The Release of Nickel from Stainless Steel into Cooked Foods

By

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Abstract

Toxicological studies show that oral doses of nickel can cause allergic contact dermatitis, and routes of exposure, such as nickel leached from stainless steel cookware are not well characterized. In this study, four variables: grade of stainless steel, cook time, stainless steel seasoning or cooking cycles, and commercial tomato sauces, were tested to for their effect on nickel leaching and their possible effects on human health. Two grades of stainless steel, two, six, and 20 hour cooking times, ten cooking cycles, and four commercially obtained tomato sauces were tested. The stainless steel grades tested were equivalent to those typically found in cookware (grade 316 and 304). We found after a single cooking cycle of six hours, depending on grade of stainless steel, nickel concentrations increased 30 to 60 fold. Increased cook times of 20 hours resulted in additional nickel leaching, about 70 fold higher than tomato sauce cooked in the absence of stainless steel. The first cooking cycle resulted in the largest increase in nickel concentration at 5.8mg/kg. However, with sequential cooking cycles, the total amount of nickel leached was less than in the first cycle. There was no change in the amount of nickel leached between the sixth and tenth cooking cycle. Nickel was still leaching into tomato sauce after 10 cooking cycles about 10 fold higher than the original tomato sauce. After 10 cooking cycles, each six hours in duration, an average of 88μg of nickel was leached per 126g serving of tomato sauce. In addition to dietary intakes, stainless steel can be an overlooked source of nickel, and the amount of additional exposure is dependent on stainless steel grade, cooking time, and repeated usage.

Abbreviations Used

UL, Tolerable Upper Intake Level; ACD, Allergic Contact Dermatitis; ICP-MS, Inductively Coupled Plasma-Mass Spectrometry; SRM, Standard Reference Material; CRM, Certified Reference Material; LOQ, Limit of Quantitation

Introduction

Nickel is a trace metal which is ubiquitous in the environment and occurs naturally in soils, plants, and animals. Surface waters are estimated to contain 15-20 µg/L[1]. Though nickel is known to be essential to the health of some species, it has not been proven to be essential to the health of humans[2]. No known human enzymes or cofactors are dependent on nickel for normal function[1]. Despite its unknown essentiality, humans are exposed to nickel via the diet. Foods high in nickel include peanuts, peas, oatmeal, and milk chocolate; 0.956, 0.699, 0.495, 0.871mg/kg respectively[3]. In 2001, the Tolerable Upper Intake Level (UL) of nickel was decreased to 1000 µg per day by the Institute to Medicine's Food and Nutrition Board[4]. Adults in the U.S. are estimated to ingest an average of 69 to 162µg of nickel per day[5].

The toxicity of nickel is not well characterized. Animal studies which do exist show carcinogenic effects after oral exposure to nickel salts, and speciation differences were observed[1,5]. Known case studies show increased rates of lung and nasal cancers associated with occupational inhalation exposures. The metabolism of nickel in humans is unkown[1]. Yet, toxicological studies indicate that a single oral doses of metallic nickel as low as 3000 µg cause recurrence of allergic contact dermatitis (ACD) in individuals sensitive to nickel[6].

Oral doses of nickel can lead to symptoms of ACD, such as skin rashes, where symptom severity displays a dose dependent relationship[6]. Approximately 10% of people are afflicted by ACD which is most common in women[7]. The mechanism of nickel allergy is not well known. However, nickel sensitive individuals are shown to have increased levels of memory T lymphocytes, which may result in the cascading effect of the allergic response[6]. It is recommended that individuals sensitive to nickel lower their exposure[6,7,8]. However, an overlooked source of nickel may be from stainless steel used during cooking processes[9,10,11].

Nickel containing 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 common steels used in the food and beverage industry and in cookware[12]. These grades differ by their chemical compositions of metals including nickel and chromium. Grade 304 stainless steel contains approximately 18% mass fraction chromium, and 8% nickel, whereas grade 316 stainless steels contain approximately 16% chromium, and 10% nickel[12]. These stainless steels often maintain direct and prolonged contact with food during cooking and manufacturing processes.

Previous research conducted on the release of nickel from stainless steel during cooking procedures have generally only tested one grade of nickel containing stainless steel cookware (grade 304), and a few varied food matrixes including acidic solutions, dried fruits, and basic soups or other meals [8,9,10,11]. Results show that nickel does leach from stainless steel into acidic solutions and foodstuff during cooking processes [8,9,10,11]. However, results were inconsistent likely due to variations in experimental conditions such as food type, cooking duration, and other uncontrolled variables. Additionally, upon interpretation of the results, these studies reached contradicting conclusions on the severity and significance of nickel leaching and the factors, such as grade of stainless steel and cooking time, which contribute to nickel leaching.

The objective of this study was to quantify the amount of nickel leached from stainless steel into tomato sauce during cooking procedures, and to identify contributing variables to nickel leaching. In this study, stainless steel chips of certified chemical compositions were tested, and compared to grade 316 stainless steel cookware (Table 1). Experimental parameters tested for their effects on nickel leaching were grade of stainless steel, cooking time, stainless steel usage or cooking cycles, multiple commercial tomato sauces, and commercial cookware.

Materials

Reagents.

A plasma grade nickel standard solution from Alfa Aesar (Ward Hill, MA) was used for instrument calibration and sample fortification. Plasma grade germanium and indium solutions from Alfa Aesar were used for internal calibration of all samples. Fisher (Pittsburgh, PA) Optima grade concentrated nitric acid was used in all digestion processes. Sample and standard were diluted with 18MΩ-cm water from a Barnstead EasypureUV D7401 (Dubuque, IA) in a 1% Fisher trace metal grade nitric acid solution. Five Certified Reference Materials (CRMs), Tomato Leaves NIST 1573a, Oyster Tissue NIST 1566b, Montano Soil NIST 2710, San Joaquin Soil NIST 2709, and New York/New Jersey Waterway Sediment NIST 1944, from National Institute of Standards and Technology (Gaithersburg, MD), were used in the validation of the methods in this study. Three stainless steel Standard Reference Materials (SRMs), NIST 123c, NIST 160b, 316a, from National Institute of Standards and Technology (Gaithersburg, MD) were tested for effects on nickel leaching. The SRMs were purchased in chip form and equivalent in chromium and nickel mass fraction to grades of stainless steel commonly used in cookware (Table 1). Pure nickel pellets, NI-131, from Atlantic Equipment Engineers (Bergenfield, NJ) were used as a positive control. One commercially obtained grade 316 stainless steel saucepan was also tested for nickel leaching. Four traditional style commercially obtained tomato sauces were used as the food matrix. The acidity of the tomato sauces tested ranged between 4.17-4.3 in pH.

Table 1. Materials used in simulated cooking procedures

Description	Identification Number	Stainless Steel Grade Equivalence	Chemical Composition (mass fraction %)	
			Cr	Ni
316a	NIST 121d	316	17.5	11.18
316b	NIST 123c	316	17.4	11.34
304	NIST 160b	304	18.34	12.35
Nickel Pellet	NI-131	–	–	99.9
Saucepan	Saucepan	316	–	–

Instrumentation.

The acidity of the tomato sauces were analyzed using a Thermo Scientific Orion 2 Star pH meter with an Orion Double Junction pH electrode (Waltham, MA). Samples were digested using an Environmental Express AutoBlock (Charleston,SC). A Perkin Elmer (Norwalk, CT) Sciex Elan 6000 Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with a Ryton spray chamber and Crossflow nebulizer with GemTips, and a PE AS91 auto sampler, was used to analyze samples for nickel. ICP-MS parameters included: 50 psi, nebulizer gas flow, 0.91L/min; dual detector, peristaltic pump rate, approximately 2.5mL/minute; PTFE tubing, 3 replicates, 1 reading/ replicate, 30 sweeps/reading; sample flush delay, 35s; read delay, 15s; wash delay, 45s. Nickel, germanium, and indium were quantified through the detection of the isotopes in in table 2.

Table 2. Isotopes detected for quantitation

Metal	Isotope
Nickel	^{60}Ni
Germanium (internal Standard)	^{74}Ge
Indium (internal Standard)	^{115}In

Method Validation

The acid digestion and trace metal analysis by ICP-MS methods used in this study were validated using certified reference materials (CRMs) from NIST. The purpose of the method validation was to ensure laboratory capability and suitability for acid digestions and trace metal analysis by ICP-MS. Through the method validation procedure calibration, accuracy, precision, and limits of quantitation were demonstrated for both the acid digestion and trace metal analysis.

The method validation consisted of the acid digestion of each CRM sample over three different days. For each CRM, 0.25g was weighed out into a clean digest tube. Analytes where then added to fortified quality control samples such as pre-digest fortification and laboratory preparation fortification samples. The digest tubes were placed into the Autoblock, and two mL of concentrated nitric acid was added to each tube. Samples were allowed to digest at ambient temperatures over night. In the morning an additional one mL of nitric acid was added. The samples were initially heated to 50°C. Over the course of 75 minutes the temperature was ramped to 85°C, then held constant for the remainder of the digestion. The digestion was complete when nitrogen oxide fumes (orange/brown gas) were no longer evolving from the sample; approximately 12 hours (Equation 1). The digests were cooled and18MΩ-cm water added to a final volume of 10mL, vortexed, and filtered with 0.45µm PVDF membrane filters into storage containers.

$$HNO_3 + Ni^0{}_{(solid)} \rightarrow NO_2 \uparrow + Ni^{2+}(NO_3) + xCO_2 \uparrow \qquad \text{(Equation 1)}$$

Aliquots of each sample were combined with internal standards solution of germanium and indium, and diluted with 1% HNO_3. From the plant tissue samples, 100µL and 200µL aliquots were taken. From the soil or sediment samples, 250µL and 2mL aliquots were taken. The diluted samples were then ready for analysis using ICP-MS for 16 trace metals including nickel. The ICP-MS analysis method validation included a five point (0.1-50ppb) and a six point (100-500ppb) calibration curves for nickel, with a regression lines of 0.99 or greater. Quality control samples employed including instrument blanks, and calibration check standards, which were used to ensure accuracy and precision.

