

Stainless Steel Leaches Nickel and Chromium into Foods during Cooking

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ABSTRACT: Toxicological studies show that oral doses of nickel and chromium can cause cutaneous adverse reactions such as dermatitis. Additional dietary sources, such as leaching from stainless steel cookware during food preparation, are not well characterized. This study examined stainless steel grades, cooking time, repetitive cooking cycles, and multiple types of tomato sauces for their effects on nickel and chromium leaching. Trials included three types of stainless steels and a stainless steel saucepan, cooking times of 2–20 h, 10 consecutive cooking cycles, and four commercial tomato sauces. After a simulated cooking process, samples were analyzed by ICP-MS for Ni and Cr. After 6 h of cooking, Ni and Cr concentrations in tomato sauce increased up to 26- and 7-fold, respectively, depending on the grade of stainless steel. Longer cooking durations resulted in additional increases in metal leaching, where Ni concentrations increased 34-fold and Cr increased approximately 35-fold from sauces cooked without stainless steel. Cooking with new stainless steel resulted in the largest increases. Metal leaching decreases with sequential cooking cycles and stabilized after the sixth cooking cycle, although significant metal contributions to foods were still observed. The tenth cooking cycle resulted in an average of 88 μg of Ni and 86 μg of Cr leached per 126 g serving of tomato sauce. Stainless steel cookware can be an overlooked source of nickel and chromium, where the contribution is dependent on stainless steel grade, cooking time, and cookware usage.

KEYWORDS: chromium, nickel, stainless steel, contact dermatitis, allergic sensitivity, food safety

INTRODUCTION

Over the last several decades, the prevalence of allergic contact dermatitis (ACD) has significantly increased.^{1,2} Nickel and to a less extent chromium are considered a frequent cause of ACD. Both metals present many diverse potential sources. Nickel is a trace metal that occurs naturally in soils, water, plants, and animals. Although Ni is known to be essential to the health of some species, it has not been proven to be essential to the health of humans.³ There are no known human enzymes or cofactors dependent on Ni for normal function.⁴ Despite its unknown essentiality, humans are exposed to Ni via the diet. Foods high in nickel include peanuts, peas, oatmeal, and milk chocolate, 956, 699, 495, and 871 $\mu\text{g}/\text{kg}$, respectively.⁵ In 2001, the Tolerable Upper Intake Level (UL) of Ni was decreased to 1000 μg per day.⁶ Adults in the U.S. are estimated to ingest an average of 69–162 μg of Ni per day.⁷

Toxicological studies indicate that a single oral dose of Ni as low as 67 μg can cause recurrence of ACD, flare up eczema, or lead to systemic dermatitis in individuals sensitive to nickel.^{8,9} Studies have shown the severity of dermatitis has a dose-dependent relationship to oral doses of nickel.⁸ Approximately 10% of people are afflicted by systemic dermatitis from nickel exposure, which is more prevalent in women.⁹ While there are some studies on the release of nickel from stainless steel jewelry,¹⁰ there is less data available on other exposure routes such as from cookware.^{2,11,12}

Like Ni, Cr can cause ACD. A single oral dose of 2500 μg of Cr can cause dermatitis in sensitized individuals.¹³ Humans are exposed to Cr through food and drinking water. Chromium levels in foods are generally estimated to be low, about 10–1300 $\mu\text{g}/\text{kg}$.¹⁴ Chromium concentrations in U.S. drinking waters range from 0.2 to 35 $\mu\text{g}/\text{L}$, and the U.S. EPA has set a

maximum contamination level at 100 $\mu\text{g}/\text{L}$ for drinking water.¹⁴ Low levels of Cr(III) are essential for human health and metabolism of glucose, protein, and fat; however, adverse effects of oral Cr exposures, such as dermatitis, are also known.¹⁴ The average daily intake of chromium in the U.S. population has been estimated at 76 μg , while the US FDA recommended daily intake is 120 μg Cr.¹⁴ It is recommended that individuals sensitive to metals lower their exposure.^{8,9,15} However, an overlooked source of Cr may be leaching from stainless steel used during cooking processes.^{16–18}

Stainless steels are used in the food and beverage industry due to their thermal conductivity and resistance to corrosion. Stainless steel grades 304 and 316 are the most commonly used in the food and beverage industry.¹⁹ These SS grades differ by their chemical compositions of metals including nickel and chromium. SS grade 304 contains approximately 18–20% mass fraction chromium, and 8–12% nickel, whereas SS grade 316 contain approximately 16–18% chromium, and 10–14% nickel; other metals may also vary within the grades.²⁰ Stainless steels often maintain direct and prolonged contact with food during cooking and manufacturing processes.

