Surface changes and metal release in the presence of citric acid for food applications
Stainless steel grades 201, 304, 204, 2101, 316L, 430, and EN1.4003

Final report, December 2014

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Commissioned by Team Stainless
Metal release from stainless steel into citric acid and tap water solutions of relevance for food applications with a surface perspective

KTH – Team Stainless project, Aug 2012 – Aug 2014

Background: Implementation of the new CoE protocol, using citric acid instead of acetic acid (Italian decree) as test medium.

Important research questions answered:
1. Differences in released metal quantities from stainless steel grades when using the new CoE protocol, compared to the Italian decree?
2. How is the surface of stainless steels changed upon exposure in citric acid? Is there any possibility of formation of Cr(VI) due to the oxidizing potential of any manganese oxides in the surface oxide of manganese-containing stainless steels?
3. How will different stainless steel grades of diverse surface finish behave following exposure according to the CoE protocol? Which grades will pass and which grades will fail the requirements, and at what specific conditions (loading, temperature, repeated exposures, etc.)?
4. Influence of the pH and citric acid concentration of the solution, respectively, on the released amount of metals from stainless steel?
5. How is the influence of repeated exposure in citric acid and surface abrasion on the metal release from some stainless steel grades?
Pilot study

Step 1

• Quantification of metal release from grades 201 and 304 in citric acid solutions
• Identification of surface changes upon citric acid exposure

M1: agreement on details step 2

M (every 3 months): discussion and agreement on experimental details

Step 2

• Screening of different stainless steel grades

M: agreement on details step 3

Step 3

• Effect of repeated exposure
• Effect of pH and citric acid concentration
• Investigation of different surface finishes for 316 and 304
• Effect of loading (surface area to solution volume ratio) for as-received 304 (2B)

Final draft report:
latest December 2014

M – meeting (email, telephone conference, meeting) between KTH and working group (sponsor(s))

START:
Aug 2012

Step 1 finished:
April 2013
(preliminary in Feb 2013)

Step 2 finished:
January 2014
(preliminary in Oct 2013)

Preliminary report in May 2014

Project finished:
Aug 2014

Project finished:
Aug 2014

Preliminary report in May 2014

Final draft report:
latest December 2014
# Investigated grades

## Investigated grades of stainless steels (based on supplier information)

<table>
<thead>
<tr>
<th>Name (in this report)</th>
<th>UNS (ASTM A 240)</th>
<th>EN</th>
<th>Surface finish</th>
<th>Cr wt%</th>
<th>Mn wt%</th>
<th>Ni wt%</th>
<th>Mo wt%</th>
<th>Cu wt%</th>
<th>N wt%</th>
<th>C wt%</th>
<th>S wt%</th>
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<tbody>
<tr>
<td>EN1.4003</td>
<td>S40977</td>
<td>1.4003</td>
<td>2B</td>
<td>11</td>
<td>&lt;1</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>430</td>
<td>S43000</td>
<td>1.4016</td>
<td>2B</td>
<td>16</td>
<td>0.3</td>
<td>0.1</td>
<td>0.02</td>
<td>0.04</td>
<td>0.03</td>
<td>0.03</td>
<td>0.002</td>
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<tr>
<td>204</td>
<td>S20431 (+Cu)</td>
<td>1.4597 (+Cu)</td>
<td>2B</td>
<td>16</td>
<td>9.1</td>
<td>1.1</td>
<td>0.2</td>
<td>1.6</td>
<td>0.19</td>
<td>0.1</td>
<td>0.004</td>
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<tr>
<td>201</td>
<td>S20100</td>
<td>1.4372</td>
<td>2D</td>
<td>16.9</td>
<td>5.8</td>
<td>3.6</td>
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<td>0.11</td>
<td>0.002</td>
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<tr>
<td>316L</td>
<td>S31603</td>
<td>1.4404</td>
<td>2B</td>
<td>17</td>
<td>1.3</td>
<td>10.2</td>
<td>2.0</td>
<td>0.5</td>
<td>0.05</td>
<td>0.02</td>
<td>-</td>
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<tr>
<td>316L</td>
<td>S31603</td>
<td>1.4404</td>
<td>Sc.-Br. (2J)</td>
<td>using a Scotch-Brite brush</td>
<td></td>
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<tr>
<td>316L</td>
<td>S31603</td>
<td>1.4404</td>
<td>No. 4 (2G)</td>
<td>polishing with a 220 grit grinding belt</td>
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<tr>
<td>304</td>
<td>S30400</td>
<td>1.4301</td>
<td>2B</td>
<td>17.9</td>
<td>1.2</td>
<td>9.0</td>
<td>0.4</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.003</td>
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<tr>
<td>304</td>
<td>S30400</td>
<td>1.4301</td>
<td>Sc.-Br. (2J)</td>
<td>using a Scotch-Brite brush</td>
<td></td>
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<td></td>
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<tr>
<td>304</td>
<td>S30400</td>
<td>1.4301</td>
<td>No. 4 (2G)</td>
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<tr>
<td>LDX 2101</td>
<td>S32101</td>
<td>1.4162</td>
<td>2B</td>
<td>21.4</td>
<td>4.8</td>
<td>1.6</td>
<td>0.3</td>
<td>0.3</td>
<td>0.22</td>
<td>0.02</td>
<td>0.001</td>
</tr>
</tbody>
</table>

