponge. Vegetables were peeled and washed in tap water. The menu, in an

amount corresponding to two adult portions, was divided into 3 parts. Each part was weighed exactly to an accuracy of ± 0.01 g.

Cooking procedures

Home cooking procedures were used; each of the 3 parts was cooked separately in the same saucepan. When cooking in water, 2 g of NaCl (measured to the nearest cg) were added and the volume of water measured (1000 ml for vegetables and pasta; meat and fish without water). Boiling and cooking times were noted: after cooking, the vegetables and starch foods were strained and weighed; meat and fish were weighed.

Preparation of samples for analysis

Once cooked, the 3 parts of each menu were homogenized separately in a blender with a martensitic stainless steel blade, then each part was divided into 2 aliquots of around 50 g which were mineralized in a quartz capsule in an oven (temperature program: 20–150°C, 120 mn; 150–250°C, 120 mn; 250–600°C, 300 mn). The volume of water strained from the vegetables and pasta was evaporated and mineralized. Hence, for each menu, 6 mineralized samples and 1 sample of strained water were obtained for determination of nickel and chromium levels. This methodology was repeated for each pan.

Validation protocol

Sample homogenization and mineralization. Blank tests were performed to ensure control of any fortuitous contamination. Nickel/chromium contamination from the blender was examined by testing on ice-frozen demineralized water, while contamination from glass pans was tested on boiled water. The mineralization step was validated by a recovery technique (addition of known concentrations of nickel nitrate and chromium nitrate) to different substrates: (a) a homogenized typical menu: addition of 80 $\mu\text{g/kg}$ of nickel nitrate and 40 $\mu\text{g/kg}$ of chromium nitrate. Test was performed 4×. (b) 5 g dry cellulose MN 300 (Macherey, Nagel): addition of 1 $\mu\text{g/g}$ of nickel nitrate and 1 $\mu\text{g/g}$ of chromium nitrate. Test was performed in duplicate.

Table 1. Chemical composition of stainless steel utensils

Stainless steel grades	Chemical composition (%)							
	C	Mn	Si	Cr	Ni	Mo	Nb	S
grade 436	0.04	0.47	0.33	16.6	—	0.95	0.67	0.001
grade 304	0.04	1.36	0.33	18.2	8.64	—	—	0.003

Table 2. (a) Ni(a) and Cr(b) concentrations expressed as $\bar{m} \pm 3s/\sqrt{n}$ (m =average; s =standard deviation; n =number of determinations) in $\mu\text{g/kg}$ of 11 habitual menus cooked in glass or stainless steel saucepans; the pH is expressed for each menu; strained water from vegetables and pasta is expressed in $\mu\text{g/volume}$ of strained water.