The limit of quantitation (LOQ) for nickel was calculated using equation one. The LOQ was calculated from seven replicates of a 1µg/L calibration standard solution, and determined to be 0.085µg/L.

The average percent recovery of nickel in the plant, soil and sediment reference samples was 88.9%. The average percent recovery of the five pre-digest sample fortifications was 103%.

Specific method validation results for multiple trace metals, including nickel, are presented in appendix 1. These results show that the methods are appropriate for producing high quality trace metal data for multiple matrices. The acid digest and ICP-MS trace metal analysis methods can be used to quantify the release of nickel from stainless steel into cooked foods.

Methods

Sampling and Preparation.

To simulate home cooking processes, the following sampling procedure was conducted. For each sample, 5g of tomato sauce was added to an Environmental Express digest tube along with 1g of SRM. Tomato sauces without presence of stainless steel and in the presence of a pure nickel pellet were also prepared, serving as a matrix blank and positive control respectively. The digest tubes were placed in the AutoBlock, and the samples heated to 85°C. This temperature was maintained for the given experimental cook time. The samples were then allowed to cool, and the tomato sauce was separated from the metal sample via quantitative transfer into clean digest tubes. This sampling method was used in all experiments with the exception of the saucepan test. To test the grade 316 saucepan for nickel leaching, ~751g (an entire commercially purchases container) of tomato sauce was cooked in a two quart stainless steel saucepan. The sauce was heated to approximately 85°C on a hotplate, and the temperature maintained for the experimental cook time of 20 hours. After cooling, the sauce was homogenized, and 5g aliquots were weighed out into clean digest tubes.

After the simulated home cooking of tomato sauce, all samples were digested using an adapted EPA method 3050b. In this method, each 5g tomato sauce sample was placed in the autoblock, received 2mL of concentrated nitric acid, and was left to react at room temperature overnight. In the morning, an additional 1mL of nitric acid was added. The samples were then ramped to 85°C over the course of 75 minutes in the autoBlock. Thereafter, they were held at approximately 85°C until nitrogen oxide fumes (orange/brown gas) were no longer evolving from the samples (approximately 12 hours). The digests were cooled and18MΩ-cm water added to a final volume of 10mL, vortexed, and filtered with 0.45µm PVDF membrane filters into storage containers. A 250µL aliquot of each sample were combined with internal standards solution of germanium and indium, and diluted to 5mL. A 250µL aliquot of each sample was diluted to a final volume of 5mL with 18MΩ-cm water. The samples were then analyzed for nickel using ICP-MS.

Experimental conditions: grade of stainless steel, cooking time, cooking cycle, and tomato sauce used were modified in each test set. Each experimental condition was sampled in replicates of four or five, resulting in 100 tomato sauce samples analyzed for nickel. Specific experimental conditions for each variable tested are defined in Table 3.

Table 3. Experimental Conditions

Experimental Variable	n Total	NIST SRM	Cook Time (hours)	Cooking Cycles	Tomato Sauce	Replicates / Variable
Stainless Steel Grade	20	316a, 316b, 304, NI-131*	6	1	Sauce 1	5
Cooking Time	12	316b	2,6,20	1	Sauce 1	4
Cooking Cycle	16	316b	6	1,3,6,10	Sauce 1	4
Tomato Sauce	20	316b	6	1	Sauce 1-4	5
Saucepan	5	Grade 316	20	1	Sauce 1	5

* Purchased from AEE (Bergenfield, NJ)

**All experimental variables also encluded control tomato sauce samples

Grade of Stainless Steel:

All three SRMs were cooked with tomato sauce in order to test the effect of stainless steel grade on nickel leaching. Tomato sauce A was used for all grades of unseasoned stainless steel, over a cook time of six hours then samples were processed using the preparation protocol described in the previous section. Samples were collected in replicates of 5. Additionally, a new grade 316 saucepan was tested for nickel leaching into tomato sauce using a 20 hour cook time. After the cooking process samples were handled using the previously described protocols.

Cooking Time:

To test the effects of time on nickel leaching during cooking processes, three cooking times (two, six, and twenty hours) were tested using tomato sauce A. All samples were cooked with new 316b stainless steel. Samples were collected in replicates of 4. Samples were processed and analyzed as previously stated.

Cooking Cycles:

To test the effect of stainless steel seasoning on nickel leaching, up to ten cooking cycles of 316b were tested. Each cooking cycle consisted of a six hour cook time with tomato sauce A. After each cycle, the tomato sauce was removed via quantitative transfer, and the stainless steel sample rinsed with 18MΩ-cm water. Sequential cooking cycles repeated this procedure using the same 1g metal sample. Tomato sauce samples for the first, third, sixth, and tenth cycle were collected and analyzed for nickel content.

Commercial Tomato Sauce:

Four commercially obtained tomato sauces (sauce A-D) were tested for their effects on nickel leaching from 316b. A six hour cooking time, and first cooking cycle were used. Each tomato sauce was a traditional style, and manufactured by differing companies and locations.

Quality Control

Quality control (QC) samples were employed throughout the study, accounting for 30% of all samples. QC samples included pre digestion nickel fortification at 50ug/L. Percent recoveries of the pre-digest fortification samples ranged from 102-107% (Table 4). A six point calibration with a regression of 0.999 or greater was used in analyzing samples with ICP-MS. Continuing calibration verification (CCV) standards and instrument blanks were analyzed at a minimum of ever ten samples in order to ensure instrumentation accuracy. The CCVs were approximately ±10% of the true value, and instrument blanks ranged from 0.011 to 0.042μg/L (Table 4).

Table. 4 Quality Control Samples

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

Statistical Analysis

Differences in nickel concentrations between experimental samples were evaluated for statistical significance using SigmaPlot 11 (Systat; Chicago, IL). For normal data, a one way analysis of variance with a Bonferroni correction for pairwise multiple comparison procedure was conducted. Samples were considered statistically significant at $p \leq 0.05$.

Results and Discussion.

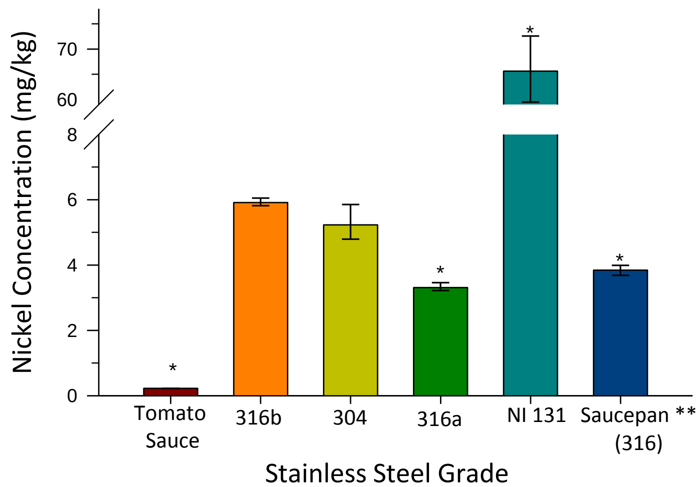
Grade of Stainless Steel:

When testing grade of stainless steel samples were treated as detailed in Table 3. Tomato sauce samples cooked in the absence of stainless steel, treated under these conditions, showed nickel concentrations of 0.224 mg/kg of sauce. This corresponds well to previously reported nickel concentration in tomatoes that ranged from 0.04 mg/kg to 1.21 mg/kg[13]. Tomato sauce exposed to a pure nickel pellets during the simulated cooking procedure contained significantly higher concentrations of nickel than all other samples at 66.0mg/kg of sauce. Tomato sauce samples cooked with 316b and 304 stainless steels showed similar nickel concentrations, 5.93 and 5.32 mg/kg respectively (Figure 1a). The similarity in nickel leached occurred despite differences in chemical composition (Table 1). The average percentage of nickel leached from 1g samples 316b and 304 stainless steels was 5.04% and 4.13% respectively (Table 5). The stainless steel chips used in this study had a similar range in particle size (between 0.5 and 1.18mm millings.) Therefore surface area differences between samples were not a major variable contributing to the percentage of nickel leached. Stainless steel 304, has a larger nickel mass fraction, but did not show the greatest nickel leaching. Stainless steel 304 also has the greatest chromium mass fraction. The result may be explained by the increase in chromium oxide on the surface of stainless steel, which is known to have protective properties[12]. Tomato sauce samples cooked with 316a, which has the lowest mass fraction of nickel, was found to have the smallest amount of nickel leached into the sauce, averaging 3.34 mg/kg of nickel (Figure 1a). Tomato sauce samples cooked with 316b stainless steel were found to have the largest amount of nickel leached into tomato sauce, and 316b therefore used in succeeding experiments. No clear relationship between stainless steel chemical composition and nickel leaching exists. The amount of nickel leached is likely due to multiple variables rather than nickel and chromium mass fractions (Table 5).