## Surface preparation of test coupons

**As-received:** Edges ground (abraded) by 1200 grit SiC, coupon areas not abraded, cleaned ultrasonically in ethanol and acetone for 5 min, respectively, dried with cold nitrogen gas, and aged for 24 ± 1 h in a desiccator (at room temperature).

**Abraded:** Edges + coupon surfaces abraded (1200 grit SiC), otherwise identical preparation as for as-received coupons.
Synthetic fluids + exposure conditions

CoE protocol

Exposures after 2, 4, 8, 26, 240 h (70°C (first 2 h) / 40°C), CoE protocol

All citric acid test solutions were buffers with pH changes during exposure of less than 0.19

Temperature, surface preparation, solution, loading, and exposure duration differ, as described for each result.

Citric acid, pH 2.4 (CA 2.4) 5 g/L citric acid

Citric acid, pH 3.1 (CA 3.1)
5 g/L citric acid + 850 µg/L (NaOH 50%)

Citric acid, pH 4.8 (CA 4.8)
5 g/L citric acid + 2980 µg/L (NaOH 50%)

Citric acid, pH 6.4 (CA 6.4)
5 g/L citric acid + 4280 µg/L (NaOH 50%)

Citric acid, pH 11 (CA 11)
5 g/L citric acid + 4550 µg/L (NaOH 50%)

Citric acid, pH 4.5 (CA 4.5)
20.8 g/L citric acid, 6 g/L NaOH

Artificial tap water, pH 7.5 (TW)
0.12 g/L NaHCO₃, 0.07 g/L MgSO₄·7H₂O, 0.12 g/L CaCl₂·2H₂O

Investigation of the effect of pH and citric acid concentration

Same CA amount and pH as in artificial lysosomal fluid (previous studies)

6 mL test solutions

Samples - total surface area: approx. 6 cm²

Loading of 1 cm²/mL
Experimental strategy

Surface characterization (prior and after exposure, selected samples):
- Scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS)
- Confocal Raman microscopy (CRM)
- X-ray photoelectron spectroscopy (XPS)
- Electron Backscattered Diffraction (EBSD)

Solution analysis:
Atomic absorption spectroscopy – graphite furnace (GF-AAS):
Fe, Cr, Ni, Mn, Mo (only for grade 316)

Speciation analysis (grades 201 and 304):
Stripping voltammetry:
Cr(III), Cr(VI)

Electrochemical measurements:
Open circuit potential (OCP) time- and temperature-dependence
Raman spectroscopy (201 and 2101): After exposure, especially to citric acid pH 2.4:

- different iron oxides
- possibly chromium(III)oxides
- no evidence for chromates
- different manganese oxides possible

EDS results (201, 304, and 2101) in general agreement with bulk information provided by the supplier.
Homogenous elemental distribution for 304.
**Duplex microstructure confirmed for LDX 2101**

