

The Release of Nickel from Stainless Steel into Cooked Foods

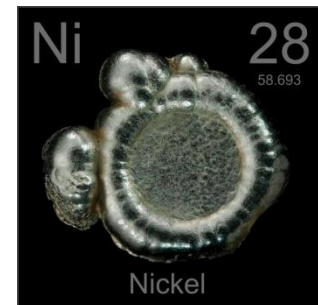
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Nickel in the Environment

- Ubiquitous in environment
 - Soils, plants, and animals
- 5th most abundant element (by weight)
 - 84 mg/kg in crust
 - 15-20 µg/L in surface waters
- Widely used in industry
 - Production of stainless steel and other nickel alloys



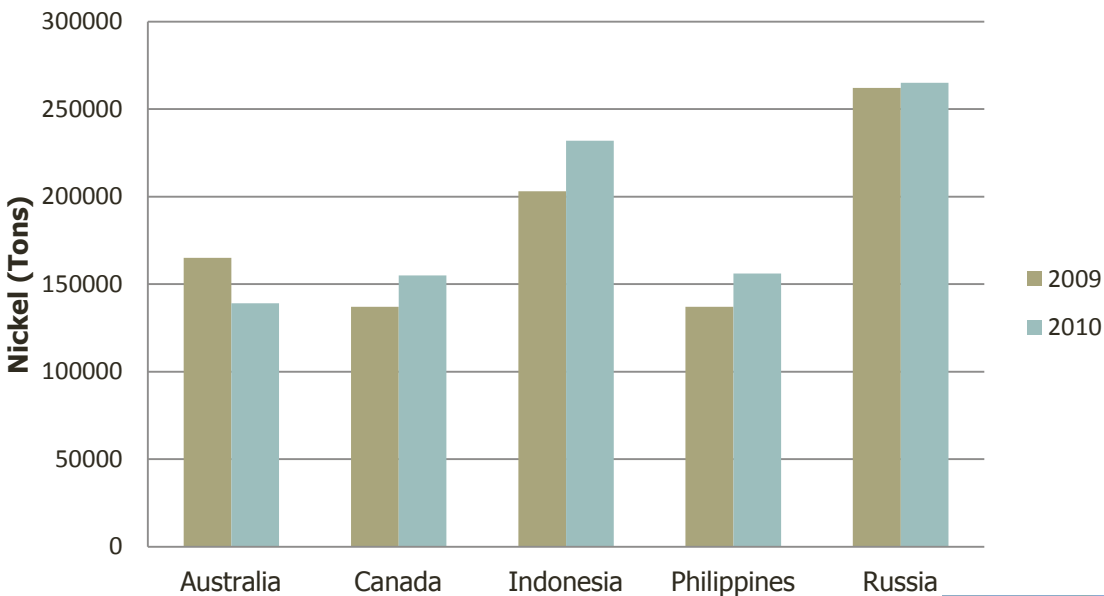
Nickel in the Environment

- Natural and anthropogenic releases of nickel
 - Weathering of rocks/soil, volcanic emissions, vegetation fires
 - Combustion of fossil fuels, tobacco smoke, industry and recycling



Global Nickel Production

Global Nickel Mine Production



Total global nickel production:
1,550,000 tons

U.S. Geological Survey, Mineral Commodity Summaries, January 2011



Pathways of Human Exposure

- Essential for some species
 - Not yet proven for humans
- Oral exposures through food and drinking water
- Estimated Intakes: up to 900 $\mu\text{g}/\text{day}$
- Tolerable upper intake level (UL):
1000 $\mu\text{g}/\text{day}$

Dietary Exposure to Nickel

Food Type	Nickel ($\mu\text{g/g}$)
Spinach	0.02-2.99
Cocoa Beans	8.2-12
Soy Beans	4.7-5.9
Beer	0.003-0.02



Nickel Toxicokinetics

- Absorption dependent on form of nickel
 - 0.09% of nickel metal
- Distribution targets
 - Kidney, cardiovascular system, blood, immune system
- Metabolism not well understood

Effects of Nickel Exposure

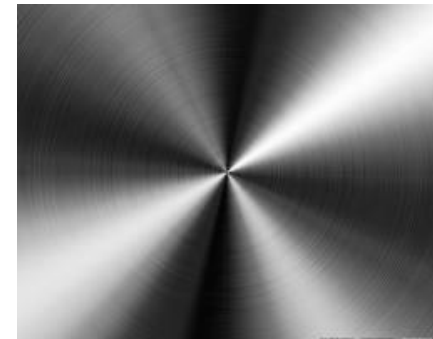
- Nickel Sensitivity
 - 10% of population
 - Allergic Contact Dermatitis (ACD)
 - Oral doses of 3000 μ g
 - Recommended to lower Nickel intake



Kreciz, Beata. "Systemic Contact Dermatitis to Nickel Present in Cocoa in 14-Year-Old Boy." *Pediatric Dermatology* 28.3 (2011): 335-36.

Stainless Steel Background

- Commonly used in food and beverage industry
 - 316, 304, 420
- Chromium oxide surface



Stainless Steel Background

- Chemical composition Ni containing stainless steels

Stainless Steel Grade	Chromium Mass Fraction (%)	Nickel Mass Fraction (%)
316	16-18	10-14
304	17-19	8-10.5
420	12-14	<0.6

Research Questions:

- Is nickel released into foods?
- Is the amount significant?
- What factors contribute to nickel leaching?