Previous research conducted on the release of metals from stainless steel during cooking procedures has generally only tested one SS grade, and of these studies few varied the foods or conditions.^{15–18,21} Often nonacidic foods were tested, such as dried fruits and basic soups, or they tested nonfood matrixes like single chemical component acidic solution.^{15–18,21} Acidic

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solutions, like acetic acid, may not be sufficiently similar to acidic foods that are composed of a complex array of chemistries. While overall the results suggest that Ni and Cr are leached from stainless steel into nonfood acidic solutions and foodstuffs during cooking processes,^{15–18} the estimated Ni or Cr contribution from cookware to a serving of acidic food is not well characterized. In addition, the studies reached contradicting conclusions concerning the severity and significance of metal leaching and the factors, such as SS grade and cooking time, which contribute to metal leaching. Results between studies were also highly inconsistent. This may be due to variations in experimental conditions such as food type, cooking duration, and other uncontrolled variables.

The objectives of this study were to quantify the amount of Ni and Cr leached from stainless steels into a real acidic food, during realistic simulated cooking procedures, and to identify contributing cooking conditions to metal leaching. In this study, three stainless steels equivalent to those used in the food industry and cooking wares and a stainless steel cooking pot were tested in a series of systematic simulated cooking scenarios. Cooking scenarios were established to test grade of stainless steel, cooking apparatus, cooking duration, cooking cycles, and tomato sauce manufacturers for their effects on metal leaching.

MATERIALS AND METHODS

Reagents and Test Materials. Plasma grade elemental standard solutions from Alfa Aesar (Ward Hill, MA) and Fisher (Pittsburgh, PA) Optima grade concentrated nitric acid were used in all experiments. Three stainless steel Standard Reference Materials (SRMs), NIST 121d, NIST 123c, and NIST 160b, from the National Institute of Standards and Technology (Gaithersburg, MD) were used. The SRMs are equivalent in Ni and Cr mass fraction to stainless steel (SS) grades commonly used in cookware; other constituents were also nominally the same, Table 1. All SRMs were in chip form and had the

Table 1. Metal Materials Exposed to Tomato Sauce during Cooking Processes

SRM description	stainless steel equivalent grade	chemical composition (% mass)	
		Ni	Cr
NIST 121d	304	11.18 ± 0.21	17.50 ± 0.15
NIST 123c	304	11.34 ± 0.15	17.40 ± 0.15
NIST 160b	316	12.35 ± 0.22	18.37 ± 0.21
Ni-131		99.9	
saucepan ^a	316	10–14	16–18

^aSaucepan Ni and Cr concentrations estimated range taken from Atlas Steel 2000.

same range of particle size and surface area. The stainless steel chips used in this study had particle size ranging between 0.5 and 1.18 mm millings. Subsamples were carefully taken to ensure representativeness. Pure Ni pellets, Ni-131, from Atlantic Equipment Engineers (Bergenfield, NJ) were used as a positive control for Ni leaching. One commercially obtained grade 316 stainless steel saucepan was tested. The stainless steel saucepan was washed with water and soap prior to use as recommended by the manufacturer, and then three additional 18 M Ω cm rinses were performed. Four traditional style commercially obtained tomato sauces (TS) were evaluated as the food matrix (tomato sauces A–D) and were manufactured by different companies and at different manufacturing locations. The acidity of the tomato sauces tested ranged between 4.17 and 4.3 pH.

Instrumentation. Samples were digested using an Environmental Express AutoBlock (Charleston, SC). A Perkin-Elmer (Norwalk, CT)

Sciex Elan 6000 inductively coupled plasma mass spectrometer (ICP-MS) with a Rytan spray chamber and Crossflow nebulizer with GemTips and a PE AS91 auto sampler were used to analyze sample extracts. ICP-MS parameters included: nebulizer gas flow, 0.91 L/min; dual detector mode; peristaltic pump rate, approximately 2.5 mL/min; PTFE tubing; 3 replicates, 1 reading/replicate, 30 sweeps/reading; sample flush delay, 35 s; read delay, 15 s; wash delay, 45 s. Quantitation was based on Ni⁶⁰ and Cr⁵² with Ge⁷⁴ used as an internal standard. To determine instrument detection limits (IDLs) and the limit of quantitation (LOQ), the lowest calibration standard that resulted in a signal-to-noise ratio greater than 3:1 was found for each metal. The lowest calibration standard was repeatedly analyzed ($n \geq 7$), and a standard deviation was calculated for each metal. IDLs were determined by multiplying the resulting standard deviation estimates by the student *t*-value corresponding to the appropriate degree of freedom and 99% confidence.²² The limits of quantitation (LOQ) for nickel and chromium was calculated by multiplying IDLs by 5 and determined to be 0.085 and 0.807 $\mu\text{g/L}$, respectively

Sampling and Preparation. To simulate home cooking scenarios, the following sampling procedure was established. For each test, 5 g of tomato sauce was weighed into high density polyethylene digest tubes. Tomato sauce background samples contained no test metal, while positive Ni leaching controls contained 1 g of Ni pellets. All SS exposure samples contained 1 g of stainless steel NIST chips, Table 2. All samples were then cooked in the AutoBlock at 85 °C. This temperature was maintained for the given experimental cook time. The TS was separated from the test metal sample via quantitative transfer into clean digest tubes.