**SEM**

**EBSD**

**EDS**

<table>
<thead>
<tr>
<th>Element</th>
<th>Based on supplier (wt%)</th>
<th>EDS results range (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Bal.</td>
<td>Bal.</td>
</tr>
<tr>
<td>Cr</td>
<td>21.4</td>
<td>20.9 - 22.2</td>
</tr>
<tr>
<td>Mn</td>
<td>4.8</td>
<td>0.5 - 6.1</td>
</tr>
<tr>
<td>Ni</td>
<td>1.6</td>
<td>0.0 - 2.4</td>
</tr>
<tr>
<td>Mo</td>
<td>0.3</td>
<td>0.0 – 1.6</td>
</tr>
<tr>
<td>Cu</td>
<td>0.3</td>
<td>0.0 – 0.6</td>
</tr>
</tbody>
</table>

As received 2101 (duplex) Unexposed

- **Ferrite (54.4%)**
- **Austenite (45.6%)**
EDS mapping for LDX 2101

As received 2101 (2B)
Unexposed

iron

chromium

manganese

nickel
No visible changes in surface topography of grade 201 after exposure in citric acid solutions or artificial tap water.

Surface - SEM

As-received 201
Unexposed

As-received 201
Citric acid pH 4.5
8 h at 70/40 °C
No visible changes in surface topography of grade 304 after exposure in citric acid solutions or tap water.

Surface - SEM

As-received 304
Unexposed

As-received 304
Citric acid pH 2.4
10 days at 70/40 ºC
No visible changes in surface topography of grade LDX 2101 after exposure in citric acid (pH 2.4) or artificial tap water.
Surface enrichment of Cr for all investigated grades. Depletion of Mn from the utmost surface oxide of 2101 after exposure in citric acid (pH 2.4).

Surface oxide – XPS

Citric acid pH 2.4, as-received, 70/40 °C, CoE protocol
Reduction in surface oxide thickness for all investigated grades after exposure to citric acid (pH 2.4). No clear changes for EN1.4003.

Citric acid pH 2.4, as-received, 70/40 °C, CoE protocol

Surface oxide – XPS

Changes in relative surface oxide thickness (%) vs. Exposure time (h)

-35
-30
-25
-20
-15
-10
-5
0
5

EN 1.4003
low Cr
430
204
201
316L
304
2101
Chromium enrichment of the surface oxide of 201 and 304 after exposure in citric acid (pH 4.5).

**Surface oxide – XPS**

<table>
<thead>
<tr>
<th>Exposure time (h)</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>8</th>
<th>26</th>
<th>240</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>201</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td><strong>304</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N/A</td>
<td></td>
</tr>
</tbody>
</table>

**Citric acid pH 4.5, as-received, 70/40 °C**

- **Cr (wt%) bulk content**

N/A= no data available
Reduction in surface oxide thickness for grades 201 and 304 after exposures in citric acid (pH 4.5).

Surface oxide – XPS

Citric acid pH 4.5, as-received, 70/40 °C

N/A= no data available
Surface enrichment of Cr for grade 201 and complete Mn depletion from the surface oxide for grade 2101 after exposure in artificial tap water (pH 7.5). No changes observed for grades 204, 304, and 316L.

**Surface oxide – XPS**

**Artificial tap water pH 7.5, as-received, 70/40 °C, CoE protocol**

<table>
<thead>
<tr>
<th>Grade</th>
<th>Cr (wt%)</th>
<th>Fe (wt%)</th>
<th>Mn (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>204</td>
<td>16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>201</td>
<td>16.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>304</td>
<td>17.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2101</td>
<td>21.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* based on one measurement
Only minor or no changes in oxide thickness upon exposure in artificial tap water.

Surface oxide – XPS

Artificial tap water pH 7.5, as-received, 70/40 °C, CoE protocol

Changes in relative surface oxide thickness (%)

Exposure time (h)

* based on one measurement
Citric acid (pH 2.4) was the most aggressive test solution.

Metal release-AAS

As-received

SRL- Fe = 40 µg/cm² (loading: 1 cm²/mL)

Release in tap water <0.03 µg Fe/cm²
Citric acid (pH 2.4) was the most aggressive test solution-cont.