Variables Tested:

- Grade of stainless steel
- Cooking time
- Cooking cycles (usage “seasoning”)
- Commercial tomato sauces

Hypotheses:

- Nickel released is inversely proportional to grade of stainless steel
- Nickel released increases with cook time
- Nickel released is constant over multiple cook cycles
- Nickel content is constant for multiple commercial tomato sauces

Materials Used

Description	Identification Number	Stainless Steel Grade Equivalence	Chemical Composition (mass fraction %)	
			Cr	Ni
316a	NIST 121d	316	17.50	11.18
316b	NIST 123c	316	17.40	11.34
304	NIST 160b	304	18.37	12.35
Nickel Pellet	NI-131	—	—	99.9
Saucepan	—	316	—	—

- Four commercially obtained tomato sauces (pH 4.17-4.3)

Study Design

Stainless Steel Grade

- Materials: SRM316/304, NI-131
- Cook time: 6 hr
- Cycles: 1
- Tomato sauce : A

Saucepan

- Materials: Grade 316
- Cook time: 20 hr
- Cycles: 1
- Tomato sauce: A

Cooking Time

- Materials: 316b
- Cook time: 2, 6, 20 hr
- Cycles: 1
- Tomato sauce: A

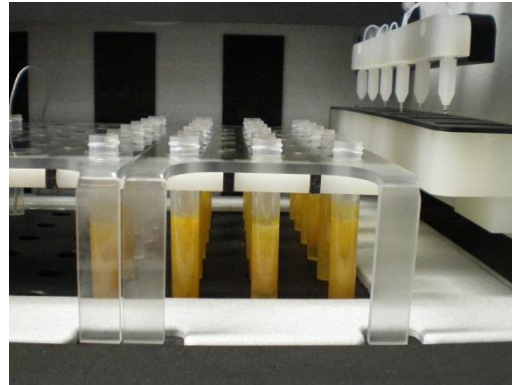
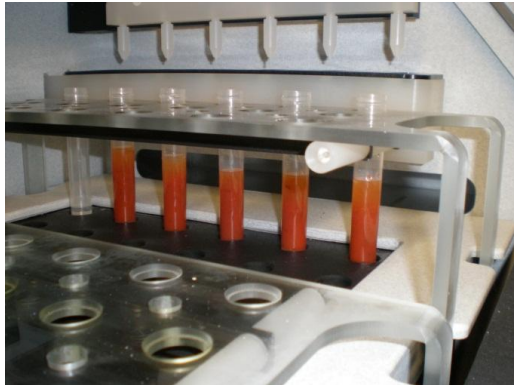
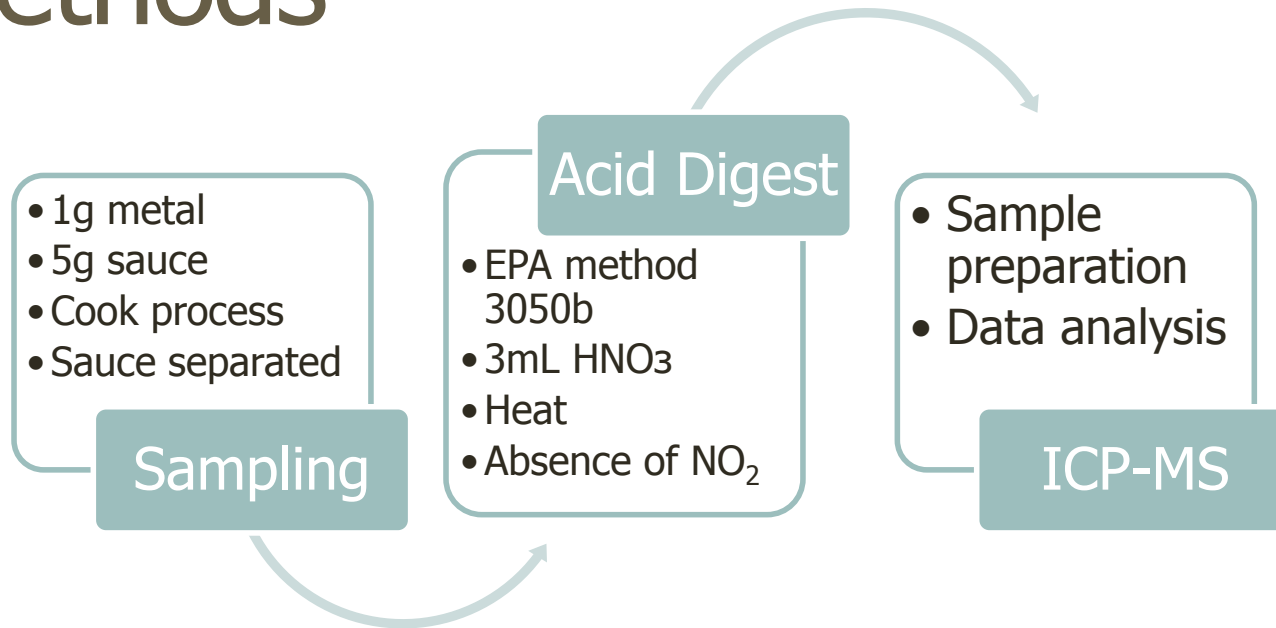
Cooking Cycles

- Materials: 316b
- Cook time: 6 hr
- Cycles: 10
- Tomato sauce: A

Commercial Tomato Sauce

- Materials: 316b
- Cook time: 6hr
- Cycles: 1
- Tomato sauce: A,B,C,D


Methods



Multi-Matrix Method Validation

- Acid digest and ICP-MS analysis validated with Certified Reference Materials
 - Tomato leave, oyster tissue, soils and sediment matrices
 - 0.25g of each CRM was digest and analyzed for 16 metals including Ni
 - Conducted over three different days
 - Replicates of three each day
 - Quality Control Samples
 - Pre-digest fortification