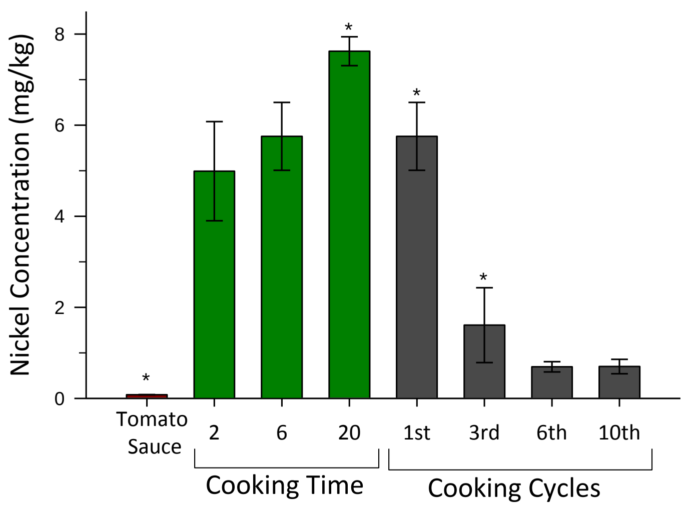
Table 5. Percent Nickel Leached from Metal Samples

Identification Number	Chemical Composition (mass fraction %)		µg Ni / g metal	Average Ni Leached (µg)	% Ni Leached
	Cr	Ni			
316a	17.5	11.18	112	3.11	2.78
316b	17.4	11.34	113	5.71	5.04
304	18.34	12.35	124	5.1	4.13
NI-131	–	99.9	999	65.8	6.59

A.


Nickel Concentration (mg/kg)
70
60
8
6
4
2
0
*
*
*
*
Tomato Sauce
316b
304
316a
NI 131
Saucepan ** (316)
Stainless Steel Grade

B.


Nickel Concentration (mg/kg)
8
6
4
2
0
*
*
*
*
Tomato Sauce
2
6
20
1st
3rd
6th
10th
Cooking Time
Cooking Cycles

C.

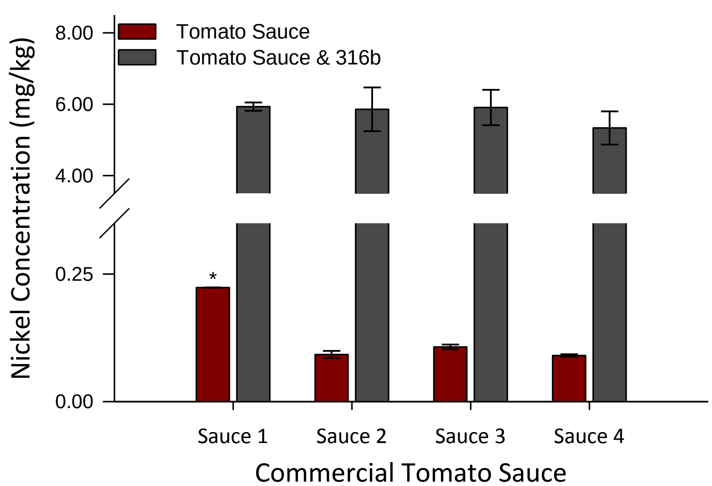

Tomato Sauce
Tomato Sauce & 316b
Nickel Concentration (mg/kg)
8.00
6.00
4.00
0.25
0.00
*
Sauce 1
Sauce 2
Sauce 3
Sauce 4
Commercial Tomato Sauce

Figure 1.

(A) Nickel concentrations (mg/kg) of commercial tomato sauce cooked in the absence of stainless steel (negative control), in the presence of stainless steel SRMs, in the presence of a pure nickel pellet (positive control), and cooked in a stainless steel saucepan (n=5) for six hours.

(B) Nickel concentrations (mg/kg) of commercial tomato sauce cooked in the absence of stainless steel, and in the presence of 316b (n=4). Two, six and twenty hour cooking times as well as first, third, sixth, and tenth cooking cycles (n=4).

(C) Nickel concentrations (mg/kg) of four commercially obtained tomatoes sauces (sauce 1-4) cooked in absence of stainless steel(n=4), and in the presence of 316b (n=5).

* Indicates statistical difference at p=0.05 or less.

**A twenty hour cook time was used in the grade 316 stainless steel saucepan test.

Cooking Time:

When testing cooking time, tomato sauce samples were treated as depicted in Table 3. After two hours of cooking, nickel concentrations in tomato sauce averaged about 5 mg/kg, about a 6000% increase above tomato sauce cooked in the absence of stainless steel. The increase in nickel leached between a two and six hour cooking time was statistically insignificant. However, after twenty hours of cooking, nickel concentrations reached 7.63 mg/kg, nearly a 9500% increase from tomato sauce cooked in the absence of stainless steel (Figure 1b). This data shows significant increases in nickel leaching with increased cooking time.

Cooking Cycles:

Ten cooking cycles were conducted in order to test the effects of repeated stainless steel usage on nickel leaching. All measured nickel values were statistically different than the nickel content of tomato sauce cooked in the absence of stainless steel, 0.088 mg/kg. Nickel concentrations were highest in the first cooking cycle at 5.93 mg/kg, approximately a 2600% increase from tomato sauce cooked in the absence of stainless steel. After the third cooking cycle, the tomato sauce contained 1.61mg/kg of nickel approximately an 1800% increase from tomato sauce cooked in the absence of stainless steel. The reduction in nickel concentration became insignificant between the sixth and tenth cooking cycle, with nickel leaching resulting in similar concentrations of 0.694 mg/kg and 0.700 mg/kg respectively (Figure 1b). However, nickel concentrations of the sixth and tenth cooking cycle samples were still significantly different than tomato sauce cooked in the absence of stainless steel, with increased nickel concentrations of approximately 800%. Although the amount of nickel initially decreased with cooking cycles, after the sixth cycle the amount of leached was stable. Reduction of the nickel leached in the later cycles was likely not due to less nickel left in the material, as only a few percent of the total nickel was removed with any cooking cycle, but rather the formation of protective oxides like chromium oxide. However, although seasoning the stainless steel had some initial benefit of reducing the amount of nickel leached in the early cooking cycles, the protective effect seems to have been maximized by the sixth cooking cycle. No further leaching protection was observed between the sixth and tenth cooking cycle were the nickel leached was still about an 800% increase.

Commercial Tomato Sauce:

A total of four commercially obtained tomato sauces were analyzed for nickel leaching when cooked in the presence of stainless steel. All tomato sauces had similar initial nickel concentrations when cooked in the absence of stainless steel. Nickel concentrations means of the four tomato sauces ranged from 0.090-0.224 mg/kg in tomato sauce cooked in the absence of stainless steel. All four tomato sauces were cooked 316b, and were found to have similar effects on the total amount of nickel leached from stainless steel. Mean nickel concentrations of tomato sauces cooked 316b stainless steel ranged from 5.86-6.14 mg/kg, and resulted in approximately 3000-7000% increases above nickel concentrations of tomato sauces cooked in the absence of stainless steel (Figure 1c). Tomato sauce had similar effects on stainless steel despite originating from different commercial tomato sauce manufacturing companies. This is likely because all tomato sauces tested were similar in pH, which ranged from 4.17-4.3.

Saucepan

A 2 quart grade 316 saucepan, typical of home cookware, was used to directly estimate nickel leaching into tomato sauce. A relationship between nickel leached from the stainless steel grade 316 saucepan and 316b samples can be made. The nickel concentration in tomato sauce cooked in the saucepan increased from 0.130 mg/kg to 3.84 mg/kg after a twenty hour cook time (Figure 1a). This represents nominally a 300% increase in nickel concentrations in tomato sauce cooked the saucepan. A single 126g serving of tomato sauce would result in the addition of 484μg of nickel. Multiple servings of tomato sauce would result in even larger additions to total daily nickel intakes. This data shows that there are significant variations in nickel concentration between samples prepared with different grades of stainless steel.

When comparing nickel concentrations of tomato sauce cooked for twenty hours with grade 316 stainless steel, average nickel concentrations were 50.3% lower in tomato sauces cooked in the saucepan (3.84 mg/kg) than those cooked in the 316b stainless steel (7.63mg/kg) despite being the same stainless steel grade(Figure 1a-b). However, the sauce to metal or saucepan ratio differed between these samples. Metal leaching from stainless steel is dependent on the ratio of surface area of the stainless steel and the volume of sauce it is in direct contact with[14]. The reduction of nickel leaching seen from the saucepan is likely due to the geometry of the saucepan used, and the amount of tomato sauce used relative to the surface area of stainless steel exposed to the tomato sauce. The ratio of tomato sauce: surface area of the saucepan in contact with the tomato sauce (approximately 486 cm^2) was approximately 1:0.62. A 1g sample of the stainless steel chips had a surface area of approximately 25.0 cm^2, with only 5g of sauce for these samples; the tomato sauce to surface area ratio was much great at 1:5. Based on sauce to surface area we would have expected nearly a 10 fold reduction in nickel in the saucepan compared to the stainless steel chips, however, we only observed a two-fold reduction in nickel in the saucepan compared to the stainless steel. Additional factors, such as the specific chemical composition and saucepan manufacturing, may be contributing to the variability between the grade 316 stainless steel saucepan and 316b. Additionally, although there are minimum requirements for specific grades of stainless steel, they still represent a range in nickel and chromium concentrations (Table 6). In contrast to the saucepan, the stainless steel SRMs used

Table 6. Stainless Steel Chemical Composition

Stainless Steel Grade	Chromium Mass Fraction (%)	Nickel Mass Fraction (%)
316	16-18%	10-14%
304	18-20%	8-10.5%
420	12-14%	<0.6

in this study are of known and certified chemical compositions, encompassed by stainless steel chemical composition ranges. Differences in the saucepan's chemical composition compared to 316b may have contributed to the observed reduction in nickel concentration. The percentage nickel leaching from cookware may be lower than the surrogate stainless steels measured here. The relationship however, may be used as a reference to other experimental conditions in order to estimate real nickel exposure scenarios. However, it would also be beneficial to test multiple stainless steel saucepans of different geometries and manufactures.