As-received

Metal release-AAS

- 5 g/L Citric acid pH 2.4 (70/40 °C)
- 20.8 g/L Citric acid pH 4.5 (70/40 °C)
- Artificial tap water pH 7.5 (70/40 °C)

Release in tap water <0.006 µg Cr/cm²

SRL- Cr = 0.25 µg/cm² (loading: 1 cm²/mL)
Citric acid (pH 2.4) was the most aggressive test solution-cont.

**Metal release-AAS**

- 5 g/L Citric acid pH 2.4 (70/40 °C)
- 20.8 g/L Citric acid pH 4.5 (70/40 °C)
- Artificial tap water pH 7.5 (70/40 °C)

As-received

- Release in tap water <0.02 µg Mn/cm²
- SRL- Mn = 1.8 µg/cm² (loading: 1 cm²/mL)
Citric acid (pH 2.4) was the most aggressive test solution-cont.

As-received

Metal release-AAS

5 g/L Citric acid pH 2.4 (70/40 °C)
20.8 g/L Citric acid pH 4.5 (70/40 °C)
Artificial tap water pH 7.5 (70/40 °C)

SRL- Ni = 0.14 µg/cm² (loading: 1 cm²/mL)

Release in tap water <0.006 µg Ni/cm²
More Fe released from grade EN1.4003 (low Cr) in citric acid (pH 2.4) compared with the other grades.

Metal release-AAS

As-received

\[
\text{SRL- Fe} = 40 \mu g/cm^2 \text{ (loading: 1 cm}^2/\text{mL)}
\]

- EN1.4003 11 wt%Cr
- 430 16 wt%Cr
- 204 16 wt%Cr
- 201 16.9 wt%Cr
- 316L 17 wt%Cr
- 304 17.9 wt%Cr
- LDX 2101 21.4 wt%Cr

5 g/L Citric acid pH 2.4 (70/40 ºC)  
Artificial tap water pH 7.5 (70/40 ºC)

Release in tap water <0.07 µg Fe/cm²
More Mn released from grade 204 compared with the other grades. Released amounts of Mn proportional to the Mn bulk alloy content.

SRL- Mn = 1.8 µg/cm² (loading: 1 cm²/mL)

- 204: 16 wt%Cr, 9.1 wt% Mn
- 201: 16.9 wt%Cr, 5.8 wt% Mn
- 316L: 17 wt%Cr, 1.3 wt% Mn
- 304: 17.9 wt%Cr, 1.2 wt% Mn
- LDX 2101: 21.4 wt%Cr, 4.8 wt% Mn

Release in tap water <0.03 µg Mn/cm²

Exposure time (h)

- 204
- 201
- 316L
- 304
- LDX 2101

5 g/L Citric acid pH 2.4 (70/40 °C)
Artificial tap water pH 7.5 (70/40 °C)
More Cr released from grade 304 in citric acid (pH 2.4) compared with the other investigated grades.

**Metal release-AAS**

**As-received**

Release in tap water <0.006 µg Cr / cm²

*SRL- Cr = 0.25 µg/cm² (loading: 1 cm²/mL)*

**Graph Description**

- **Y-axis:** Released amount of chromium (µg/cm²)
- **X-axis:** Exposure time (h)
- **Data Points:**
  - **EN1.4003** 11 wt%Cr
  - **430** 16 wt%Cr
  - **204** 16 wt%Cr
  - **201** 16.9 wt%Cr
  - **316L** 17 wt%Cr
  - **304** 17.9 wt%Cr
  - **LDX 2101** 21.4 wt%Cr
More Ni released from grades 316L and 304 in both test solutions compared with the other investigated grades.

**Metal release-AAS**

As-received

![Graph showing released nickel amounts over exposure time for different grades and test solutions.](image)

- **SRL- Ni = 0.14 µg/cm² (loading: 1 cm²/mL)**

- **Release in tap water <0.006 µg Ni/cm²**

- **5 g/L Citric acid pH 2.4 (70/40 °C)**

- **Artificial tap water pH 7.5 (70/40 °C)**

- Grades:
  - 204: 16 wt%Cr, 1.1 wt% Ni
  - 201: 16.9 wt%Cr, 3.6 wt% Ni
  - 316L: 17 wt%Cr, 10.2 wt% Ni
  - 304: 17.9 wt%Cr, 9 wt% Ni
  - LDX 2101: 21.4 wt%Cr, 1.6 wt% Ni
More Mo released from grade 316L in citric acid (pH 2.4) compared with artificial tap water (pH 7.5).