Method Validation

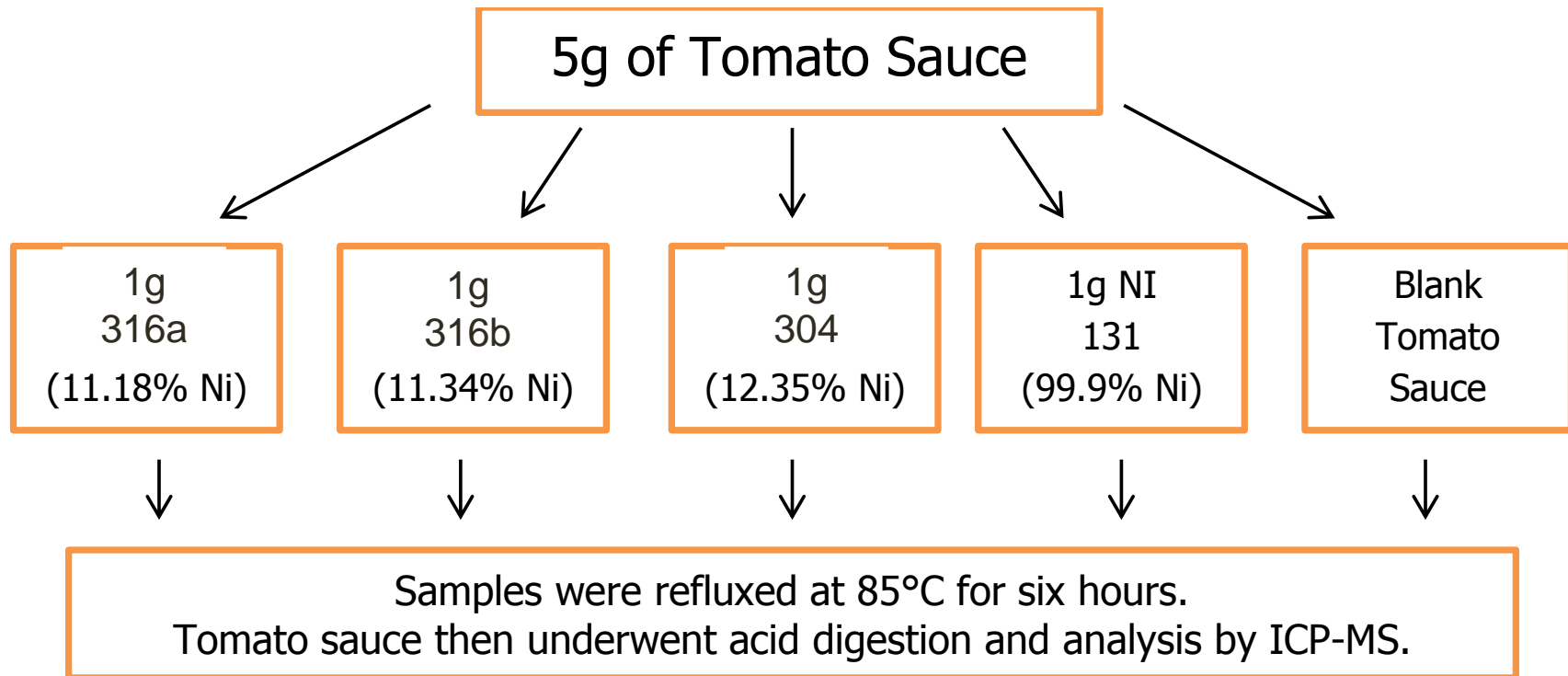
- Precision & Accuracy
 - Average nickel % recovery: 91.3%
 - %RSD: 1.35
 - Average pre-digest sample fortification % recovery: 103%
- Limit of Quantification: 0.085µg/L
 - 
 - n=7

Quality Control Results

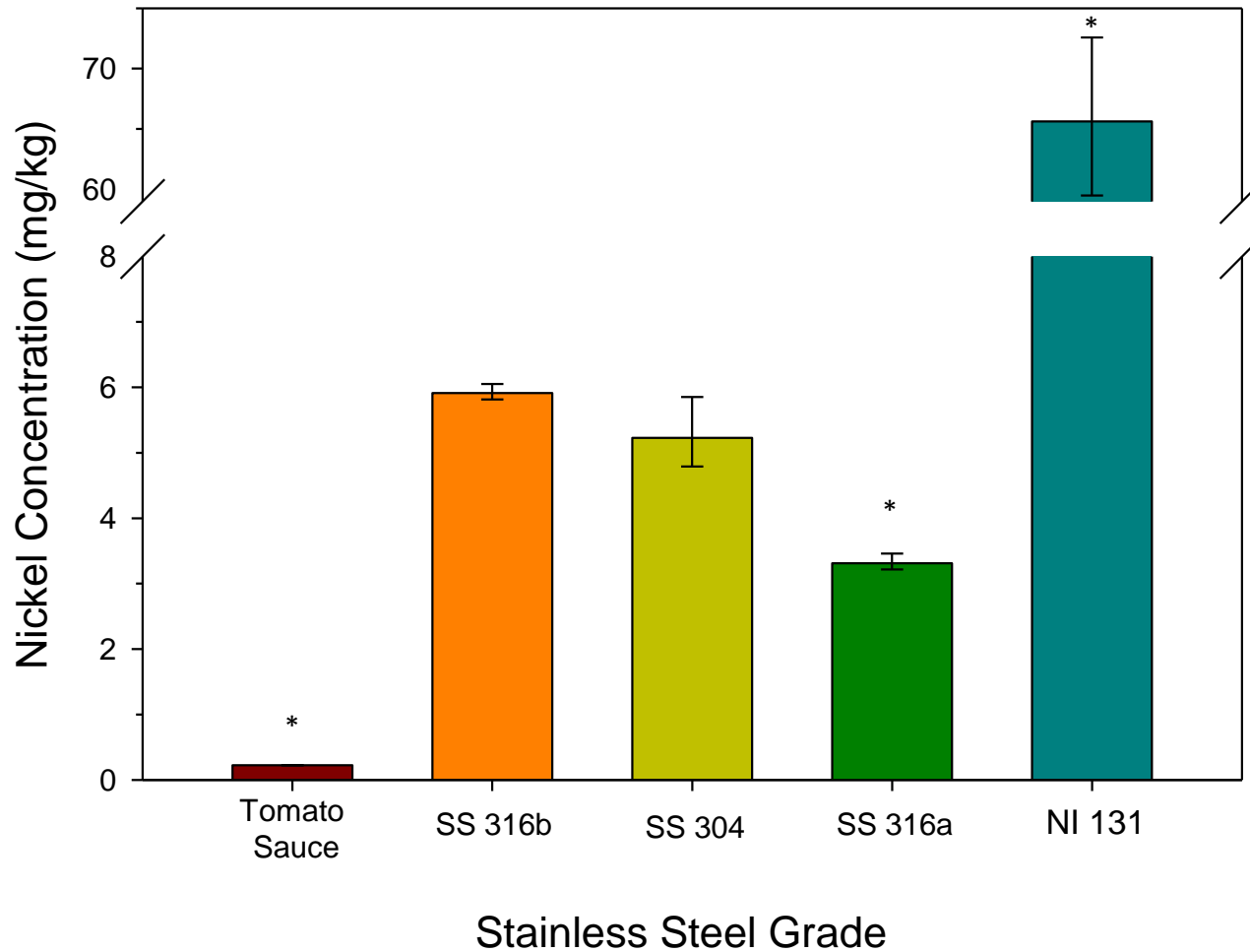
- Quality Control Samples
 - Meet QC data quality objectives