Menu	1	2	3	4	5	6	7	8	9	10	11
Container	($n=12$)	($n=12$)	($n=12$)	($n=12$)	($n=12$)	($n=12$)	($n=12$)	($n=12$)	($n=12$)	($n=12$)	($n=12$)
glass	88 $\pm$ 8	62 $\pm$ 10	22 $\pm$ 5	86 $\pm$ 5	93 $\pm$ 17	20 $\pm$ 2	91 $\pm$ 2	16 $\pm$ 2	8 $\pm$ 1	28 $\pm$ 6	75 $\pm$ 10
stainless steel 436	112 $\pm$ 4	85 $\pm$ 6	38 $\pm$ 3	91 $\pm$ 5	67 $\pm$ 3	14 $\pm$ 2	65 $\pm$ 2	10 $\pm$ 3	17 $\pm$ 4	27 $\pm$ 1	42 $\pm$ 4
stainless steel 304	131 $\pm$ 2	75 $\pm$ 5	22 $\pm$ 2	98 $\pm$ 2	93 $\pm$ 3	21 $\pm$ 3	75 $\pm$ 6	18 $\pm$ 3	17 $\pm$ 3	33 $\pm$ 3	54 $\pm$ 4
stainless steel 304 polished	55 $\pm$ 1	65 $\pm$ 4	24 $\pm$ 2	78 $\pm$ 1	84 $\pm$ 3	18 $\pm$ 2	70 $\pm$ 4	19 $\pm$ 2	21 $\pm$ 2	17 $\pm$ 6	43 $\pm$ 2
pH after cooking	8.7	7.5	7.5	8.5	8	8	8.5	8.0	7.0	7.5	8
vegetable and pasta:		54		49							
strained water		$n=2$		$n=2$							
(b)											
glass	41 $\pm$ 6	47 $\pm$ 4	7 $\pm$ 4	31 $\pm$ 3	17 $\pm$ 6	26 $\pm$ 4	17 $\pm$ 1	28 $\pm$ 2	29 $\pm$ 7	11 $\pm$ 3	17 $\pm$ 6
stainless steel 436	62 $\pm$ 8	79 $\pm$ 23	13 $\pm$ 8	16 $\pm$ 2	28 $\pm$ 1	10 $\pm$ 2	25 $\pm$ 5	31 $\pm$ 2	20 $\pm$ 10	15 $\pm$ 2	28 $\pm$ 6
stainless steel 304	16 $\pm$ 1	63 $\pm$ 17	12 $\pm$ 5	16 $\pm$ 4	15 $\pm$ 1	19 $\pm$ 4	15 $\pm$ 1	59 $\pm$ 2	28 $\pm$ 1	18 $\pm$ 6	22 $\pm$ 8
stainless steel 304 polished	26 $\pm$ 2	28 $\pm$ 1	7 $\pm$ 1	13 $\pm$ 2	14 $\pm$ 2	13 $\pm$ 2	13 $\pm$ 2	37 $\pm$ 3	28 $\pm$ 3	7 $\pm$ 2	13 $\pm$ 1
pH after cooking	8.7	7.5	7.5	8.5	8	8	8.5	8.0	7.0	7.5	8
vegetable and pasta:		31		17							
strained water		$n=2$		$n=2$							

Note: Stainless steel 436 is a 17% Cr and 1% Mo containing stainless steel.

Stainless steel 304 is a 18% Cr and 9% Ni containing stainless steel.

Analytical validation. Methods of analysis were validated according to recommendations (8) on the following criteria: detection limit, inter and intra-assay reproducibility. The detection limit was determined by successive assays of the reagent blank (0.1M HNO₃) in the same series of analyses. Reproducibility was tested on 2 samples, one containing 25 $\mu\text{g/l}$ nickel, the other containing 34 $\mu\text{g/l}$ chromium. Intra-assay reproducibility was estimated by successive assays of nickel (20 $\times$) and chromium (17 $\times$). Inter-assay reproducibility was estimated by determination of nickel and chromium on 8 consecutive days.

Determination of nickel and chromium

All mineralized samples (6 for each pan: 24 for 4 pans) were mixed with 10% nitric acid (MERCK, suprapur) and deionized water (w/w) prior to determination of nickel and chromium levels by electrothermal atomic absorption spectrometry. The instrument used was a Varian ZAA 300 equipped with a heated graphite analyzer (without platform) and a Zeeman corrector. The radiation source was either a nickel or a chromium hollow-cathode lamp operated at 10 mA. Measurements of nickel and chromium were performed at wavelengths of 232 nm and 357.9 nm respectively with a 0.5 nm spectral pathlength. The sample volume dispersed by the autosampler was 10 μl . The ashing temperature was 800°C for nickel and 1000°C for chromium. Atomization was 2400°C for nickel and

2600°C for chromium. The tests were made with a pyrolytically coated graphite tube (Varian L6310001200) as atomizer. Data were read at peak height.