Metal release-AAS

As-received

$SRL - Mo = 0.12 \mu g/cm^2$ (loading: 1 cm$^2$/mL)

316L  
17 wt% Cr  
2 wt% Mo

Release in tap water <0.003 µg Mo/cm$^2$
Most metals released from grade EN1.4003 (low Cr) upon exposure in citric acid (pH 2.4).

Metal release-AAS

* Only Fe and Cr were analyzed by AAS for grades 430 and EN1.4003 containing Mn, Ni, and Mo <1 (wt%)

As-received grades
240 h at 70 °C/40 °C
5 g/L Citric acid (pH 2.4) and Artificial tap water (pH 7.5)
Most Fe released into citric acid (pH 2.4) during the first 2 hours of exposure.

**As-received surfaces**

Exposure in citric acid (pH 2.4) for 2 h at 70 °C, 2 h at 70 °C followed by 24 h at 40 °C, and 2 h at 70 °C followed by 238 h at 40 °C.
Most Cr released into citric acid (pH 2.4) during the first 2 hours of exposure.

*As-received surfaces*

*Exposure in citric acid (pH 2.4) for 2 h at 70 °C, 2 h at 70 °C followed by 24 h at 40 °C, and 2 h at 70 °C followed by 238 h at 40 °C.*
Most Ni released into citric acid (pH 2.4) during the first 2 hours of exposure.

As-received surfaces
Exposure in citric acid (pH 2.4) for 2 h at 70 °C, 2 h at 70 °C followed by 24 h at 40 °C, and 2 h at 70 °C followed by 238 h at 40 °C.
Most Mn released into citric acid (pH 2.4) during the first 2 hours of exposure.

As-received surfaces
Exposure in citric acid (pH 2.4) for 2 h at 70 °C, 2 h at 70 °C followed by 24 h at 40 °C, and 2 h at 70 °C followed by 238 h at 40 °C.
Most Mo released into citric acid (pH 2.4) during the first 2 hours of exposure.

As-received surfaces
Exposure in citric acid (pH 2.4) for 2 h at 70 °C, 2 h at 70 °C followed by 24 h at 40 °C, and 2 h at 70 °C followed by 238 h at 40 °C.
Lower release rates of all metals with time for grade 304.

As-received surface – 304 (2B)
Exposure in citric acid (pH 2.4) for 2 h at 70 °C, 2 h at 70 °C followed by 24 h at 40 °C, and 2 h at 70 °C followed by 238 h at 40 °C.
Lower release rates of all metals with time for grade 201.

As-received surface – 201 (2D)
Exposure in citric acid (pH 2.4) for 2 h at 70 °C, 2 h at 70 °C followed by 24 h at 40 °C, and 2 h at 70 °C followed by 238 h at 40 °C.
Fe and Mn preferentially released from all grades into citric acid. No correlation with relative surface oxide or bulk nominal composition.

As-received surfaces
Exposure in citric acid (pH 2.4) for 10 days (2 h at 70 °C followed by 238 h at 40 °C).
Increased passivity with time. No active corrosion observed. (As-received 304 (2B)).

Same trends for all grades.

Electrochemical measurements (open circuit potential)

As-received 304 (2B) at 70 °C (2 h) + 40 °C (24 h)
5 g/L Citric acid (pH 2.4)

Open circuit potential vs. Ag/AgCl (V)

Time (s)
Stripping voltammetry measurements: No Cr(VI) detected in artificial tap water (pH 7.5) or citric acid solutions (pH 2.4 and 4.5) after exposure of as-received 201 and 304 up to 10 days (70/40 °C).

Limit of determination – 0.1 µg/L
Effect of pH and citric acid concentration
Cr enrichment in the surface oxide of grades 316L and 304 upon exposure to citric acid solutions of varying pH (3.1 to 6.4).