Estimated Exposure Scenarios:

In order to estimate oral exposures, nickel per serving of tomato sauce was calculated from the mean nickel concentrations of select experimental samples. A single serving of tomato sauce is defined by the manufacturer to be 126g. Figure 2 presents the amount of nickel per serving of tomato sauce in comparison to maximum estimated daily dietary nickel intake for U.S. adults of 162µg/day[5], as well as the tolerable upper intake level (UL) for nickel of 1000µg/day4. Tomato sauce cooked in the absence of stainless steel made minimal additions to total daily intakes, with 28 µg per serving of tomato sauce. Samples cooked in the new saucepan contained 483µg of nickel per serving of tomato sauce. Tomato sauce cooked with first cycle 316b stainless steel approached the UL of 1000µg for both twenty and six hour cook times with 961µg and 747µg of nickel per serving respectively. After the tenth cooking cycle, tomato sauce prepared with 316b showed significant additions of nickel to dietary intakes, 88.2µg (Figure 2). These estimated exposures are based on a single 126g tomato sauce serving. However, additional servings would increase daily nickel exposure.

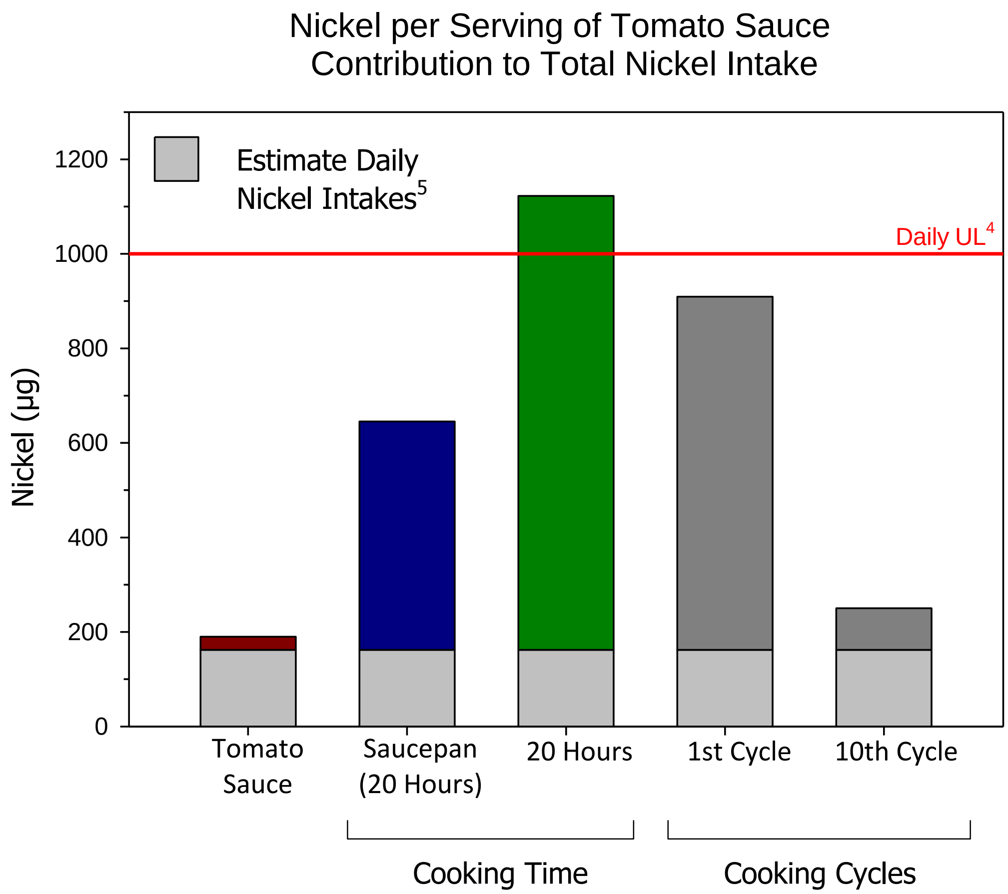


Figure 2.

Nickel (µg) per serving of tomato sauce for samples which underwent simulated cooking procedures. Tomato sauce samples were cooked with either 316b, or a stainless steel grade 316 saucepan. Nickel levels in experimental samples are compared with the Tolerable Upper Intake Level (UL) (1000µg/day[2]) and estimated range of daily nickel intakes for U.S. adults (69-162µg/day[3]).

Conclusion

The method validation showed that acceptable recoveries for trace metals from multiple matrices can be achieved through acid digestion, and accurate and precise measurements of those trace metals can be achieved through analysis by ICP-MS. The use of these methods for the analysis of nickel released from stainless steel into tomato sauce was appropriate, and resulted in reliable data from which conclusions can be drawn.

Tomato sauce cooked in the absence of stainless steel, showed minimal nickel concentrations compared to the estimation of total dietary nickel intake, nominally less than 0.224mg/kg. All tomato sauce samples that were cooked in the presence of stainless steel using typical cooking procedures showed significantly elevated nickel concentrations. This indicates that the increases in nickel concentrations are due to interactions of tomato sauce with stainless steel. In addition to natural dietary sources, stainless steel cookware can significantly contribute to overall nickel consumption. The amount of nickel leached from stainless steel into tomato sauce is dependent on the grade of stainless steel, cooking time, and previous usage or seasoning of the stainless steel.

Previous research on other toxic metals, such as lead, has shown leaching from cookware into foods[14,15,16]. These studies conclude that the avoidance of cookware containing lead may have beneficial health effects. Chromium and lead leaching into acetic acid solutions was shown to increase with stainless steel surface area[14]. Concentrations of lead in acidic solutions are shown to increase as the duration of contact with glazed cookware and storage containers increases[15]. These reports are consistent with our observations that nickel leaching increases with cooking time.

The effectiveness of avoiding stainless steel cookware to reduce nickel exposure and its effects on diminishing the effects of ACD is still unknown. However, it appears that recommendations for those with nickel sensitivity to avoid the use of stainless steel are not futile. When cooked in the presence of stainless steel, tomato sauce contains significant levels of nickel. The avoidance of cooking tomato sauce in stainless steel cookware can be helpful in reducing overall nickel consumption.

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Appendix 1

Demonstration of Accuracy and Precision

SRM 1573a-Tomato Leaf

		Digest date	1/11/2012	1/11/2012	1/11/2012	3/8/2012	3/8/2012				
		Analysis Date	5/18/2012	5/18/2012	5/18/2012	5/18/2012	5/18/2012				
		Certified Values	Concentration (µg/g)					Average	Standard Deviation	%RSD	Average % Recovery
Low Calibration	Be		0.029	0.027	0.028	0.034	0.034	0.030	0.003	11.1	
	Cr	1.99	2.15	2.13	2.14	2.21	2.33	2.20	0.084	3.81	110
	Mn	246	274	276	275	284	288	280	6.32	2.259	114
	Co	0.54	0.575	0.575	0.571	0.581	0.585	0.58	0.006	0.961	107
	Cu	4.7	4.00	4.04	4.04	4.07	4.1	4.05	0.036	0.894	86.2
	As	0.112	0.093	0.09	0.092	0.093	0.093	0.092	0.001	1.41	82.3
	Sr	85	93.5	93.2	93.5	93.6	95.0	93.8	0.712	0.759	110
	Cd	1.52	1.41	1.40	1.41	1.42	1.42	1.41	0.011	0.788	92.8
	Ba	63	67.8	67.6	67.0	67.7	68.1	67.6	0.395	0.585	107
		Digest date	1/11/2012	1/11/2012	1/11/2012	3/8/2012	3/8/2012				
		Analysis Date	3/27/2012	3/27/2012	3/27/2012	3/27/2012	3/27/2012				
		Certified Values	Concentration (µg/g)					Average	Standard Deviation	%RSD	Average % Recovery
high Cal.	Mg	12000	9910	10025	10105.873	10347	10288	10135	175	1.73	84.5
	P	1260	2060	2047	2091.904	2141	2139	2096	39.3	1.87	84.5
	K	27000	25472	25543	26167.27	26493	26452	26025	446	1.71	96.4
	Ca	50500	46510	46456	48377.864	49210	48697	47850	1165	2.43	94.8

SRM 1566b-Oyster Tissue

		Digest date	1/11/2012	1/11/2012	1/11/2012	3/8/2012	3/8/2012				
		Analysis Date	5/18/2012	5/18/2012	5/18/2012	5/18/2012	5/18/2012				
Low Calibration		Certified Values	Concentration (ug/g)					Average	Standard Deviation	%RSD	Average % Recovery
	Be		0.01	0.012	0.011	0.014	0.013	0.012	0.002	13.176	
	Cr		1.49	1.47	1.48	1.41	1.35	1.44	0.059	4.095	
	Mn	18.5	19.3	18.9	19.1	19.6	19.8	19.3	0.331	1.711	105
	Co	0.371	0.352	0.349	0.35	0.354	0.354	0.3518	0.002	0.648	94.8
	Ni	1.04	0.946	1.265	0.925	0.91	0.925	0.994	0.152	15.281	95.6
	Cu	71.6	76.8	75.3	75.3	75.1	76.2	75.7	0.760	1.004	106
	Zn	1424	1247	1228	1224	1216	1233	1230	11.3	0.920	86.4
	As	7.65	8.65	8.48	8.52	8.23	8.29	8.43	0.171	2.026	110
	Sr	6.8	6.20	6.05	6.12	6.11	6.22	6.14	0.070	1.139	90.3
	Cd	2.48	2.49	2.49	2.48	2.48	2.49	2.48	0.005	0.183	100
	Ba	8.6	5.98	6.05	5.83	5.89	6.38	6.03	0.214	3.549	70.1
	Pb	0.31	0.283	0.274	0.278		0.266	0.28	0.006	2.290	88.8
		Digest date	1/11/2012	1/11/2012	1/11/2012	3/8/2012	3/8/2012				
		Analysis Date	3/27/2012	3/27/2012	3/27/2012	3/27/2012	3/27/2012				
high Cal.		Certified Values	Concentration (ug/g)					Average	Standard Deviation	%RSD	Average % Recovery
	Mg	1082	1009	1022	1029	1001	1010	1014	9.96	0.98	93.7
	P		7032	7163	7188	6910	7013	7061	103	1.47	
	K	6520	6230	6274	6410	6155	6264	6266	83.4	1.33	96.1
	Ca	838	764	777	790	773	771	775	9.04	1.17	92.5