Sample Type	Concentration (µg/L)			% Recovery	n Total
Instrument Blank	BDL			—	16
Reagent Blank	BDL			—	16
10µg/L Check Standard	10.4	±	0.572	96.0	9
20µg/L Check Standard	21.2	±	0.399	106	5
Pre-digest Fortification	52.1	±	1.01	104.2	3

Grade of Stainless Steel



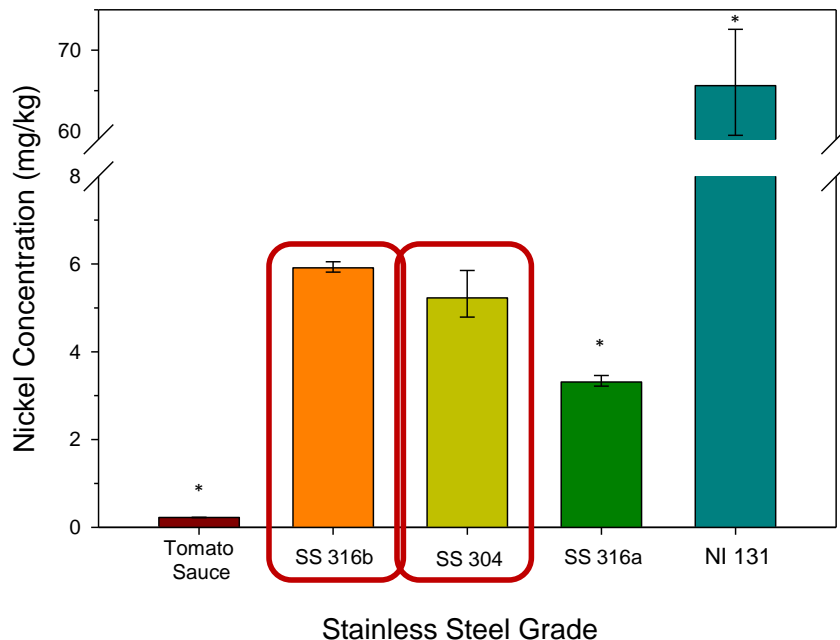
Stainless Steel Grade



n=5; samples deemed significant at $p < 0.05$
* Statistical difference between one or more samples

Discussion

Description	Identification Number	Stainless Steel Grade Equivalence	Chemical Composition (mass fraction %)	
			Cr	Ni
316a	NIST 121d	316	17.50	11.18
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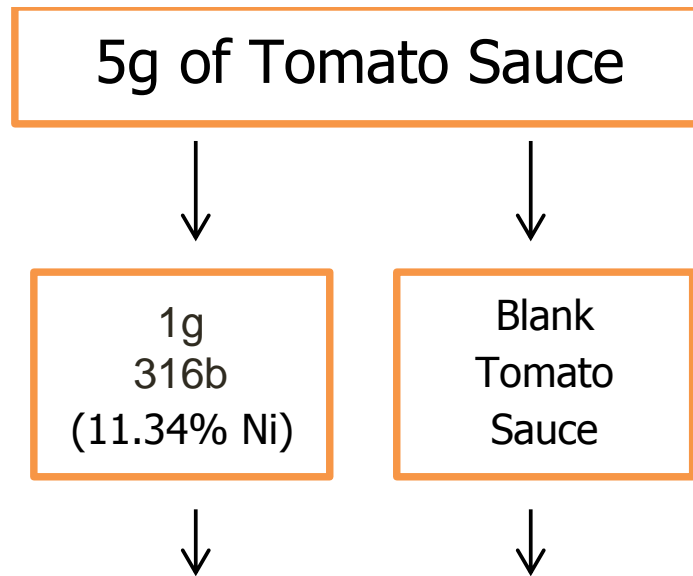
- Expectations:
 - 316a and 316b about equal
 - 304 high response
- Results show 316b and 304 equivalent
 - Protective properties of Cr

Percent Nickel Released

Experimental Tomato Sauce Sample	Chemical Composition (mass fraction %)		Average Ni Leached (μg)	% Ni Leached
	Cr	Ni		
316a	17.50	11.18	3.11	2.78
316b	17.40	11.34	5.71	5.04
304	18.37	12.35	5.1	4.13
Nickel Pellet	—	99.9	65.8	6.59