Surface oxide – XPS

abraded (1200 SiC) and 24 h-aged
70 °C (first 2 h) + 40 °C (24 h)
Reduction and/or minor changes in surface oxide thickness of grades 316L and 304 after exposure to citric acid solutions of varying pH (3.1 to 6.4)

Surface oxide – XPS

Grades 316L and 304
Abraded (1200 SiC) and 24 h-aged
Citric acid pH 3.1, 4.8, and 6.4
70 °C (first 2 h) + 40 °C (24 h)
Both pH and the presence of citric acid govern the Fe release.

**Metal release-AAS**

**Grades 316L and 304**
Abraded (1200 SiC) and 24 h-aged
Citric acid pH 3.1, 4.8, and 6.4
70 °C (first 2 h) + 40 °C (24 h)

<table>
<thead>
<tr>
<th>pH</th>
<th>Grade 316L Released</th>
<th>Grade 304 Released</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>5 g/L citric acid pH 3.1 (70/40 °C)</td>
<td>5 g/L citric acid pH 3.1 (70/40 °C)</td>
</tr>
<tr>
<td>4.8</td>
<td>5 g/L citric acid pH 4.8 (70/40 °C)</td>
<td>5 g/L citric acid pH 4.8 (70/40 °C)</td>
</tr>
<tr>
<td>6.4</td>
<td>5 g/L citric acid pH 6.4 (70/40 °C)</td>
<td>5 g/L citric acid pH 6.4 (70/40 °C)</td>
</tr>
<tr>
<td>11</td>
<td>5 g/L citric acid pH 11 (70/40 °C)</td>
<td>5 g/L citric acid pH 11 (70/40 °C)</td>
</tr>
</tbody>
</table>
Both pH and the presence of citric acid govern the Cr release, pH is more important.

Metal release-AAS

<table>
<thead>
<tr>
<th>Grade</th>
<th>304</th>
<th>316L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr (wt%)</td>
<td>17.9</td>
<td>17.0</td>
</tr>
</tbody>
</table>

Grades 316L and 304
Abraded (1200 SiC) and 24 h-aged
Citric acid pH 3.1, 4.8, and 6.4
70 °C (first 2 h) + 40 °C (24 h)

![Graph showing released amount of chromium (µg/cm²) for grades 316L and 304 with different pH values.](image)

- 5 g/L citric acid pH 3.1 (70/40 °C)
- 5 g/L citric acid pH 4.8 (70/40 °C)
- 5 g/L citric acid pH 6.4 (70/40 °C)
- 5 g/L citric acid pH 11 (70/40 °C)
Both pH and the presence of citric acid govern the Mn release.

**Metal release-AAS**

<table>
<thead>
<tr>
<th>Grade</th>
<th>304</th>
<th>316L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn (wt%)</td>
<td>1.2</td>
<td>1.3</td>
</tr>
</tbody>
</table>

**Grades 316L and 304**

Abraded (1200 SiC) and 24 h-aged

Citric acid pH 3.1, 4.8, and 6.4

70 °C (first 2 h) + 40 °C (24 h)
Both pH and the presence of citric acid govern the Ni release.

Metal release-AAS

<table>
<thead>
<tr>
<th>Grade</th>
<th>304</th>
<th>316L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (wt%)</td>
<td>9.0</td>
<td>10.2</td>
</tr>
</tbody>
</table>

Grades 316L and 304
Abraded (1200 SiC) and 24 h-aged
Citric acid pH 3.1, 4.8, and 6.4
70 °C (first 2 h) + 40 °C (24 h)

![Graph showing released amount of nickel (µg/cm²) vs. pH for different grades and conditions.](image)
Citric acid contributes largely to the extent of released metals from grade 304, independent of solution pH.

\[
\begin{align*}
Fe_{\text{citric acid}} & \approx (200-800) \times Fe_{\text{tap water}} \\
Cr_{\text{citric acid}} & \approx (15-240) \times Cr_{\text{tap water}} \\
Ni_{\text{citric acid}} & \approx (0.5-17) \times Ni_{\text{tap water}} \\
Mn_{\text{citric acid}} & \approx (3-8) \times Mn_{\text{tap water}}
\end{align*}
\]

pH 3.1, 4.8, 6.4, 11

As-received (2B), edge-ground, and aged surfaces (304)
Correlation between repeated use and metal release behavior of abraded (stainless steel wool) grades 304 and 316L.
More Fe released during the 1st 30 min exposure at 100 °C, and after SS wool abrasion compared with the 2nd and 3rd exposure for grades 316L and 304 in citric acid (pH 2.4).