Nickel and chromium levels of each sample were deduced from a standard addition curve determined on mineralized sample. The standard addition curve was drawn from 0 to 80 $\mu\text{g/l}$ for nickel and from 0 to 20 $\mu\text{g/l}$ for chromium. Measurements were performed in duplicate for each mineralized sample and strained water; hence, in total, for each habitual menu, 48 determinations of mineralized sample and 8 of strained water were performed for each element. Nickel and chromium levels are expressed in $\mu\text{g/kg}$ of cooked, homogenized food for mineralized samples and in $\mu\text{g/vol}$ of strained water. For evaluation of accuracy, National Institute of Standards and Technology (NIST) certified reference materials were submitted to the entire analytical protocol.

Results

For homogenization and mineralization validation, no nickel and chromium release by the blender was noted. On the one hand, 80 $\mu\text{g/kg}$ of nickel and 40 $\mu\text{g/kg}$ of chromium added to each habitual menu were recovered at levels of 80 $\mu\text{g/kg} \pm 0.1$ and 39.5 $\mu\text{g/kg} \pm 0.1$ respectively; on the other hand, 1 $\mu\text{g/g}$ of nickel and chromium added to 5 g cellulose were recovered at $0.99 \pm 0.01 \mu\text{g/g}$ and $1.02 \pm 0.01 \mu\text{g/g}$, respectively. So, we can conclude

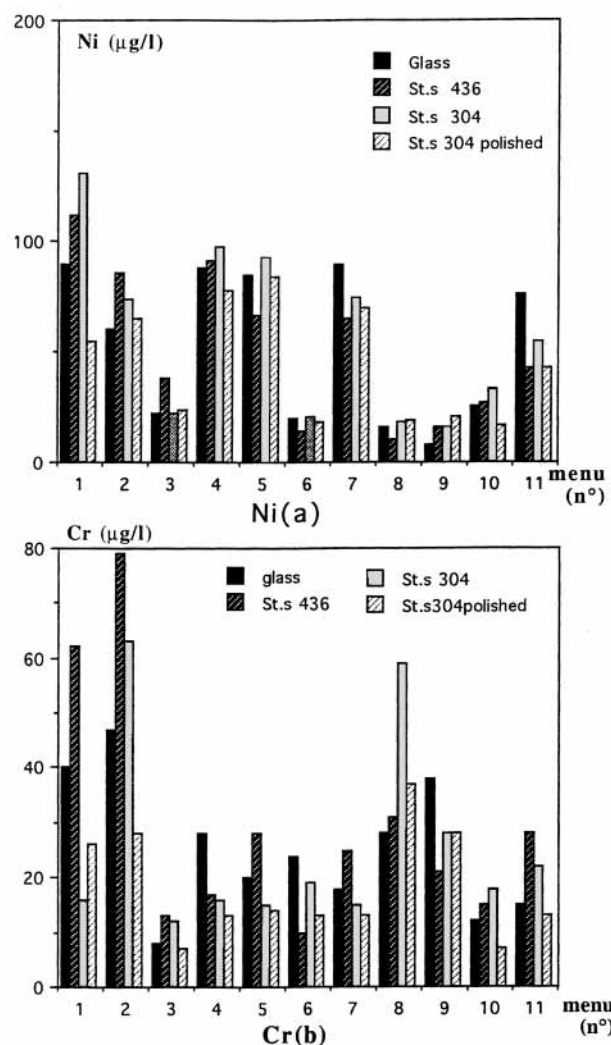


Fig. 1. Ni (a) and Cr (b) intakes from 11 habitual menus cooked in glass or stainless steel (St.s) saucepans.

that no loss or contamination was observed during the overall procedure employed. For analytical validation, the limit of detection obtained for nickel and chromium was $0.5 \mu\text{g/l}$. Intra- and inter-assay reproducibility were within acceptable values: – for nickel 7.8% and 8.4%, respectively, for a sample of approximately $25 \mu\text{g/l}$; – for chromium 8.2% and 9.4%, respectively, for a sample of approximately $34 \mu\text{g/l}$.