A new SS grade 316 saucepan was tested for metal leaching using ~751 g of TS cooked for 20 h. The sauce pan was placed on a hot plate and was heated to 85 °C, and the temperature was maintained for a cook time of 20 h. This time point was chosen to illustrate a realistic yet high exposure scenario.

All TS samples were then homogenized and digested using an adapted U.S. EPA method 3050b. Briefly, the TS samples were placed into AutoBlock, and 2 mL of nitric acid was added and left to react at room temperature overnight. An additional milliliter of nitric acid was added, and the samples were heated to 85 °C, typically for 12 h. Samples were diluted to 10 mL with 18 M Ω cm water, vortexed, and filtered with PALL (Port Washington, NJ) 0.45 μm polyvinylidene difluoride membrane filters. 0.25 mL of sample extracts was combined with an internal standard solution of Ge, and diluted to 5 mL in 1% nitric acid. The samples were then analyzed by ICP-MS.

Each cooking scenario and tested condition are listed and defined in Table 2. Test conditions include four stainless steels/test metals and a cooking pot, four cooking times, 10 cooking cycles, and four tomato sauces each in replicates of four to five.

Quality Control. Quality control (QC) samples were employed throughout the study, accounting for 30% of all samples analyzed. QC samples included blanks, predigestion fortifications of nickel and chromium, continuing calibration verifications (CCV), and certified reference materials. A six-point calibration with a regression coefficient of 0.998 or greater for both nickel and chromium was used in analyzing samples with ICP-MS. CCV standards and instrument blanks were analyzed prior to and post sequence and at a minimum of every 10 samples during each sequence to ensure instrumentation accuracy. The CCVs were 96–111% recovery, and all instrument blanks were below detection limits. Fortification samples ranged from 102–107% for Ni and 101–109% for Cr, Table 3.

Statistical Analysis. Differences in metal concentrations between experimental samples were evaluated for statistical significance using *R*.²³ For normal data, a one-way analysis of variance (ANOVA) for pairwise multiple comparison procedure was conducted. Generalized linear regression analysis was performed to determine if experimental variables were correlated with leaching. Regression coefficients and ANOVAs were considered to be statistically significant at $p \leq 0.05$.

Table 2. Cooking Scenarios and Materials Used to Test Experimental Variables with Ni and Cr Results in Percent Leached from SRM

experimental variable	<i>n</i>	SRM	SS grade equivalent	cook time (h)	cooking cycles	tomato sauce	mean % Ni leached	mean % Cr leached
stainless steel grade	5	NIST 121d	304	6	1	sauce A	2.85%	1.32%
	5	NIST 123c	304	6	1	sauce A	5.10%	3.25%
	5	NIST 160b	316	6	1	sauce A	4.20%	2.61%
	5	Ni-131		6	1	sauce A	6.60%	
	5	saucepan	316	20	1	sauce A		
cooking time	4	NIST 123c	304	2	1	sauce A	4.26%	3.35%
	4	NIST 123c	304	6	1	sauce A	4.94%	3.71%
	4	NIST 123c	304	20	1	sauce A	6.59%	4.00%
cooking cycle	4	NIST 123c	304	6	1	sauce A	5.10%	3.25%
	4	NIST 123c	304	6	3	sauce A	1.28%	1.11%
	4	NIST 123c	304	6	6	sauce A	0.48%	0.30%
	4	NIST 123c	304	6	10	sauce A	0.48%	0.34%
tomato sauce	5	NIST 123c	304	6	1	sauce A	5.10%	3.25%
	5	NIST 123c	304	6	1	sauce B	5.08%	3.25%
	5	NIST 123c	304	6	1	sauce C	5.11%	3.16%
	4	NIST 123c	304	6	1	sauce D	4.62%	2.67%

Table 3. Quality Control Results for Ni and Cr

sample type	<i>n</i>	concentration (ug/L) Ni ± SD	Ni mean % recovery
instrument blank	16	BLOD ^a	
reagent blank	16	BLOD	
10 ug/L check standard	9	10.4 ± 0.572	96.0%
20 ug/L check standard	5	21.2 ± 0.399	106%
predigest fortification	3	52.1 ± 1.01	104%
sample type	<i>n</i>	concentration (ug/L) Cr ± SD	Cr mean % recovery
instrument blank	16	BLOD	
reagent blank	16	BLOD	
10 ug/L check standard	8	9.64 ± 0.870	96.4%
20 ug/L check standard	8	22.2 ± 0.566	111%
predigest fortification	3	52.3 ± 1.91	104%