SRM 1944-New York/New jersey Waterway Sediment

MicroCal-100uL aliquot

	Certified Value					Conc (ug/g)					Average	Deviatio n	%RSD	Average % Recovery
Digest Date		7/31/12	7/31/12	7/31/12	8/7/12	8/7/12	8/7/12	8/15/12	8/15/12	8/15/12				
Analysis Date		8/27/12	8/27/12	8/27/12	8/13/12	8/13/12	8/13/12	8/16/12	8/16/12	8/16/12				
Be		0.967		0.935				1.01	1.01	1.03	0.990	0.04	3.54	
Ti								442	464	441	449	10.3	2.29	
Cr	266	206		208	178	182	176	189	199	191	191	11.5	6.00	71.8
Mn	505	326		327				330	349	341	335	8.84	2.64	66.2
Co	14	10.3		10.5	9.15	10.2	8.96	9.97	10.3	9.96	9.91	0.52	5.29	70.8
Ni	76.1	68.6		69.7	60.5	64.2	59.0	65.2	69.8	65.6	65.3	3.79	5.79	85.8
Cu		373		384	347	345	367	367	400	388	371	18.0	4.85	
Zn	656	710		711	618	592	617	652	675	640	652	41.2	6.32	99.4
As	18.9	18.8		18.7	16.9	18.1	17.3	18.4	19.7	20.2	18.5	1.04	5.64	97.9
Sr	231	58.7		60.3				60.8	61.4	60.1	60.3	0.90	1.50	26.1
Cd	8.8	10.3		9.46	8.75	8.87	8.46	9.36	10.6	9.64	9.42	0.69	7.28	107
Ba		197		238				213	210	202	212	14.2	6.71	
Pb	330													

MicroCal-200uL aliquot

	Certified Value					Conc (ug/g)					Average	Standard Deviatio	%RSD	Average % Recovery
Digest Date		7/31/12	7/31/12	7/31/12	8/7/12	8/7/12	8/7/12	8/15/12	8/15/12	8/15/12				
Analysis Date		8/2/12	8/2/12	8/2/12	8/9/12	8/9/12	8/9/12	8/16/12	8/16/12	8/16/12				
Be		0.698		0.642				0.971	0.970	1.00	0.857	0.2	17.99	
Ti								424	456	464	448	17.1	3.82	
Cr	266							182	195	203	193	8.4	4.34	72.7
Mn	505	262		242				302	299	312	283	26.7	9.40	56.1
Co	14	10.6		9.64	9.00	10.0	9.18	9.98	10.4	10.7	9.95	0.6	6.04	71.1
Ni	76.1	69.0		64.3	58.2	62.2	59.0	63.6	69.1	70.0	64.4	4.3	6.66	84.7
Cu		385		355	344	346	380	352	390	404	369	21.4	5.80	
Zn	656	669		613	609	588	626	608	636	660	626	25.7	4.10	95.4
As	18.9	19.3		17.1	16.1	17.4	17.3	17.5	19.1	21.3	18.1	1.5	8.53	96.0
Sr	231	63.5		58.9				59.2	61.9	64.3	61.6	2.2	3.56	26.7
Cd	8.8	10.5		9.14	8.65	8.97	9.03	8.95	10.2	10.2	9.47	0.7	7.31	108
Ba		173		155				200	205	197	186	19.1	10.28	
Pb	330	308		255	495	420		276	353	353	351	77.5	22.04	106

MacroCal-200uL aliquot

	Certified Value					Conc (ug/g)					Average	Standard Deviatio	%RSD	Average % Recovery
Digest Date		7/31/12	7/31/12	7/31/12	8/7/12	8/7/12	8/7/12	8/15/12	8/15/12	8/15/12				
Analysis Date		8/3/12	8/3/12	8/3/12	8/9/12	8/9/12	8/9/12	8/17/12	8/17/12	8/17/12				
Be														
Ti														
Cr	266	306		290	283	290	279	203	234	180	258	43.5	16.84	97.0
Mn	505	338		324	305	316	301	402	382	396	346	38.8	11.22	68.4
Co	14							-78.915	-77.732	-80.295	-79.0	1.0	-1.33	
Ni	76.1							68.0	76.7	62.4	69.0	5.9	8.53	90.7
Cu		445		433	399	412	438	403	461	388	422	24.1	5.71	
Zn	656	851		808	749	722	740	770	834	701	772	50.5	6.54	118
As	18.9	13.6		11.9	8.79	10.1	9.33				10.7	1.8	16.36	56.8
Sr	231				86.2	92.4	89.4	55.1	61.4	47.1	71.9	18.0	25.02	31.1
Cd	8.8							8.78	10.7	8.23	9.2	1.1	11.49	105
Ba		169		215							192	22.6	11.78	
Pb	330													

SRM 2709-San Joaquin Soil

MicroCal-100uL aliquot

	Certified Value	Conc (ug/g)									Average	Standard Deviation	%RSD	Average % Recovery
Digest Date		7/31/12	7/31/12	7/31/12	8/7/12	8/7/12	8/7/12	8/15/12	8/15/12	8/15/12				
Analysis Date		8/27/12	8/27/12	8/27/12	8/13/12	8/13/12	8/13/12	8/16/12	8/16/12	8/16/12				
Be		1.08		1.11				1.16	1.15	1.11	1.12	0.03	2.61	
Ti	3420							490	501	464	485	15.43	3.18	14.2
Cr	130	76.3		74.3	70.2	74.4	83.9	71.7	72.1	69.6	74.1	4.27	5.77	57.0
Mn	538	489		481				507	512	488	496	12.09	2.44	92.1
Co	13.4	12.5		12.3	11.3	12.0	13.4	12.3	12.5	11.9	12.3	0.58	4.75	91.5
Ni	88	80.2		80.3	75.0	79.8	89.2	82.0	82.2	78.6	80.9	3.79	4.68	92.0
Cu	34.6	29.9		28.9	28.7	29.9	33.5	30.9	30.9	29.1	30.2	1.47	4.86	87.3
Zn	106	95.5		97.5	82.4	87.2	97.3	97.5	97.7	91.8	93.4	5.39	5.77	88.1
As	17.7	16.2		16.1	15.5	16.5	18.7	17.0	17.5	17	16.8	0.92	5.50	94.6
Sr	231	109		108				113	114	109	111	2.55	2.30	47.9
Cd	0.38				0	0	0	0	0	0	0.127	0.02	17.84	33.4
Ba	968	422		421				403	434	415	419	10.16	2.42	43.3
Pb	18.9													

MicroCal-200uL aliquot

	Certified Value	Conc (ug/g)									Average	Standard Deviation	%RSD	Average % Recovery
Digest Date		7/31/12	7/31/12	7/31/12	8/7/12	8/7/12	8/7/12	8/15/12	8/15/12	8/15/12				
Analysis Date		8/2/12	8/2/12	8/2/12	8/9/12	8/9/12	8/9/12	8/16/12	8/16/12	8/16/12				
Be		0.79		0.77				1.02	1.08	1.05	0.941	0.14	14.54	
Ti	3420							485	504	464	484	16.57	3.42	14.2
Cr	130							73.4	76.5	72.5	74.2	1.70	2.29	57.0
Mn	538	366		359				411	424	403	393	25.38	6.46	73.0
Co	13.4	11.6		11.5	11.1	10.9	11.1	12.4	12.7	12.1	11.7	0.63	5.36	87.1
Ni	88	77.6		77.2	73.5	72.1	72.9	80.1	84.1	79.5	77.1	3.87	5.02	87.6
Cu	34.6	30.2		30.0	26.0	25.5	25.5	31.3	32.3	30.9	29.0	2.66	9.17	83.7
Zn	106	87.0		89.4	87.8	88.6	86.7	94.3	97.7	93.8	90.7	3.81	4.21	85.5
As	17.7	14.9		15.1	15.0	14.9	15.0	16.9	17.7	16.5	15.8	1.05	6.65	89.1
Sr	231	106		106				113	117	112	111	4.06	3.67	47.9
Cd	0.38	0.275		0.270	0.312	0.300	0.302	0.266	0.265	0.276	0.283	0.02	6.10	74.5
Ba	968	293		284				336	350	334	319	25.91	8.11	33.0
Pb	18.9	14.4		13.0							13.7	0.71	5.17	72.3