The field blank studies demonstrated that no detectable contamination of the test samples occurred during sample preparation (peeling, homogenization, mineralization). Variability linked to the different steps in the procedure (weighing and cooking of foods, homogenization, mineralization and measurement) was controlled in the course of the study (coefficient of variation (CV) < 10%). The levels of nickel and chromium contained in the 11 habitual menus cooked in glass or stainless steel

saucepans and the respective pH are given in Table 2 and Fig. 1. The NIST certified reference material with a theoretical value of $50 \mu\text{g/l}$ gave a value of $50.1 \mu\text{g/l}$, that is, a difference of 0.05%.

ANOVA statistical analysis permitted calculation of variances relative to the menus, containers and also to the different steps in sample preparation (peeling, cooking, homogenization, mineralization) and analysis (Fig. 2). In order to compare our results with other authors, we evaluated the nickel and chromium intake for an average food portion taking into account the food groups (Fig. 3).

Discussion

The levels of nickel and chromium found in the 11 habitual menus cooked in glass and stainless steel saucepans fall within or are close to the range of nickel and chromium contents of these foods reported in the literature.

Statistical analysis of the data (Fig. 2) revealed the following points:

- 86.5% (for nickel) and 55% (for chromium) of the variability was due to the great difference in nickel and chromium intake from the different

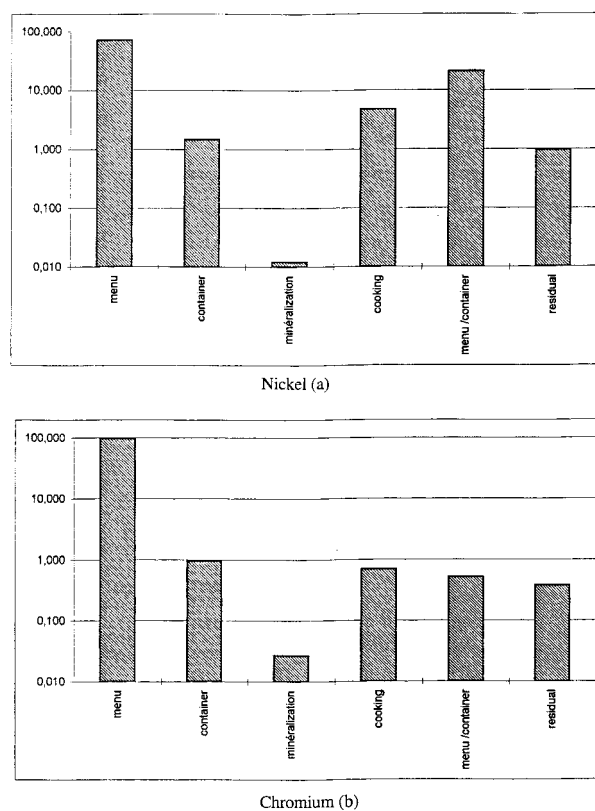


Fig. 2. Relative variability of different variances (Ni (a), Cr (b); logarithmic scale).