^aBLOD = below limit of detection

RESULTS

Grade of Stainless Steel. Four metal SRMs were tested: three are equivalent to stainless steel grades, and one was a nickel metal, Table 1. Tomato sauce samples, cooked in the absence of stainless steel, were found to have on average 0.130 mg/kg Ni and 0.200 mg/kg Cr. This agrees well with previous reports of Ni in tomatoes that ranged from 0.04 to 1.21 mg/kg.²⁴ Tomato sauce exposed to Ni pellets during the simulated cooking procedure contained significantly higher concentrations of Ni than all other samples at 66.0 mg/kg. Tomato sauce cooked with NIST 123c contained 5.93 mg/kg Ni and 5.75 mg/kg Cr, Figure 1A. After 6 h of cooking TS with NIST123c, there was a 26-fold increase in Ni as compared to the control TS and a nearly 30-fold increase in Cr. Tomato sauce cooked with NIST 160b resulted in 5.32 mg/kg Ni and 4.88 mg/kg Cr. Cooking tomato sauce with NIST160b resulted in a 24-fold and a 26-fold increase in Ni and Cr over the control TS. Tomato sauce samples cooked with NIST 121d were found to have the smallest amount of Ni and Cr leached, averaging 3.34 mg/kg and 2.39 mg/kg, respectively. Cooking TS for 6 h with NIST121d resulted in 15- and 12-fold increases in Ni and Cr

over the control TS. There was a small difference between the final amount of Ni and Cr leached into tomato sauce between NIST 123c and 160b: however, both were significantly higher than NIST121d. The average percentages of Ni leached from the stainless steels during the 6 h experiments were 2.78%, 4.13%, and 5.04% for NIST 123c, 160b, and 121d, respectively. The average Cr leached during the 6 h experiments was 1.37%, 2.66%, and 3.30% for NIST 123c, 160b, and 121d, Table 2. All SS equivalent samples resulted in significant increases in both Ni and Cr concentrations in TS during simulated cooking scenarios.

Cooking Time. Figure 1B illustrates the effects of cooking time on Ni and Cr leaching into tomato sauce. We found no significant increases in metal leached between a 2 and 6 h cooking time. However, after 20 h of cooking, Ni concentrations reached 7.63 mg/kg, approximately a 95-fold increase from TS cooked in the absence of stainless steel. Similarly, after 20 h of cooking, Cr concentrations averaged 7.06 mg/kg, nearly a 9-fold increase from the control TS. These data show that significant increases in Ni and Cr leaching occur with increased cooking times.

Cooking Cycles. Ten cooking cycles were conducted to test the effects of repeated stainless steel usage on metal leaching. All samples exposed to SS during cooking resulted in significantly higher concentrations of Ni and Cr as compared to the control TS regardless of the number of cooking cycles. Nickel and chromium concentrations were highest in the first cooking cycle. Sequential cooking cycles resulted in decreased Ni and Cr content; after three cooking cycles, samples contained 1.61 mg/kg of Ni and 2.03 mg/kg of Cr. While this represents about a 65% reduction in Ni from the first cook cycle, it is still about a 20-fold increase from unexposed tomato sauce. Similarly, by the third cooking cycle, Cr decreased about 35% from the first cooking cycle, but still was 2.5-fold above the unexposed tomato sauce. Metal contributions from the stainless steel appeared to reach a steady condition after six cooking cycles; there was no statistical difference between the sixth and tenth cooking cycle for either Ni or Cr. Nonetheless, after the sixth cooking cycle, Ni and Cr contributions were still significantly above the control TS. There was approximately an 8-fold increase in Ni and 3-fold increase in Cr observed above the unexposed control TS. Although the amount of metal