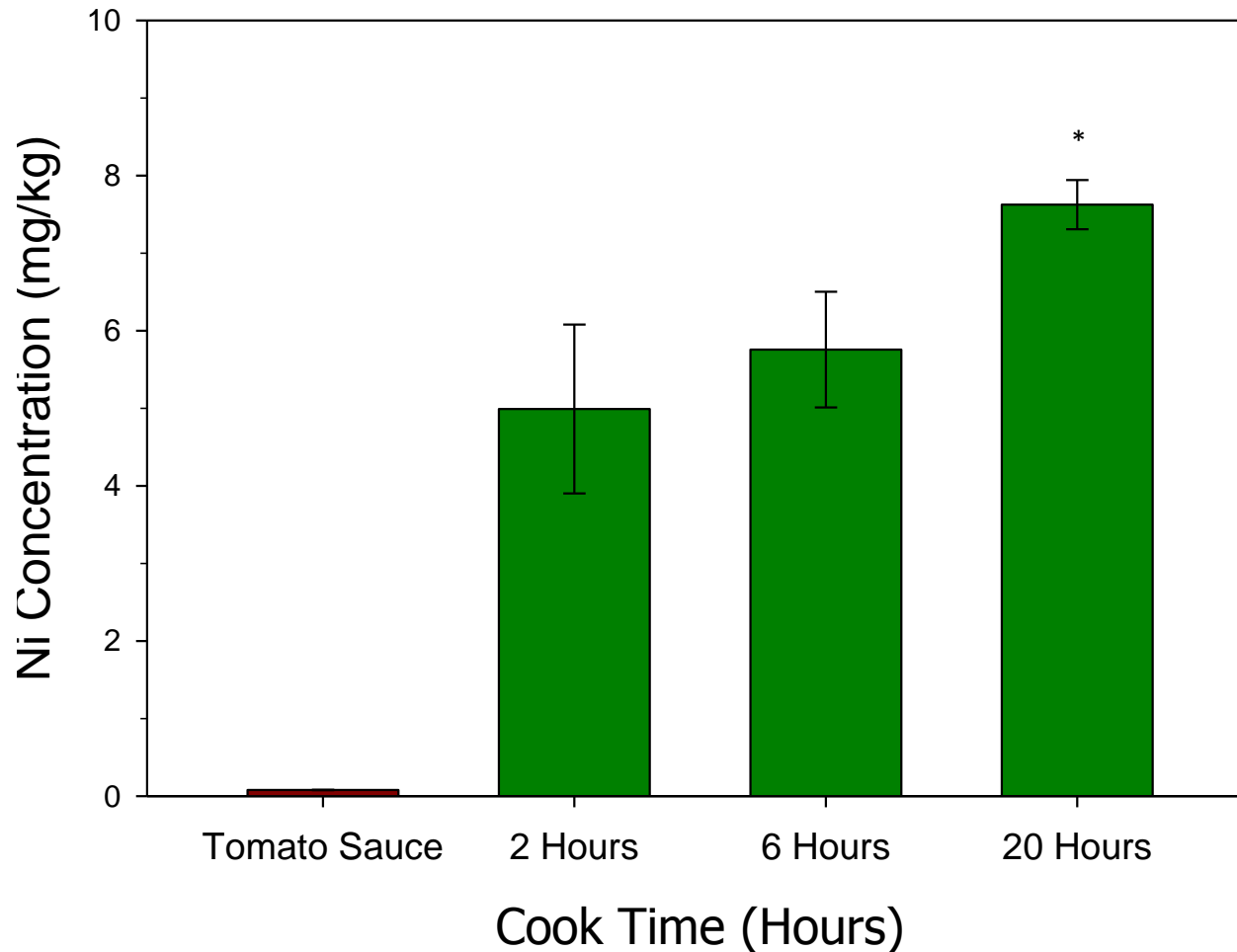
- Grade of stainless steel experimental samples
 - $n=5$

Cooking Time



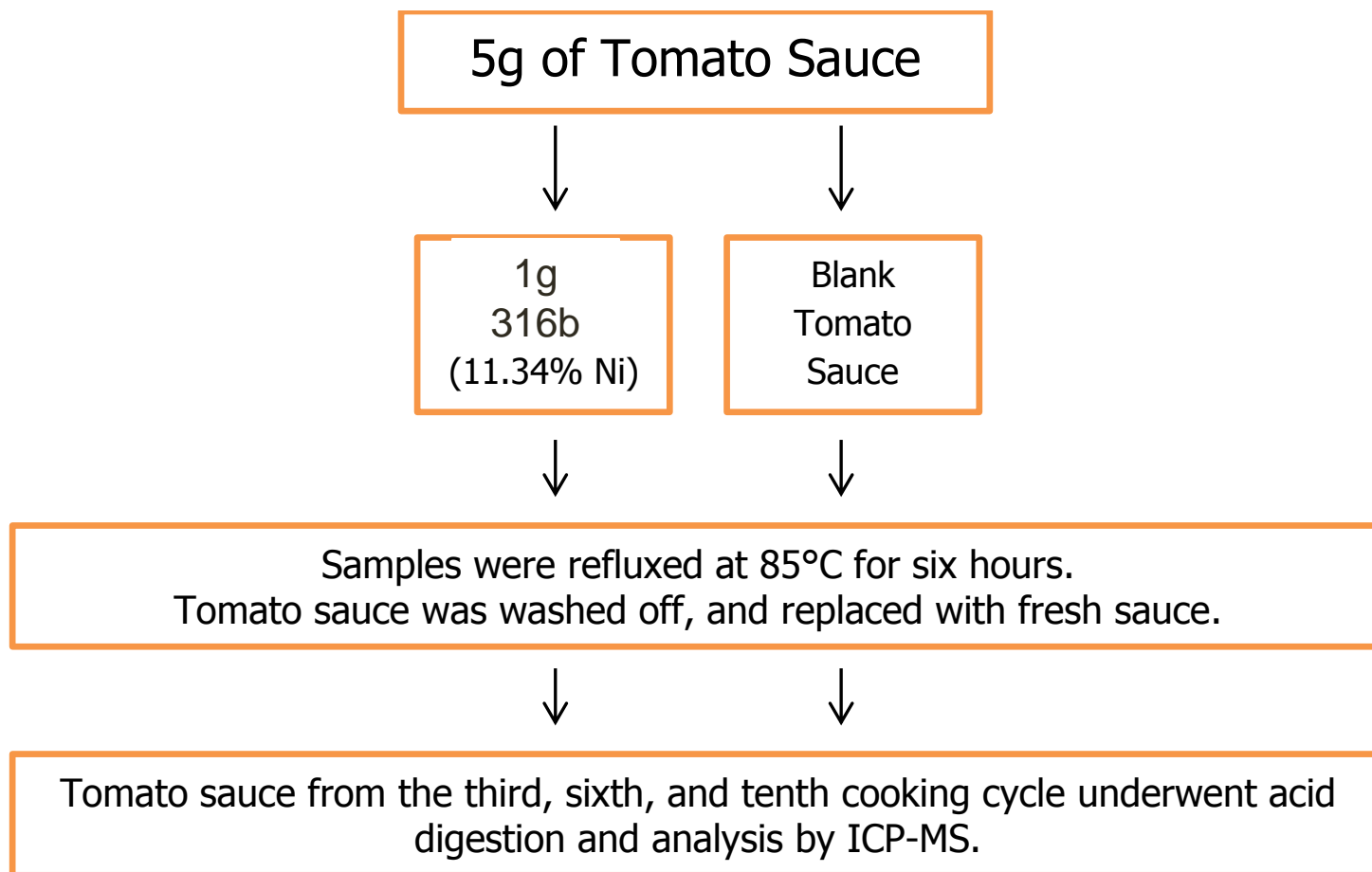
Samples were refluxed at 85°C for two, six, or twenty hours.
Tomato sauce then underwent acid digestion and analysis by ICP-MS.