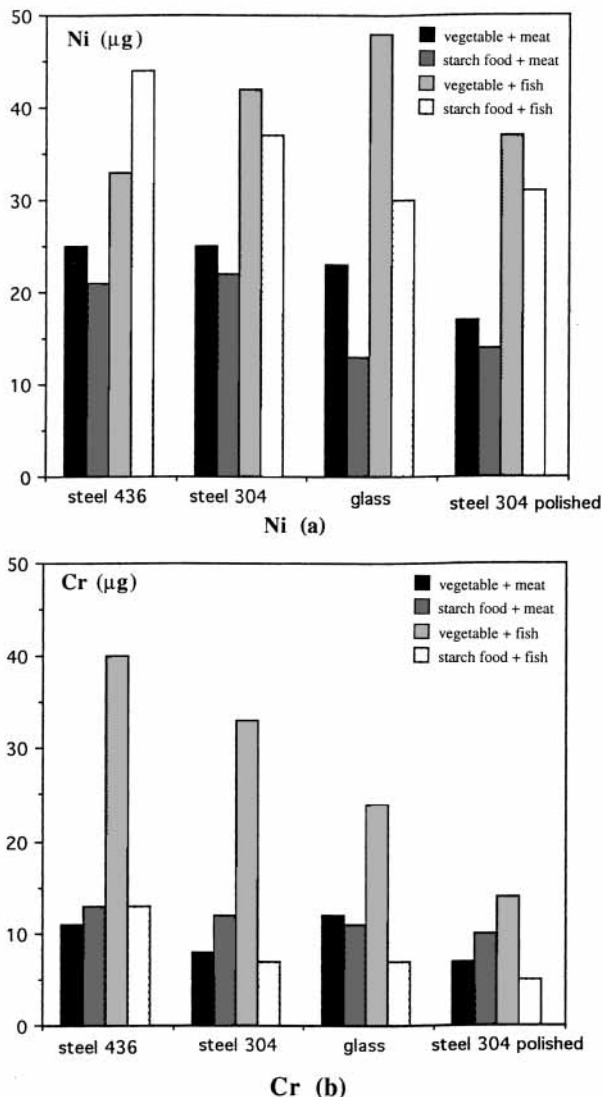


Fig. 3. Ni (a) and Cr (b) intakes from an average portion of food.

menus. Apart from a hypothetical release from utensils, the different menus showed very high nickel levels which, in addition, varied greatly from one menu to another (Table 2, Fig. 1; see results in glass pan). We noted high CV: 61% for nickel and 70% for chromium.

- only 2% (for nickel) and 6% (for chromium) of the variability seemed to be linked to different nickel release depending on the type of cooking utensil used. We noted a significant difference between the glass and stainless steel saucepans (particularly in the as delivered state), but this was very low compared to the levels of nickel and chromium contained in the menus. Release from the polished stainless steel 304 saucepan was the lowest (Table 2, Fig. 1).
- 10% (for nickel) and 25.5% (for chromium) of

the variability can be explained by the very significant utensil/menu interaction, that is, the difference in metal release by the container depending on the menu. Although statistically significant, this difference only concerned very low nickel levels.

- 1.5% (for nickel) and 13.5% (for chromium) of the variability was due to different factors of preparation (weighing of the food, cooking, homogenization, mineralization) and corresponded to residual variance. This source of variation was controlled and it appeared that it was insignificant.

All values fall within or are close to the range of nickel content of these foods reported in the literature (9–12).

The pick-up of nickel and chromium by several menus cooked in the same stainless steel utensils was different according to the type of food (Fig. 3), but we can observe that the values remain at low levels. The present study was based on analysis of classical mixed diets served for consumption and not only of raw foods; preliminary studies used acidic foods (7, 9–13) which do not reflect daily French consumption. We treated the menus according to a well-established protocol and a validated analytical method. The different sources of variability such as cooking, homogenization and mineralization were validated; statistical analysis showed that the variance linked to these last factors was insignificant.

We have compared the statistical results of our study with World Health Organization (WHO) recommendations concerning daily intakes of nickel and chromium. To do this, we evaluated for each pair “type of menu/cooking utensil” the nickel and chromium intake for an average food portion (Fig. 3). Statistical tests indicated that daily nickel and chromium intake from food cooked in stainless steel utensils was insignificant. Mean intakes of nickel and chromium were under the tolerable daily intake (TDI) recommended by the WHO: (i) TDI for nickel (food+water)=5 µg/kg of body weight (considering the mean body weight of a man to be 60 kg); (ii) TDI for chromium (water)=50 µg/l (the WHO gives no recommendations for chromium in food).

Our results show that the contribution made by stainless steel cooking utensils to nickel and chromium content of the diet is minimal and within the normal day-to-day variation of nickel intake. Some authors noted a high pick-up by food cooked in stainless steel utensils but insisted on the quality of the material which was poor in chromium (7); in fact, it has been recognized that chromium improves resistance to corrosion.

It may be concluded that there is no advantage to be gained by nickel-sensitive persons who suffer from contact allergy, in avoiding the use of stainless steel utensils, provided that they are of good quality.

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