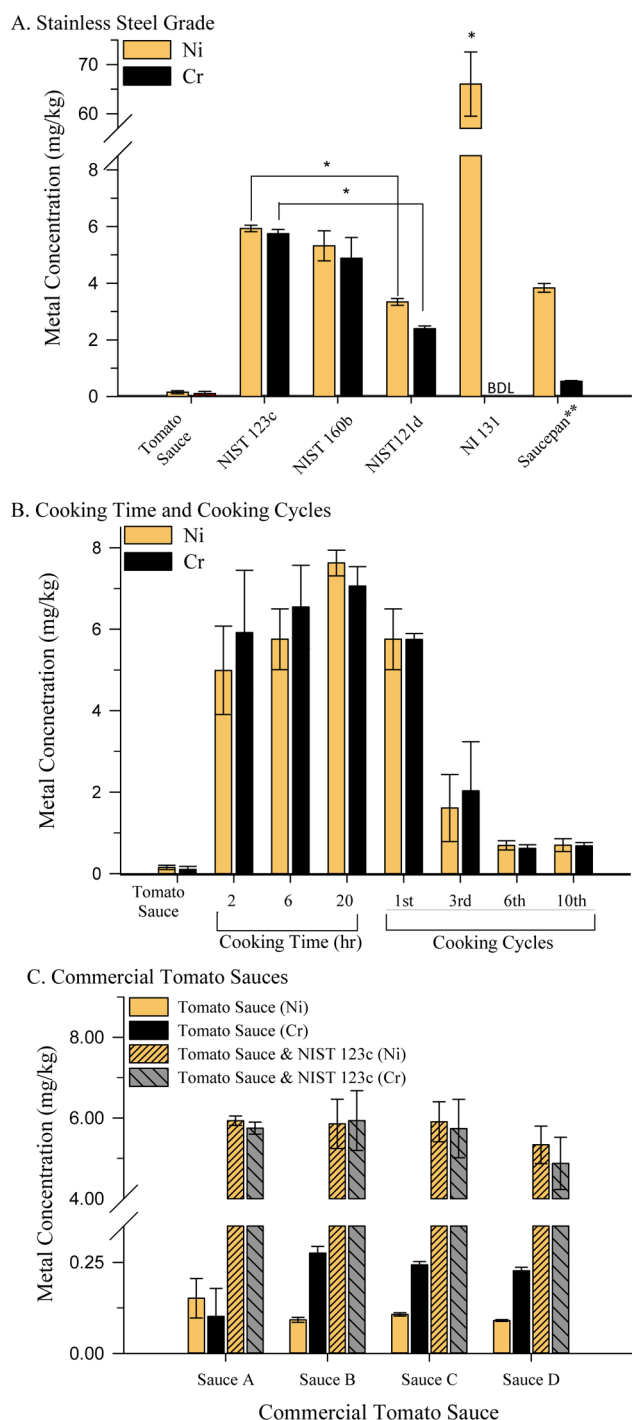


Figure 1. Metal released from stainless steel into tomato sauce. (A) Nickel and chromium concentrations (mg/kg) in commercial tomato sauce cooked for 6 h in the absence of stainless steel, with stainless steel SRMs, nickel pellets, or a stainless steel saucepan ($n = 5$). (B) Nickel and chromium concentrations (mg/kg) in commercial tomato sauce cooked in the absence of stainless steel or with NIST 123c, the equivalent of 304 stainless steel ($n = 4$). 2, 6, and 20 h cooking times are shown. Also, the first, third, sixth, and tenth cooking cycles ($n = 4$) each shown. (C) Nickel and chromium concentrations (mg/kg) in four commercially obtained tomato sauces (sauces A–D) cooked in the absence of stainless steel ($n = 4$), and with NIST 123c, the equivalent of SS grade 304 ($n = 5$). *Indicates statistical difference at $p = 0.05$ or less. **A 20 h cook time was used while testing the SS grade 316 saucepan.

leaching initially decreased with cooking cycles, significant amounts of both Ni and Cr continue to leach after multiple cooking cycles and appear to reach a constant condition.

Commercial Tomato Sauce (TS). Four different commercially obtained tomato sauces were analyzed for their effect on metal leaching when cooked in the presence of NIST123c stainless steel. All tomato sauces had similar initial Ni and Cr concentrations when cooked in the absence of stainless steel, ranging from 0.090 to 0.224 mg/kg Ni, and 0.200–0.275 mg/kg Cr. All four tomato sauces were found to have similar effects on the total amount of Ni and Cr leached. Mean Ni concentrations of tomato sauces cooked with stainless steel ranged from 5.86 to 6.14 mg/kg, and resulted in approximately 64–68-fold increases in Ni as compared to the control TS. Mean Cr concentrations of TS cooked with stainless steel ranged from 4.87 to 5.96 mg/kg, and resulted in approximately 21-fold increases in Cr as compared to the unexposed TS. The four TS were not significantly different for either Ni or Cr. With a similar matrix and pH, as expected, all tomato sauces had similar effects on metal leaching despite originating from different commercial tomato sauce manufacturing companies.

SS Saucepan. A two quart SS 316 grade saucepan, typical of home cookware, was used to directly estimate metal leaching into tomato sauce. The Ni concentration in TS cooked in the saucepan increased to 3.84 mg/kg after a 20 h cook time, Figure 1A. This represents nominally a 50-fold increase in Ni concentration in TS cooked in the saucepan. While less dramatic, Cr also increased significantly in TS from 0.200 to 0.6 mg/kg, nominally a 3-fold increase when cooked in a SS saucepan.

After 20 h of cooking, TS cooked with the equivalent SS SRM, NIST123c, had about twice the concentration of Ni as that found in TS cooked with the saucepan, Figure 1A and B. Likewise, Cr concentrations were lower in saucepan (0.536 mg/kg) TS than when cooked with NIST123c (7.06 mg/kg). The sauce to surface area ratio was different between the two. The ratio of tomato sauce to surface area of the saucepan in contact with the tomato sauce (approximately 486 cm²) was approximately 1:0.62. In contrast, the NIST stainless steel chips had a surface area of approximately 25.0 cm², and the tomato sauce to surface area ratio was 1:5. The difference in ratio of sauce to surface areas between the saucepan and the NIST SS is about a factor of 10.

DISCUSSION

Stainless Steels and Cooking Scenarios. We found that different SS grades have different leaching properties in tomato sauce. The mass of Ni in stainless steels did not correlate with the amount leached. NIST 160b has a larger Ni mass fraction than the other SS tested; however, we observed that it did not have the largest amount of Ni leached considering both Ni mass or % Ni leached, Table 2. Further illustration is that NIST 121d and 123c have similar Ni content, but the amount of Ni and Cr leached was significantly different. NIST 123c leached about 56% more Ni and 42% more Cr than NIST 121d, yet both are equivalent to SS grade 304. Other constituents beyond Ni content in SS contribute to Ni leaching. For example, it has been reported that an increased chromium oxide layer on the surface of SS is known to have protective properties against corrosion.¹⁹ A chromium oxide protection layer is consistent with our findings; NIST160b has the highest Cr content and Ni content, but does not have the highest nickel leaching, suggesting that Cr alone or with potentially other constituents

reduces Ni leaching. Not all SRM have certified values for all elements, but for those that were available for all three SS (C, Cr, Mn, Ni, Cu, and Mo), no single element correlated with the Ni or Cr leaching trends observed.