Cooking Time

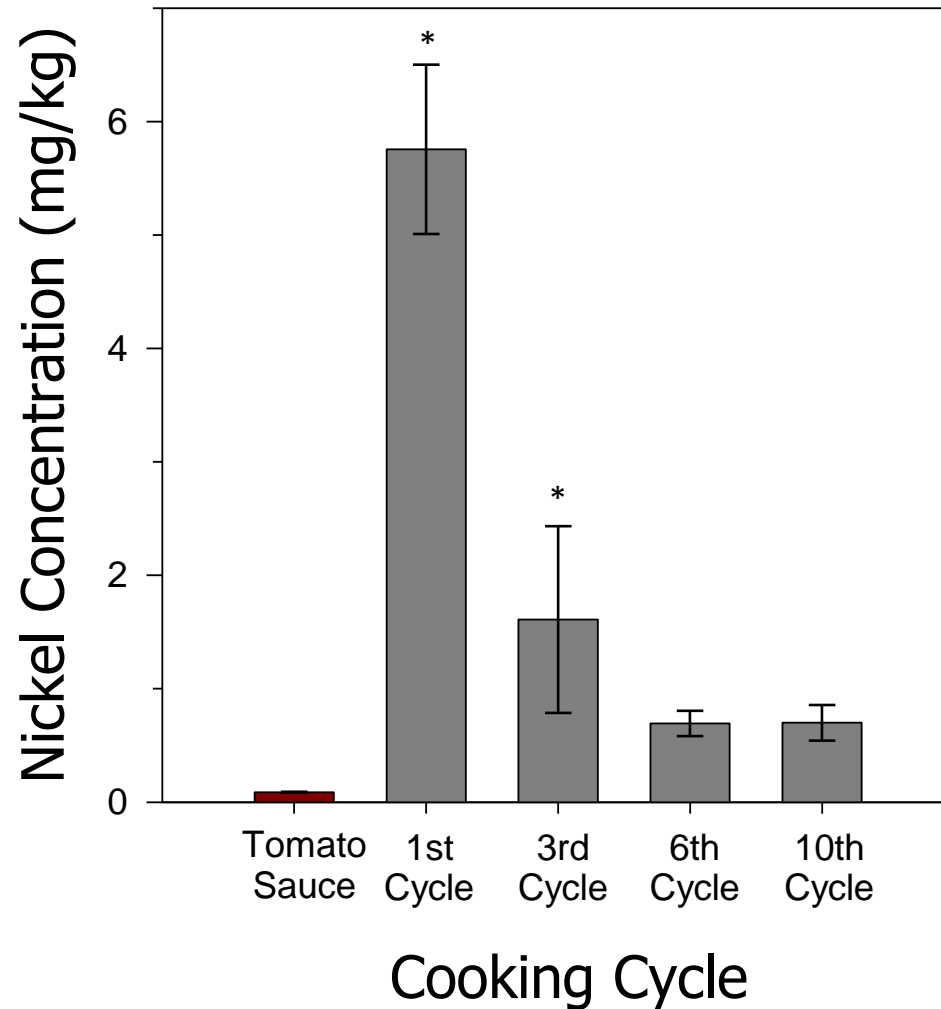


n=4; samples deemed significant at $p < 0.05$
* Statistical difference between one or more samples