316L and 304 (with a preliminary 2B surface finish)
SS wool abraded → 24 h aged → 3x30 min → SS wool abraded → 24 h aged → 3x30 min
5 g/L citric acid solution (pH 2.4, BC≈ 0.02)
100°C

SRL- Fe = 40 µg/cm² (loading: 1 cm²/mL)

Sum of release during first 2 exposures for grade 316L. 99 times lower than 7 x SRL
More Cr released during the 1st exposure cycle at 100 °C, and after SS wool abrasion compared with the 2nd and 3rd exposure for grades 316L and 304 in citric acid (pH 2.4).

SRL- Cr = 0.25 µg/cm² (loading: 1 cm²/mL)

316L and 304 (with a preliminary 2B surface finish)
SS wool abraded → 24 h aged → 3x30 min → SS wool abraded → 24 h aged → 3x30 min
5 g/L citric acid solution (pH 2.4, BC≈ 0.02)
100°C

Sum of release during first 2 exposures for grade 316L. 8 times lower than 7 x SRL

<table>
<thead>
<tr>
<th>Grade</th>
<th>316L</th>
<th>304</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr (wt%)</td>
<td>17.0</td>
<td>17.9</td>
</tr>
</tbody>
</table>
More Mn released during the 1st exposure cycle at 100 °C, and after SS wool abrasion compared with the 2nd and 3rd exposure for grades 316L and 304 in citric acid (pH 2.4).

316L and 304 (with a preliminary 2B surface finish)
SS wool abraded → 24 h aged → 3×30 min → SS wool abraded → 24 h aged → 3×30 min
5 g/L citric acid solution (pH 2.4, BC≈ 0.02)

SRL- Mn = 1.8 µg/cm² (loading: 1 cm²/mL)

Sum of release during first 2 exposures for grade 316L.
375 times lower than 7 x SRL

Grade | 316L | 304
Mn (wt%) | 1.3 | 1.2
More Ni released during the 1st exposure cycle at 100 °C, and after SS wool abrasion compared with the 2nd and 3rd exposure for grades 316L and 304 in citric acid (pH 2.4).

SRL- Ni = 0.14 µg/cm² (loading: 1 cm²/mL)

316L and 304 (with a preliminary 2B surface finish)
SS wool abraded → 24 h aged → 3x30 min → SS wool abraded → 24 h aged → 3x30 min
5 g/L citric acid solution (pH 2.4, BC≈ 0.02)
100°C

<table>
<thead>
<tr>
<th>Grade</th>
<th>316L</th>
<th>304</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (wt%)</td>
<td>10.2</td>
<td>9.0</td>
</tr>
</tbody>
</table>

Sum of release during first 2 exposures for grade 316L. 13 times lower than 7 x SRL
Investigation of different surface finishes (No. 4 and Scotch-Brite) for the same grade (304 and 316L)
Investigated grades + synthetic fluids + exposure conditions.

Investigated grades of stainless steels (based on supplier information)

<table>
<thead>
<tr>
<th>Name (in this report)</th>
<th>UNS (ASTM A 240)</th>
<th>Surface finish</th>
<th>Cr wt%</th>
<th>Mn wt%</th>
<th>Ni wt%</th>
<th>Mo wt%</th>
<th>Cu wt%</th>
<th>N wt%</th>
<th>C wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>304</td>
<td>S30400</td>
<td>2B</td>
<td>17.9</td>
<td>1.2</td>
<td>9.0</td>
<td>0.4</td>
<td>0.4</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>304</td>
<td>S30400</td>
<td>Sc.-Br. (2J)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>304</td>
<td>S30400</td>
<td>No. 4 (2G)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>S31603</td>
<td>2B</td>
<td>17</td>
<td>1.3</td>
<td>10.2</td>
<td>2</td>
<td>0.5</td>
<td>0.05</td>
<td>0.02</td>
</tr>
<tr>
<td>316L</td>
<td>S31603</td>
<td>Sc.-Br. (2J)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>S31603</td>
<td>No. 4 (2G)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As-received 304 (SB, N4, and 2B)
As-received 316L (SB, N4, and 2B)