Longer cook times in the first cooking cycle produced statistically higher Ni and Cr leaching concentrations at 20 h consistent with findings for other metals and cookware. It has been demonstrated that Pb in glazed cookware and storage containers can leach with test acidic solutions and increased with duration of contact.²⁵ Seasoning of the samples through multiple cook cycles reduced the amount of Ni and Cr leached, although it did not eliminate either. The reduction of metal leached in the later cooking cycles was not due to less metal left in the material, as only a very small percentage (<0.00004%) of the total nickel and chromium was removed with any given cooking cycle. As discussed above, the formation of protective oxides, like chromium oxide, likely contributed to the reduction in Ni and Cr leaching with seasoning. The protective effect seems to have been maximized by the sixth cooking cycle, as no further change in leaching was observed.

Chromium and lead leaching into acetic acid solutions has been shown to increase with stainless steel surface area.²⁶ Metal leaching from stainless steel has been found to be dependent on the ratio of surface area of the stainless steel to the volume of solution it is in direct contact with.²⁶ We found the TS cooked in a SS grade 316 saucepan had lower Ni concentrations than the 20 h NIST 123c SS. As well, the saucepan had lower Ni than the NIST 160d, SS grade 316 equivalent. Both the NIST samples and the saucepan had different sauce to surface area ratios. On the basis of sauce to SS surface area, we would have expected nearly a 10-fold reduction in Ni and Cr in the saucepan as compared to the stainless steel NIST chips. Interestingly, we only observed a 2-fold reduction in nickel in the saucepan as compared to the stainless steel. Chromium was, however, about 10-fold less in the saucepan as compared to the NIST SS chips consistent with our sauce to surface area calculations and expectations. Additional factors, such as the specific chemical composition and saucepan manufacturing, may be contributing to the variability observed between the SS 316 grades and with the saucepan for the Ni leaching. Although there are minimum requirements for specific grades of stainless steel, they still represent a range in nickel and chromium concentrations as well as other elements.²⁰

Effects of Cooking Scenarios on Dietary Exposure and ACD. To estimate potential oral exposures, nickel and chromium per serving of tomato sauce were calculated from the mean concentrations of select experimental samples. A single serving of tomato sauce is defined by the manufacturer to be 126 g (about 4.5 oz). Figure 2A presents the amount of Ni per serving of tomato sauce in addition to the maximum estimated daily dietary Ni intake for U.S. adults reported as 162 $\mu\text{g}/\text{day}$.⁷ As well, the UL for Ni of 1000 $\mu\text{g}/\text{day}$ ⁶ is displayed in Figure 2A. Dermatitis resulting from dietary nickel has been demonstrated in multiple studies.² Tomato sauce cooked in the absence of stainless steel would comprise a minimal portion of the total daily intakes, with 16 μg per serving of tomato sauce. However, these results suggest that TS cooked in a new saucepan would contain 483 μg of Ni per serving of tomato sauce, nearly one-half the tolerable upper intake level for a day. A dose of only 67 μg of nickel was associated with cutaneous reactions in 40% of nickel-sensitive participants.^{2,11} The Ni leached from the saucepan exceeds the levels found by Jensen that caused cutaneous reactions.¹¹ Tomato sauce cooked in