Cooking Cycles

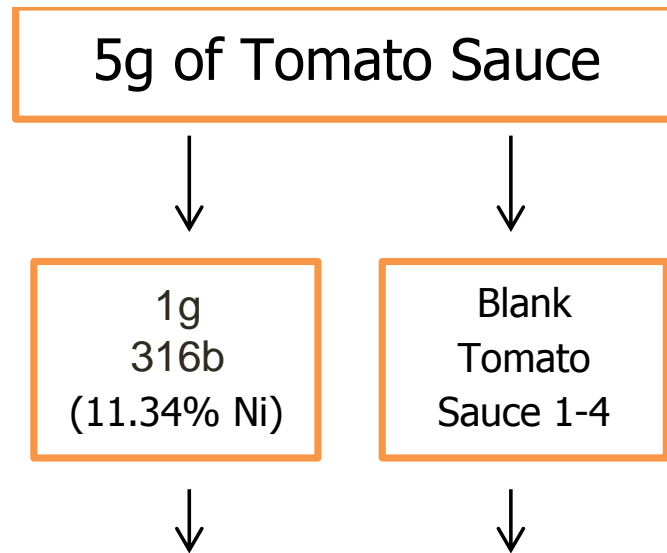


Cooking Cycles



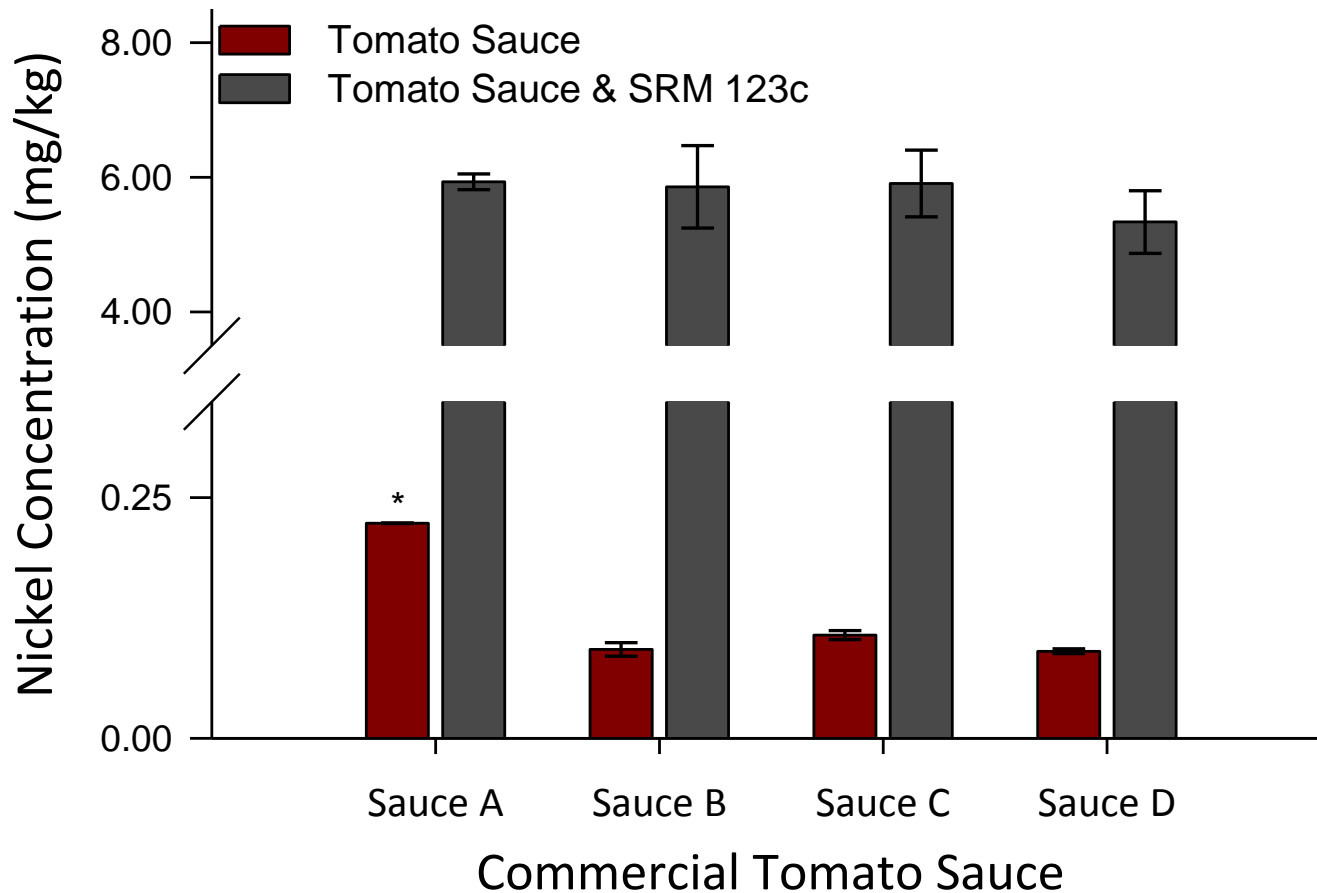
n=4; samples deemed significant at $p < 0.05$
* Statistical difference between one or more samples

Commercial Tomato Sauces



Samples were refluxed at 85°C for six hours.
Tomato sauce then underwent acid digestion and analysis by ICP-MS.

Commercial Tomato Sauce



n=4; samples deemed significant at $p < 0.05$

* Statistical difference between one or more samples

Saucepan

571g of Tomato Sauce

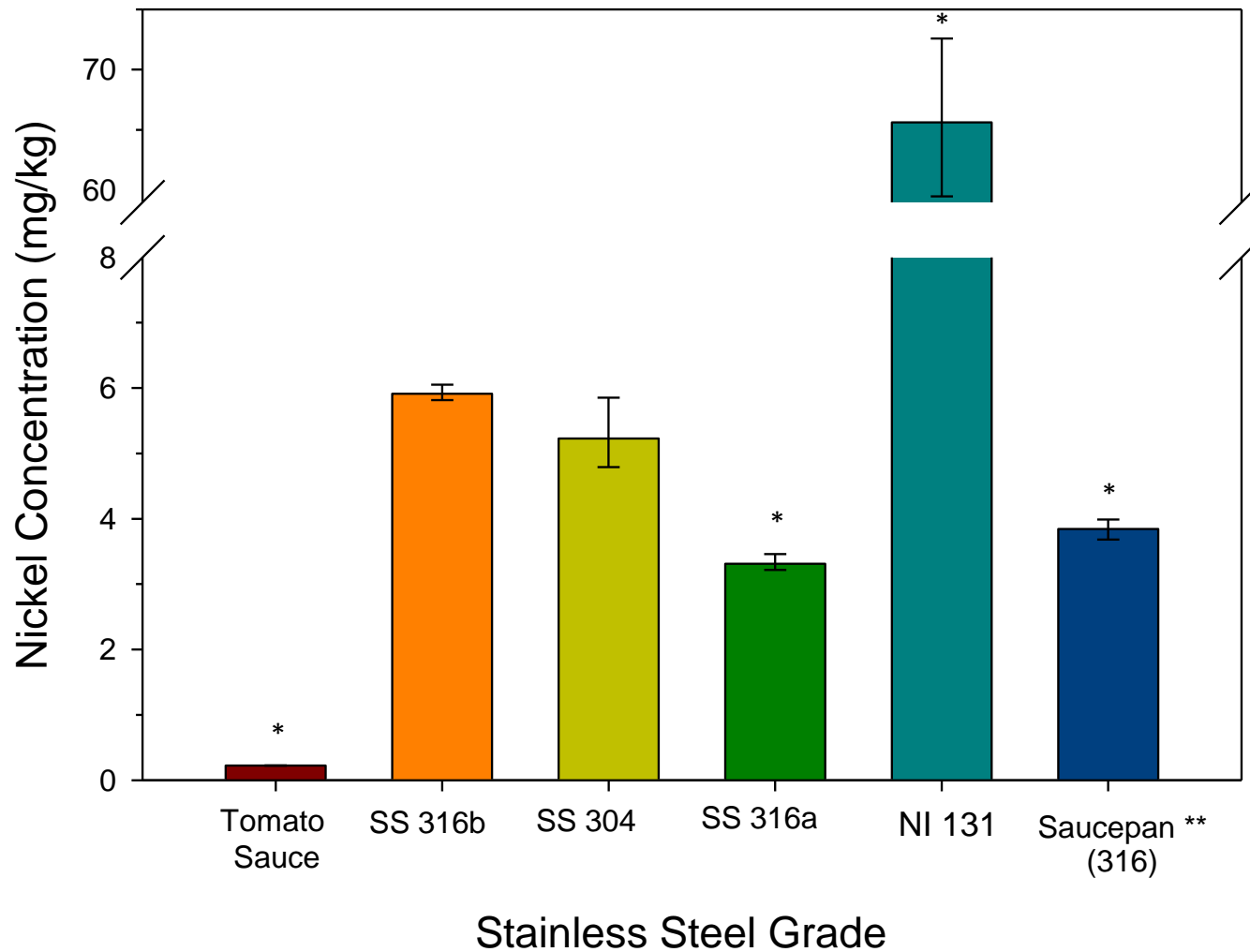


Grade 316
Stainless Steel
Saucepan



Sauce was refluxed at 85°C for twenty hours.
5g aliquots were taken and underwent acid digestion and analysis by ICP-MS.