MacroCal-200uL aliquot

	Certified Value	Conc (ug/g)									Average	Standard Deviation	%RSD	Average % Recovery
Digest Date		7/31/12	7/31/12	7/31/12	8/7/12	8/7/12	8/7/12	8/15/12	8/15/12	8/15/12				
Analysis Date		8/3/12	8/3/12	8/3/12	8/9/12	8/9/12	8/9/12	8/17/12	8/17/12	8/17/12				
Be														
Ti	3420													
Cr	130	110		108	118	117	117	17.2	18.3	16.2	77.7	46.94	60.41	59.8
Mn	538	502		493	491	494	489	512	521	507	501	10.67	2.13	93.1
Co	13.4													
Ni	88							81	81	79	80.4	1.08	1.35	91.3
Cu	34.6													
Zn	106	108		110	110	110	109	109	111	109	110	0.88	0.81	103
As	17.7	9		9	8	8	8				8.07	0.49	6.11	45.6
Sr	231				164	166	166	116	117	113	140	25.20	17.96	60.8
Cd	0.38													
Ba	968	436		423							430	6.62	1.54	44.4
Pb	18.9													

SRM 2710a-Montan I Soil

MicroCal-100uL aliquot

	Certified Value	Conc (ug/g)									Average	Standard Deviation	%RSD	Average % Recovery
Digest Date		7/31/12	7/31/12	7/31/12	8/7/12	8/7/12	8/7/12	8/15/12	8/15/12	8/15/12				
Analysis Date		8/27/12	8/27/12	8/27/12	8/13/12	8/13/12	8/13/12	8/16/12	8/16/12	8/16/12				
Be		1.44	1.50	1.48				1.43	1.46	1.42	1.45	0.03	1.77	
Ti	2830							1212	1174	1132	1173	32.75	2.79	41.4
Cr	39	15.4	16.3	16.1	14.5	14.3	15.1	13.7	12.8	12.3	14.5	1.30	8.97	37.2
Mn	10100	6664	6385	6364				6956	6587	6390	6558	210.54	3.21	64.9
Co	10	7.70	8.07	8.07	7.72	7.66	7.90	7.85	7.53	7.31	7.76	0.23	2.99	77.6
Ni	14.3	11.7	11.7	11.7	10.5	10.4	10.7	11.3	10.8	10.5	11.0	0.53	4.79	77.1
Cu	2950	2404	2373	2366	1992	2014	2040	2460	2327	2275	2250	173.08	7.69	76.3
Zn	6952	5658	5708	5640	4503	4542	4631	5717	5427	5287	5235	496.71	9.49	75.3
As	626	644	672	677	670	673	695	675	646	629	664	19.39	2.92	106
Sr	330	105	110	111				113	108	106	109	2.74	2.51	33.0
Cd	21.8	20.7	21.1	20.9	21.0	20.9	21.7	22.0	20.6	20.1	21.0	0.54	2.55	96.4
Ba	707	335	336	334				338	324	318	331	7.46	2.26	46.8
Pb														

MicroCal-200uL aliquot

	Certified Value	Conc (ug/g)									Average	Standard Deviation	%RSD	Average % Recovery
Digest Date		7/31/12	7/31/12	7/31/12	8/7/12	8/7/12	8/7/12	8/15/12	8/15/12	8/15/12				
Analysis Date		8/2/12	8/2/12	8/2/12	8/9/12	8/9/12	8/9/12	8/16/12	8/16/12	8/16/12				
Be		1.06	1.12	1.15					1.37	1.35	1.29	0.13	9.84	
Ti	2830								1134	1133	1110	1126	101.39	39.2
Cr	39								15.4	15.6	15.1	15	101.79	38.7
Mn	10100	5648	5874	5630					6302	6268	6226	6060	97.33	61.6
Co	10	6.89	7.13	6.99	6.63	6.95	7.31	6.96	7.63	7.53	7.47	7	96.08	74.7
Ni	14.3	10.5	10.8	10.8	7.87	8.46	8.94	8.42	11.0	11.0	11.00	10	89.23	76.9
Cu	2950	1967	2001	1954	1852	1910	1917	1893	2208	2184	2173	2010	92.51	73.7
Zn	6952	4390	4459	4429	4046	4218	4211	4158	4985	4931	4889	4481	91.65	70.3
As	626	616	631	626	575	611	612	599	626	627	628	615	97.95	100
Sr	330	102	106	104					106	107	106	106	99.88	32.0
Cd	21.8	17.8	18.3	18.0	17.1	17.7	18.3	17.7	18.6	18.5	18.6	18	97.23	85.3
Ba	707	195	202	196					225	220	221	213	96.25	31.3
Pb	5532	4174	4024	4047	3986	3924	3897	4043	3868	3990	3995	87.30	2.19	72.2

MacroCal-200uL aliquaot

	Certified Value	Conc (ug/g)									Average	Standard Deviation	%RSD	Average % Recovery
Digest Date		7/31/12	7/31/12	7/31/12	8/7/12	8/7/12	8/7/12	8/15/12	8/15/12	8/15/12				
Analysis Date		8/3/12	8/3/12	8/3/12	8/9/12	8/9/12	8/9/12	8/17/12	8/17/12	8/17/12				
Be														
Ti	2830													
Cr	39	27.0	27.5	27.7	26.9	27.8	27.7				27.4	0.36	1.30	70.3
Mn	10100	8972	9054	9147	8517	8588	8294	8684	8606	8780	8738	260.86	2.99	86.5
Co	10													
Ni	14.3							8.46	8.68	8.80	8.65	0.14	1.62	60.5
Cu	2950	2930	2936	2961	3119	3154	3058	2561	2581	2605	2878	221.78	7.70	97.6
Zn	6952	5656	5705	5702	4809	4867	4689	5932	5905	6014	5475	500.28	9.14	78.8
As	626	671	677	683	624	647	633				656	22.44	3.42	105
Sr	330				156	159	159	111	111	112	135	23.48	17.42	40.8
Cd	21.8							17.9	17.9	18.3	18.0	0.18	1.02	82.6
Ba	707	267	271	276							272	3.56	1.31	38.4
Pb	5532													

Pre-digestion Fortifications

SRM 1566b-Oyster Tissue

	digest date	5/23/12						
	analysis date	5/25/12						
	1566 Background	Sample Intensity	Sample Fortifcation	Slope	Intercept	ug/L	theoretical	% Recovery
Be	0	0.154	0.154	0.007801	0	19.7	20	98.7
Ti	2.23675	2.779	0.54225	0.02018	0.004	26.7	20	133
Cr	2.4865	7.735	5.2485	0.273501	-0.139	19.7	20	98.5
Mn	34.9515	45.941	10.9895	0.396538	0.068	27.5	20	138
Co	0.55075	6.882	6.33125	0.307501	0.022	20.5	20	103
Ni	0.34175	1.621	1.27925	0.064256	0.017	19.6	20	98.2
Cu	54.417	60.871	6.454	0.144382	-0.25	46.4	20	232
Zn	274.84625	284.258	9.41175	0.04372	0.054	214	20	1070
As	1.781	2.85	1.069	0.040096	0.009	26.4	20	132
Sr	16.516	28.067	11.551	0.517363	0.052	22.2	20	111
Cd	0.094	0.248	0.154	0.007735	0	19.9	20	100
Ba	2.6415	4.433	1.7915	0.087191	-0.074	21.4	20	107
	digest date	5/23/12						
	analysis date	5/25/12						
	1566 Background	Sample Intensity	Sample Fortifcation	Slope	Intercept	ug/L	theoretical	% Recovery
Be	0	0.156	0.156	0.007801	0	20.0	20	100
Ti	2.23675	2.704	0.46725	0.02018	0.004	23.0	20	115
Cr	2.4865	7.593	5.1065	0.273501	-0.139	19.2	20	95.9
Mn	34.9515	46.827	11.8755	0.396538	0.068	29.8	20	149
Co	0.55075	7.029	6.47825	0.307501	0.022	21.0	20	105
Ni	0.34175	1.654	1.31225	0.064256	0.017	20.2	20	101
Cu	54.417	62.111	7.694	0.144382	-0.25	55.0	20	275
Zn	274.84625	294.729	19.88275	0.04372	0.054	454	20	2268
As	1.781	2.866	1.085	0.040096	0.009	26.8	20	134
Sr	16.516	28.485	11.969	0.517363	0.052	23.0	20	115
Cd	0.094	0.253	0.159	0.007735	0	20.6	20	103
Ba	2.6415	4.527	1.8855	0.087191	-0.074	22.5	20	112
	digest date	5/23/12						
	analysis date	5/25/12						
	1566 Background	Sample Intensity	Sample Fortifcation	Slope	Intercept	ug/L	theoretical	% Recovery
Be	0	0.159	0.159	0.007801	0	20.4	20	102
Ti	2.23675	1.636	-0.60075	0.02018	0.004	-30.0	20	
Cr	2.4865	8.34	5.8535	0.273501	-0.139	21.9	20	110
Mn	34.9515	575.222	540.2705	0.396538	0.068	1362	20	6811
Co	0.55075	7.121	6.57025	0.307501	0.022	21.3	20	106
Ni	0.34175	2.263	1.92125	0.064256	0.017	29.6	20	148
Cu	54.417	5.475	-48.942	0.144382	-0.25	-337	20	
Zn	274.84625	5.482	-269.36425	0.04372	0.054	-6162	20	
As	1.781	0.984	-0.797	0.040096	0.009	-20.1	20	
Sr	16.516	271.369	254.853	0.517363	0.052	492	20	2462
Cd	0.094	0.201	0.107	0.007735	0	13.8	20	69.2
Ba	2.6415	28.937	26.2955	0.087191	-0.074	302	20	1512