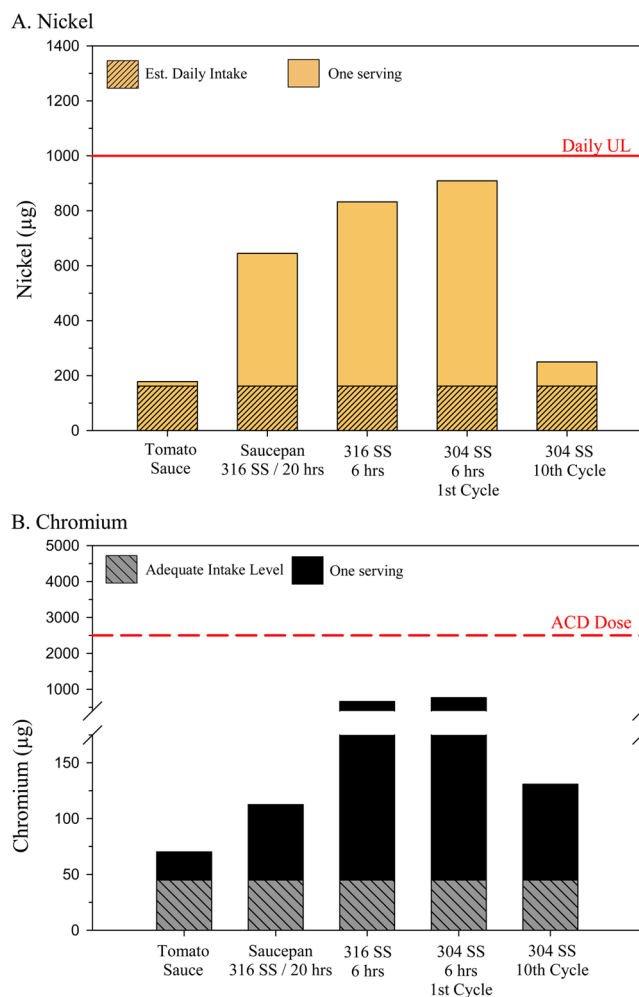


Figure 2. Total daily intake for Ni and Cr and potential contributions from cooking scenarios. Potential (A) nickel (μg) and (B) chromium (μg) from one serving (126 g) of tomato sauce from various cooking scenarios in addition to estimated maximum daily nickel intakes for U.S. adults (162 $\mu\text{g}/\text{day}$)⁷ and adequate maximum chromium intake level of a healthy individual, 45 $\mu\text{g}/\text{day}$.¹⁴ Nickel levels are compared to the tolerable upper intake level (UL) (1000 $\mu\text{g}/\text{day}$),⁶ and chromium levels are compared to the lowest dose known to cause ACD, 2500 $\mu\text{g}/\text{day}$.¹³

NIST160b, equivalent to a 316 stainless steel, approaches the UL of 1000 μg for both 20 and 6 h cook times with 961 and 747 μg of nickel per serving, respectively. At the tenth cooking cycle, TS prepared with NIST160b still showed significant nickel contributions to dietary intakes, 88.2 μg per serving of sauce, Figure 2A.

In a similar analysis, the amount of Cr per serving of TS is added to the maximum adequate intake level (as defined by the Institute of Medicine), 45 $\mu\text{g}/\text{day}$,¹⁴ then compared to the estimated dose threshold associated with ACD, 2500 $\mu\text{g}/\text{day}$.¹³ Tomato sauce cooked in the absence of stainless steel would comprise just over one-half of the maximum adequate level, with about 25 μg of Cr per serving, however, well below the estimated threshold associated with ACD. In contrast, all other TS cooked with stainless steel resulted in significantly greater additions to total daily chromium intakes. Tomato sauce cooked in the new saucepan contained 67.5 μg of Cr per serving. Tomato sauce cooked with NIST 160b, the equivalent of 316 stainless steel, contained the largest amount of Cr

measured, 890 μg Cr per serving after 20 h of cooking, and 724 μg Cr per serving after 6 h. At the tenth cooking cycle, one serving of TS still made significant additions to total daily Cr intakes, with 85.8 μg Cr per serving. While a single serving of TS did not exceed the amount known to associate with ACD, Cr from cooking in stainless steel may represent an unrecognized or poorly quantified source of Cr.

The estimated exposures presented in Figure 2 are based on a single 126 g serving of tomato sauce. Additional servings would increase daily metal exposures, and other dietary sources of Ni or Cr would contribute to the overall daily intakes. The leaching of both Cr and Ni from SS into TS may be additive, further aggravating ACD.

All tomato sauce samples that were cooked in the presence of stainless steel using typical cooking procedures showed significantly elevated Ni and Cr concentrations. In addition to other natural dietary sources, stainless steel cookware is an under-recognized source, which can potentially contribute to overall nickel and chromium consumption. For the scenarios tested, the amount of nickel and chromium leached from stainless steel into tomato sauce is independent of tomato sauce brand, but dependent on the grade of stainless steel, cooking time, and previous usage or seasoning of the stainless steel. The effectiveness of avoiding stainless steel cookware to reduce nickel and chromium exposure and its effects on diminishing the effects of ACD is still unknown. However, it appears that recommendations to avoid stainless steel for those with nickel and chromium sensitivities may be prudent.

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Notes

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ABBREVIATIONS AND NOMENCLATURE

ACD, allergic contact dermatitis; CCV, continuing calibration verification; ICP-MS, inductively coupled plasma-mass spectrometry; IDLs, instrument detection limits; LOQ, limit of quantitation; NIST, National Institute of Standards and Technology; SRM, standard reference material; SS, stainless steel; TS, tomato sauce; UL, tolerable upper intake level; BDOL, below limit of detection

REFERENCES

(1) Moennick, J.; Zirwas, M.; Jacob, S. Nickel-induced facial dermatitis: Adolescents beware of the cell phone. *Cutis* **2009**, *84*, 199–200.

(2) Zirwas, M. J.; Molenda, M. A. Dietary nickel as a cause of systemic contact dermatitis. *J. Clin. Aesthet. Dermatol.* **2009**, *2*, 39–43.

(3) Barceloux, D. G. Nickel. *J. Toxicol., Clin. Toxicol.* **1999**, *37*, 239–258.

(4) Denkhaus, E.; Salnikow, K. Nickel essentiality, toxicity, and carcinogenicity. *Crit. Rev. Oncol./Hematol.* **2002**, *42*, 35–56.