Saucepan



n=5; samples deemed significant at $p < 0.05$

* Statistical difference between one or more samples

** 20 hour cook time

Grade 316:

316b and Stainless Steel Saucepan

- Would have expected similar nickel concentrations
- ~50% less nickel leached from saucepan than 316b
 - However, tomato sauce to stainless steel surface area ratios different

Surface Area

316b

- Avg. nickel released after 20h cook time:
7.63mg/kg
- Sauce : Stainless steel ratio
 - 1:5

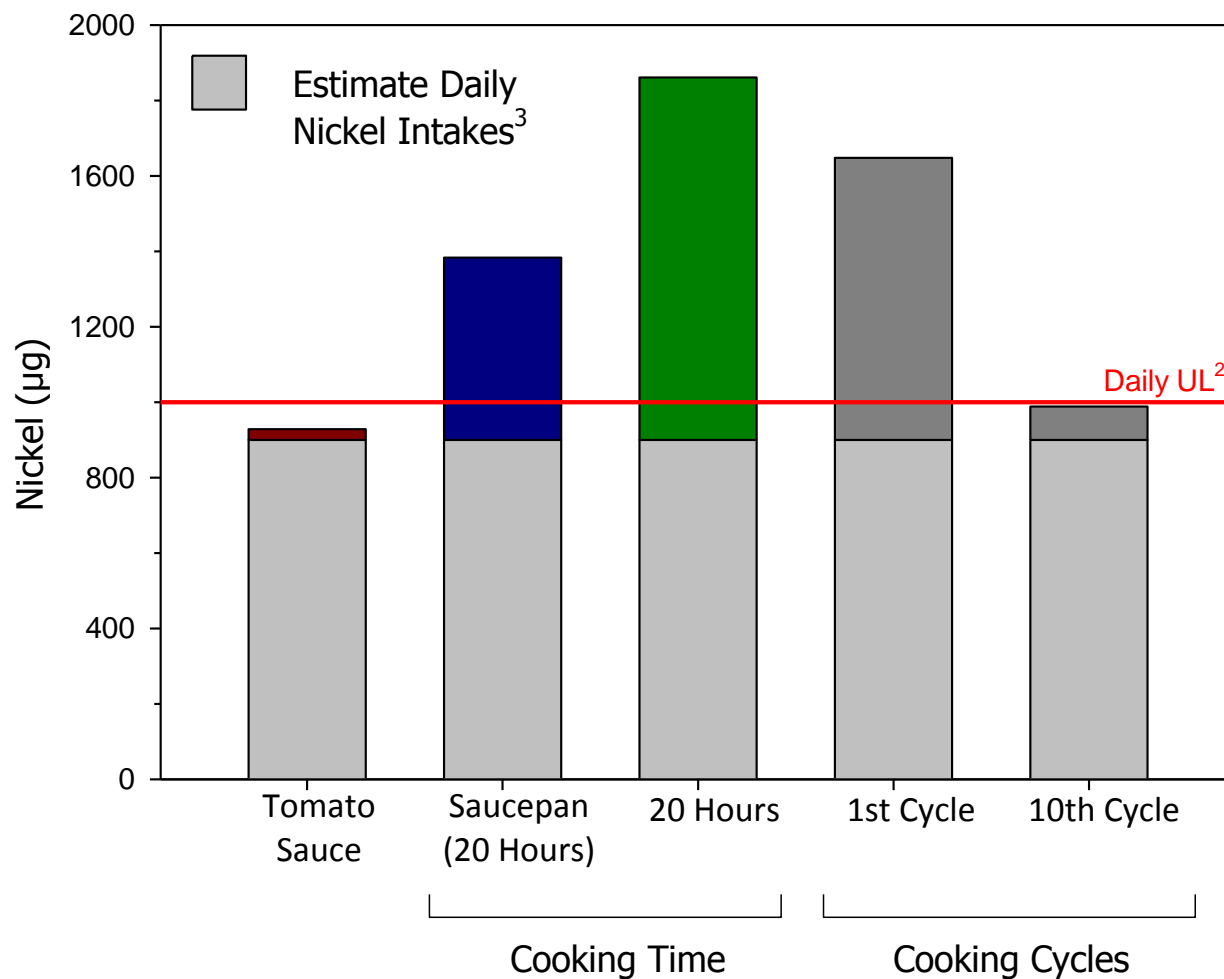
Saucepan

- Avg. nickel released after 20h cook time:
3.84mg/kg
 - ~50% less than 316b
- Sauce : Stainless steel ratio
 - 1:0.6

- Would expect a nearly a 10 fold difference, but we observed only a 2 fold difference
- Stainless steels used a good surrogate for cookware and cooking variable assessment

Ni per Serving of Tomato Sauce

Nickel per Serving of Tomato Sauce
Contribution to Total Nickel Intake



Conclusions

- Hypothesis: Nickel released is inversely proportional to grade of stainless steel
 - Nickel is leached into tomato sauce
 - 316b and 304 showed no statistical difference
 - Protective properties of Cr
 - 316a statistically different than 316b and 304
 - 316b showed greatest response
 - Dependent on chemical composition

Conclusions

- Hypothesis: Nickel released increases with cook time
 - Nickel increase with cook time
- Hypothesis: Nickel released is constant over multiple cook cycles
 - Nickel is still leaching after 10 cook cycles but the amount is less than the early cook cycles
- Hypothesis: Nickel content is constant for multiple commercial tomato sauces
 - No significant difference were seen between multiple commercial tomato sauces in their effect on nickel leaching

Conclusions

- Stainless steel cookware contributes to total nickel intakes
- Avoidance of stainless steel cookware may decrease total nickel exposure

Acknowledgements

- Kim Anderson, Ph.D.
- Kate Field, Dan Sudakin
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 - Kevin Hobbie, Norman Forsberg
- Friends & Family



Thank you for your attention.
Any Questions?