SRM 1573a-Tomato Leaf Overspikes

digest date	5/23/12							
analysis date	5/25/12							

	1573 Background	Sample Intensity	Sample Fortifcation	Slope	Intercept	ug/L	theoretical	% Recovery
Be	0.001	0.166	0.165	0.007801	0	21.2	20	106
Ti	1.02	1.62	0.6	0.02018	0.004	29.5	20	148
Cr	3.564	8.394	4.83	0.273501	-0.139	18.2	20	90.8
Mn	509.1145	586.051	76.9365	0.396538	0.068	194	20	969
Co	0.894	7.125	6.231	0.307501	0.022	20.2	20	101
Ni	0.9885	2.205	1.2165	0.064256	0.017	18.7	20	93.3
Cu	3.11625	5.438	2.32175	0.144382	-0.25	17.8	20	89.1
Zn	4.728	5.52	0.792	0.04372	0.054	16.9	20	84.4
As	0.03	0.978	0.948	0.040096	0.009	23.4	20	117
Sr	253.0245	277.431	24.4065	0.517363	0.052	47.1	20	235
Cd	0.0535	0.2	0.1465	0.007735	0	18.9	20	94.7
Ba	28.02925	29.382	1.35275	0.087191	-0.074	16.4	20	81.8

digest date	5/23/12							
analysis date	5/25/12							

	1573 Background	Sample Intensity	Sample Fortifcation	Slope	Intercept	ug/L	theoretical	% Recovery
Be	0.001	0.161	0.16	0.007801	0	20.5	20	103
Ti	1.02	1.613	0.593	0.02018	0.004	29.2	20	146
Cr	3.564	8.323	4.759	0.273501	-0.139	17.9	20	89.5
Mn	509.1145	574.153	65.0385	0.396538	0.068	164	20	819
Co	0.894	7.041	6.147	0.307501	0.022	19.9	20	100
Ni	0.9885	2.213	1.2245	0.064256	0.017	18.8	20	94.0
Cu	3.11625	5.417	2.30075	0.144382	-0.25	17.7	20	88.3
Zn	4.728	5.479	0.751	0.04372	0.054	15.9	20	79.7
As	0.03	0.981	0.951	0.040096	0.009	23.5	20	117
Sr	253.0245	272.149	19.1245	0.517363	0.052	36.9	20	184
Cd	0.0535	0.2	0.1465	0.007735	0	18.9	20	94.7
Ba	28.02925	28.895	0.86575	0.087191	-0.074	10.8	20	53.9

digest date	5/23/12							
analysis date	5/25/12							

	1573 Background	Sample Intensity	Sample Fortifcation	Slope	Intercept	ug/L	theoretical	% Recovery
Be	0.001	0.166	0.165	0.007801	0	21.2	20	106
Ti	1.02	1.62	0.6	0.02018	0.004	29.5	20	148
Cr	3.564	8.394	4.83	0.273501	-0.139	18.2	20	90.8
Mn	509.1145	586.051	76.9365	0.396538	0.068	194	20	969
Co	0.894	7.125	6.231	0.307501	0.022	20.2	20	101
Ni	0.9885	2.205	1.2165	0.064256	0.017	18.7	20	93.3
Cu	3.11625	5.438	2.32175	0.144382	-0.25	17.8	20	89.1
Zn	4.728	5.52	0.792	0.04372	0.054	16.9	20	84.4
As	0.03	0.978	0.948	0.040096	0.009	23.4	20	117
Sr	253.0245	277.431	24.4065	0.517363	0.052	47.1	20	235
Cd	0.0535	0.2	0.1465	0.007735	0	18.9	20	94.7
Ba	28.02925	29.382	1.35275	0.087191	-0.074	16.4	20	81.8

SRM 1944-New York/New Jersey Waterway Sediment

.2mL aliquot-Soils Micro
Digest Date 7/31/2012
Analysis Date 8/2/2012

	sample intensity	1944 background	Sample Fortification	slope	intcept	µg/L	Theoretical	% Recovery
Be	0.083	0.003	0.08	0.007321	0.001	10.8	10	108
Ti	3.382	3.429	-0.047	0.017784	0.006		10	
Cr	23.694	23.998	-0.304				10	
Mn	45.589	45.718	-0.129	0.347521	0.232		10	
Co	4.135	1.539	2.596	0.272612	0.091	9.19	10	91.9
Ni	2.415	1.972	0.443	0.05692	0.008	7.64	10	76.4
Cu	26.04	25.14	0.9	0.130441	0.022	6.73	10	67.3
Zn	13.209	13.739	-0.53	0.040808	0.092		10	
As	0.795	0.396	0.399	0.04018	0.009	9.71	10	97.1
Sr	20.158	16.01	4.148	0.501223	0.104	8.07	10	80.7
Cd	0.118	0.041	0.077	0.007799	0	9.87	10	98.7
Ba	5.816	0.396	5.42	0.081779	-0.003		10	

.1mL aliquot-Soils Micro
Digest Date 7/31/2012
Analysis Date 8/27/2012

	sample intensity	1944 backgrou	Sample Fortificatio	slope	intcept	µg/L	Theoretical	% Recovery
Be	0.051	0.002	0.049	0.00937	0	5.23	5	105
Cr	12.341	11.279	1.062	0.213055	0.208	4.01	5	80.2
Mn	30.947	28.267	2.68	0.343962	0.121	7.44	5	149
Co	2.029	0.701	1.328	0.264254	0.007	5.00	5	100
Ni	1.251	0.953	0.298	0.054227	0.008	5.35	5	107
Cu	13.328	11.832	1.496	0.122128	0.112	11.3	5	227
Zn	7.084	6.731	0.353	0.037486	0.064	7.71	5	154
As	0.408	0.188	0.22	0.039942	0.001	5.48	5	110
Sr	10.629	7.9	2.729	0.518005	0.095	5.08	5	102
Cd	0.064	0.019	0.045	0.007642	0.001	5.76	5	115
Ba	4.465	4.64	-0.175	0.07725	0.035	-2.72	5	-54.4

.2mL aliquot-Soils Micro
Digest Date 8/7/2012
Analysis Date 8/9/2012

	sample intensity	1944 background	Sample Fortification	slope	intcept	µg/L	Theoretical	% Recovery
Cr	22.226	20.81	1.416					
Co	3.785	1.372	2.413	0.274833	-0.003	8.79	10	87.9
Ni	2.364	1.838	0.526	0.056353	0.084	7.84	10	78.4
Cu	22.288	21.492	0.796	0.12299	0.359	3.55	10	35.5
Zn	11.565	11.698	-0.133	0.03954	0.072	-5.18	10	-51.8
As	0.737	0.365	0.372	0.040963	0.009	8.86	10	88.6
Cd	0.114	0.035	0.079	0.007879	0	10.0	10	100.3

.1mL aliquot-Soils Micro
Digest Date 8/7/2012
Analysis Date 8/13/2012

	sample intensity	1944 backgrou	Sample Fortificatio	slope	intcept	µg/L	Theoretical	% Recovery
Cr	12.411	10.282	2.129	0.2271	0.17	8.63	5	173
Co	2.042	0.571	1.471	0.266797	-0.04	5.66	5	113
Ni	1.313	0.872	0.441	0.055852	0.028	7.39	5	148
Cu	12.58	11.073	1.507	0.126797	0.083	11.2	5	225
Zn	6.678	6.279	0.399	0.040072	0.085	7.84	5	157
As	0.41	0.169	0.241	0.040525	-0.002	6.00	5	120
Cd	0.064	0.017	0.047	0.007915	0	5.94	5	119

.2mL aliquot-Soils Micro
Digest Date 8/15/2012
Analysis Date 8/16/2012

	sample intensity	1944 background	Sample Fortification	slope	intcept	µg/L	Theoretical	% Recovery
Be	0.2	0.004	0.196	0.008978	-0.00029	10.9	10	109
Ti	5.049	3.881	1.168	0.018245	0.01066	31.7	10	317
Cr	25.966	21.298	4.668	0.231731	0.159062	9.73	10	97.3
Mn	53.389	52.511	0.878	0.345305	0.291531	0.849	10	8.49
Co	6.719	1.314	5.405	0.270757	-0.03701	10.0	10	100
Ni	2.965	1.797	1.168	0.05601	0.016072	10.3	10	103
Cu	24.876	22.199	2.677	0.125771	0.07781	10.3	10	103
Zn	13.044	11.951	1.093	0.039145	0.050172	13.3	10	133
As	1.215	0.35	0.865	0.041247	-0.12155	12.0	10	120
Sr	26.573	15.185	11.388	0.508812	0.123784	11.1	10	111
Cd	0.209	0.035	0.174	0.007916	-4.8E-05	11.0	10	110
Ba	8.572	8.05	0.522	0.080795	-0.0241	3.38	10	33.8

SRM 2709- Sam Joaquin Soil

.2mL aliquot-Soils Micro

Digest Date 7/31/12

Analysis Date 8/2/2012

	sample intensity	2709 background	Sample Fortification	slope	intcept	µg/L	Theoretical	% Recovery
Be	0.084	0.004	0.08	0.007321	0.001	10.8	10	108
Ti	3.94	2.986	0.954	0.017784	0.006	53.3	10	533
Cr	10.96	8.49	2.47				10	0.0
Mn	65.949	63.913	2.036	0.347521	0.232	5.19	10	51.9
Co	4.345	1.668	2.677	0.272612	0.091	9.49	10	94.9
Ni	2.801	2.217	0.584	0.05692	0.008	10.1	10	101
Cu	3.218	1.993	1.225	0.130441	0.022	9.22	10	92.2
Zn	2.425	1.867	0.558	0.040808	0.092	11.4	10	114
As	0.719	0.309	0.41	0.04018	0.009	10.0	10	99.8
Sr	32.627	26.722	5.905	0.501223	0.104	11.6	10	116
Cd	0.083	0.001	0.082	0.007799	0	10.5	10	105
Ba	12.306	11.965	0.341	0.081779	-0.003	4.21	10	42.1