(5) Capar, S. G.; Cunningham, W. C. Element and radionuclide concentrations in food: FDA total diet study 1991–1996. *J. AOAC Int.* **2000**, *83*, 157–177.

(6) Trumbo, P.; Yates, A. A.; Schlicker, S.; Poos, M. Dietary reference intakes: Vitamin A, vitamin K, arsenic, boron, chromium, copper, iodine, iron, manganese, molybdenum, nickel, silicon, vanadium, and zinc. *J. Am. Diet. Assoc.* **2001**, *101*, 294–301.

(7) ATSDR. *Toxicological Profile for Nickel*; U.S. Department of Health and Human Services: Atlanta, GA, 2005.

(8) Jensen, C. S.; Lisby, S.; Larsen, J. K.; Veien, N. K.; Menne, T. Characterization of lymphocyte subpopulations and cytokine profiles in peripheral blood of nickel-sensitive individuals with systemic contact dermatitis after oral nickel exposure. *Contact Dermatitis* **2004**, *50*, 31–38.

(9) Sharma, A. D. Relationship between nickel allergy and diet. *Indian J. Dermatol. Venereol. Leprol.* **2007**, *73*, 307–312.

(10) Haudrechy, P.; Mantout, B.; Frappaz, A.; Rousseau, D.; Chabeau, G.; Faure, M.; Claudy, A. Nickel release from stainless steels. *Contact Dermatitis* **1997**, *37*, 113–7.

(11) Jensen, C. S.; Menné, T.; Lisby, S.; Kristiansen, J.; Veien, N. K. Experimental systemic contact dermatitis from nickel: a dose–response study. *Contact Dermatitis* **2003**, *49*, 124–132.

(12) Vrochte, H.; Schätzke, M.; Dringenberg, E.; Wölwer-Rieck, U.; Büning-Pfaue, H. The question of nickel release from stainless steel cooking pots. *Z. Ernährungsweis.* **1991**, *30*, 181.

(13) Veien, N. K.; Hattel, T.; Justesen, O.; Nørholm, A. Oral challenge with metal salts. (I). Vesicular patch-test-negative hand eczema. *Contact Dermatitis* **1983**, *9*, 402–406.

(14) ATSDR. *Toxicological Profile for Chromium*; U.S. Department of Health and Human Services: Atlanta, GA, 2012.

(15) Accominotti, M.; Bost, M.; Haudrechy, P.; Mantout, B.; Cunat, P. J.; Comet, F.; Mouterde, C.; Plantard, F.; Chambon, P.; Vallon, J. J. Contribution to chromium and nickel enrichment during cooking of foods in stainless steel utensils. *Contact Dermatitis* **1998**, *38*, 305.

(16) Marzec, Z.; Marzec, A.; ZarÅba, S. Study of metal release from cookware. *Pol. J. Environ. Stud.* **2006**, *15*, 139–142.

(17) Agarwal, P.; Srivastava, S.; Srivastava, M. M.; Prakash, S.; Ramanamurthy, M.; Shrivastav, R.; Dass, S. Studies on leaching of Cr and Ni from stainless steel utensils in certain acids and in some Indian drinks. *Sci. Total Environ.* **1997**, *199*, 271–275.

(18) Flint, G. N.; Packirisamy, S. Systemic Nickel - the contribution made by stainless-steel cooking utensils. *Contact Dermatitis* **1995**, *32*, 218–224.

(19) Nickel, I. The Effective Use of Nickel in Stainless Steels; <http://www.nickelinstitute.org/en/KnowledgeBase/TrainingModules/EffectiveUseofNickelinStSt.aspx>.

(20) Atlas Steels. *Atlas Steels - Specialty Steels Product Reference Manual*; Atlas Steels: Melbourne, Australia, 2000.

(21) Kuligowski, J.; Halperin, K. Stainless steel cookware as a significant source of nickel, chromium, and iron. *Arch. Environ. Contam. Toxicol.* **1992**, *23*, 211–215.

(22) EPA. *Definition and Procedure for Determination of the Method Detection Limit*; 40 CFR Part 136, Appendix B, revision 1.11, 1995; pp 343–345.

(23) R Core Team. *R: A Language and Environment for Statistical Computing*; R Foundation for Statistical Computing: Vienna, Austria, 2013.

(24) Thomas, B.; Roughan, J. A.; Watters, E. D. *Cobalt, Chromium and Nickel Content of Some Vegetable Foodstuffs*; 1974; Vol. 25, pp 771–6.

(25) Romieu, I.; Carreon, T.; Lopez, L.; Palazuelos, E.; Rios, C.; Manuel, Y.; Hernandez-Avila, M. Environmental urban lead exposure

and blood lead levels in children of Mexico City. *Environ. Health Perspect.* **1995**, *103*, 1036–1040.

(26) Herting, G.; Odnevall Wallinder, I.; Leygraf, C. Corrosion-induced release of chromium and iron from ferritic stainless steel grade AISI 430 in simulated food contact. *J. Food Eng.* **2008**, *87*, 291–300.