.1mL aliquot-Soils Micro

Digest Date 7/31/12

Analysis Date 8/27/12

	sample intensity	2709 background	Sample Fortificatio	slope	intcept	µg/L	Theoretical	% Recovery
Be	0.054	0.002	0.052	0.00937	0	5.55	5	111
Ti								
Cr	5.446	4.27	1.176	0.213055	0.208	4.54	5	90.9
Mn	44.896	42.146	2.75	0.343962	0.121	7.64	5	153
Co	2.165	0.831	1.334	0.264254	0.007	5.02	5	100
Ni	1.418	1.096	0.322	0.054227	0.008	5.79	5	116
Cu	1.701	1.025	0.676	0.122128	0.112	4.62	5	92.4
Zn	1.257	0.959	0.298	0.037486	0.064	6.24	5	125
As	0.369	0.163	0.206	0.039942	0.001	5.13	5	103
Sr	17.195	14.164	3.031	0.518005	0.095	5.67	5	113
Cd	0.043	0	0.043	0.007642	0.001	5.50	5	110
Ba	7.572	8.177	-0.605	0.07725	0.035	-8.28	5	-166

.2mL aliquot-Soils Micro

Digest Date 8/7/2012

Analysis Date 8/9/2012

	sample intensity	2709 background	Sample Fortification	slope	intcept	µg/L	Theoretical	% Recovery
Cr	5.741	4.395	1.346	0.2271	0.17	5.18	5	104
Co	2.191	0.76	1.431	0.266797	-0.04	5.51	5	110
Ni	1.458	1.142	0.316	0.055852	0.028	5.16	5	103
Cu	1.707	1.03	0.677	0.126797	0.083	4.68	5	94
Zn	1.225	0.959	0.266	0.040072	0.085	4.52	5	90
As	0.391	0.165	0.226	0.040525	-0.002	5.63	5	113
Cd	0.045	0	0.045	0.007915	0	5.69	5	114
Cr	6.101	4.395	1.706	0.2271	0.17	6.76	5	135
Co	2.318	0.76	1.558	0.266797	-0.04	5.99	5	120
Ni	1.551	1.142	0.409	0.055852	0.028	6.82	5	136
Cu	1.821	1.03	0.791	0.126797	0.083	5.58	5	112
Zn	1.279	0.959	0.32	0.040072	0.085	5.86	5	117
As	0.413	0.165	0.248	0.040525	-0.002	6.17	5	123
Cd	0.048	0	0.048	0.007915	0	6.06	5	121

.2mL aliquot-Soils Micro

Digest Date 08/15/12

Analysis Date 08/16/12

	sample intensity	2709 background	Sample Fortification	slope	intcept	µg/L	DF	DF	µg/L	Theoretical	% Recovery
Be	0.202	0.005	0.197	0.008978	-0.00029	22.0	50	0.04	11.0	10	110
Ti	5.741	4.61	1.131	0.018245	0.01066	61.4	50	0.04	30.7	10	307
Cr	13.446	9.022	4.424	0.231731	0.159062	18.4	50	0.04	9.20	10	92.0
Mn	75.871	73.413	2.458	0.345305	0.291531	6.3	50	0.04	3.14	10	31.4
Co	6.977	1.685	5.292	0.270757	-0.03701	19.7	50	0.04	9.84	10	98.4
Ni	3.353	2.37	0.983	0.05601	0.016072	17.3	50	0.04	8.63	10	86.3
Cu	4.463	2.111	2.352	0.125771	0.07781	18.1	50	0.04	9.04	10	90.4
Zn	2.678	1.963	0.715	0.039145	0.050172	17.0	50	0.04	8.49	10	84.9
As	1.188	0.354	0.834	0.041247	-0.12155	23.2	50	0.04	11.6	10	116
Sr	39.663	29.764	9.899	0.508812	0.123784	19.2	50	0.04	9.61	10	96.1
Cd	0.173	0.001	0.172	0.007916	-4.8E-05	21.7	50	0.04	10.9	10	109
Ba	14.898	14.118	0.78	0.080795	-0.0241	10.0	50	0.04	4.98	10	49.8

SRM 2710-Montana I Soil

.2mL aliquot-Soils Micro

Digest Date 7/31/12

Analysis Date 8/2/2012

	sample intensity	2710 background	Sample Fortification	slope	intcept	µg/L	Theoretical	% Recovery
Be	0.084	0.005	0.079	0.007321	0.001	10.7	10	107
Ti	9.534	9.204	0.33	0.017784	0.006	18.2	10	182
Cr	4.148	2.081	2.067				10	
Mn	985.776	978.585	7.191	0.347521	0.232	20.0	10	200
Co	3.655	1.045	2.61	0.272612	0.091	9.24	10	92.4
Ni	0.86	0.316	0.544	0.05692	0.008	9.42	10	94.2
Cu	126.231	127.437	-1.206	0.130441	0.022	-9.41	10	
Zn	88.258	90.47	-2.212	0.040808	0.092	-56.5	10	
As	12.851	12.575	0.276	0.04018	0.009	6.65	10	66.5
Sr	31.379	26.198	5.181	0.5012234	0.104	10.1	10	101
Cd	0.138	0.07	0.068	0.007799	0	8.72	10	87.2
Ba	8.342	7.992	0.35	0.081779	-0.003	4.32	10	43.2

.1mL aliquot-Soils Micro

Digest Date 8/7/2012

Analysis Date 8/13/12

	sample intensity		Average	2710 background	Sample Fortification	slope	intcept	µg/L	Theoretical	% Recovery
Cr	2.23	2.032	2.131	0.99	1.141	0.2271	0.17	4.28	5	85.5
Co	1.953	1.756	1.8545	0.475	1.3795	0.266797	-0.04	5.32	5	106
Ni	0.486	0.433	0.4595	0.174	0.2855	0.055852	0.028	4.61	5	92.2
Cu	66.101	60.31	63.2055	63.216	-0.0105	0.126797	0.083	-0.74	5	
Zn	46.608	43.019	44.8135	45.192	-0.3785	0.040072	0.085	-11.6	5	
As	7.317	6.554	6.9355	6.783	0.1525	0.040525	-0.002	3.81	5	76.2
Cd	0.086	0.078	0.082	0.042	0.04	0.007915	0	5.05	5	101

.2mL aliquot-Soils Micro

Digest Date 8/15/12

Analysis Date 8/16/12

	sample intensity	2710 background	Sample Fortification	slope	intcept	µg/L	DF	DF	µg/L	Theoretical	% Recovery
Be	0.195	0.006	0.189	0.0089776	-0.000287542	21.1	50	0.04	10.5	10	105
Ti	11.86	10.348	1.512	0.0182446	0.0106598	82.3	50	0.04	41.1	10	411
Cr	6.127	1.968	4.159	0.231731	0.159062	17.3	50	0.04	8.63	10	86.3
Mn	1075.747	1082.406	-6.659	0.345305	0.291531	-20.1	50	0.04	-10.1	10	
Co	6.171	0.983	5.188	0.270757	-0.0370075	19.3	50	0.04	9.65	10	96.5
Ni	1.395	0.325	1.07	0.0560098	0.0160721	18.8	50	0.04	9.41	10	94.1
Cu	136.48	137.45	-0.97	0.125771	0.07781	-8.3	50	0.04	-4.17	10	
Zn	95.96	96.562	-0.602	0.0391453	0.0501717	-16.7	50	0.04	-8.33	10	
As	13.543	12.919	0.624	0.0412466	-0.121546	18.1	50	0.04	9.04	10	90.4
Sr	38.182	27.297	10.885	0.508812	0.123784	21.1	50	0.04	10.6	10	106
Cd	0.214	0.073	0.141	0.00791643	-0.000048396	17.8	50	0.04	8.91	10	89.1
Ba	10.205	8.845	1.36	0.0807946	-0.0240966	17.1	50	0.04	8.57	10	85.7

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1 **Limits of Quantitation**

Limit of Quantitation from 1μg/L Standard

	Intensities								Standard			Limit of
	R1	R2	R3	R4	R5	R6	R7	Average	Deviation	slope		Quantitation
Be	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.000	0.009	3.3	0
Cr	0.432	0.431	0.417	0.426	0.436	0.327	0.318	0.398	0.052	0.213	3.3	0.807
Mn	0.325	0.326	0.325	0.325	0.329	0.329	0.321	0.326	0.003	0.344	3.3	0.026
Co	0.276	0.273	0.276	0.273	0.267	0.257	0.26	0.269	0.008	0.264	3.3	0.097
Ni	0.056	0.056	0.055	0.055	0.057	0.057	0.053	0.056	0.001	0.054	3.3	0.085
Cu	0.332	0.326	0.328	0.33	0.325	0.273	0.279	0.313	0.026	0.122	3.3	0.693
Zn	0.044	0.045	0.043	0.045	0.045	0.038	0.037	0.042	0.003	0.037	3.3	0.304
As	0.04	0.04	0.039	0.04	0.04	0.039	0.039	0.040	0.001	0.040	3.3	0.044
Sr	0.533	0.524	0.535	0.53	0.528	0.515	0.526	0.527	0.007	0.518	3.3	0.042
Cd	0.008	0.008	0.008	0.008	0.008	0.008	0.007	0.008	0.000	0.008	3.3	0.163
Ba	0.067	0.067	0.064	0.066	0.066	0.082	0.065	0.068	0.006	0.077	3.3	0.265