Based on the CoE protocol:
Citric acid pH 2.4
70 °C (first 2 h) + 40 °C (24 h)

*loading of this study (0.5 cm²/mL), since only one of the sample surfaces was finished, the other side was blocked using a metal-free lacquer.
The release of Fe from grades 316L and 304 reduced according to: Scotch-Brite (SB) > N4 > 2B.

Metal release-AAS

![Graph showing release of Fe from different surface finishes]

- 304
  - Release of Fe from grades 316L and 304 reduced according to: Scotch-Brite (SB) > N4 > 2B.
  - SRL- Fe = 80 µg/cm² (loading: 0.5 cm²/mL)

- 316L

**Different surface finishes**

- Released amount of iron (µg/cm²)
The release of Fe from grades 316L and 304 reduced according to: Scotch-Brite (SB) > N4 > 2B.

Metal release-AAS

![Graph showing released amount of iron (µg/cm²) for different surface finishes (SB, N4, 2B) for grades 316L and 304.]

- SRL- Fe = 80 µg/cm² (loading: 0.5 cm²/mL)
The release of Cr from grade 316L reduced according to: Scotch-Brite (SB) > 2B > N4. No difference between the released amount of Cr from SB and 2B surface finishes for grade 304.

Metal release-AAS

![Graph showing released amount of chromium (µg/cm²) for different surface finishes (SB, N4, 2B) for grades 304 and 316L. The legend indicates SRL- Cr = 0.5 µg/cm² (loading: 0.5 cm²/mL).]

- SRL- Cr = 0.5 µg/cm² (loading: 0.5 cm²/mL)
- Released amount of chromium (µg/cm²)
- Different surface finishes (SB, N4, 2B)
- Grade 304
- Grade 316L
The release of Mn reduced according to: SB > N4 > 2B, for grade 316L; and SB ≈ N4 > 2B for grade 304.

Metal release-AAS

SRL- Mn = 3.6 µg/cm² (loading: 0.5 cm²/mL)
The release of Ni reduced according to SB > N4 > 2B. The release of Ni from SB surface finished grade 316L above the SRL value.

Metal release-AAS

<table>
<thead>
<tr>
<th>Surface Finish</th>
<th>Released Amount of Nickel (µg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>304 SB</td>
<td>0.18</td>
</tr>
<tr>
<td>304 N4</td>
<td>0.16</td>
</tr>
<tr>
<td>304 2B</td>
<td>0.15</td>
</tr>
<tr>
<td>316L SB</td>
<td>0.30</td>
</tr>
<tr>
<td>316L N4</td>
<td>0.28</td>
</tr>
<tr>
<td>316L 2B</td>
<td>0.27</td>
</tr>
</tbody>
</table>

SRL- Ni = 0.28 µg/cm² (loading: 0.5 cm²/mL)
Increased passivity with time. No active corrosion observed.

As-received 304 (2B)

As-received 316L (SB), since only one side of the coupons was finished, the other side was blocked using a metal-free lacquer

Exposures at 70 °C (2 h) + 40 °C (24 h)

5 g/L Citric acid (pH 2.4)
Illustration of the effect of loading (surface area to solution volume ratio) for as-received 304 (2B)
Higher metal concentrations in solution with higher loading (linear correlation, $0.91 \leq R^2 \leq 0.99$).

As-received 304 (2B) 2 h at 70 °C
5 g/L Citric acid (pH 2.4)
Surface to volume ratios: 0.25, 0.5, 0.75, 1, 1.3, and 2 cm²/mL

Loading of 1 cm²/mL
A relatively constant released amount of metals (especially for Ni and Mn) per surface area, independent of exposure condition.

As-received 304 (2B) 2 h at 70 °C 5 g/L Citric acid (pH 2.4) Surface to volume ratios: 0.25, 0.5, 0.75, 1, 1.3, and 2 cm²/mL

Loading of 1 cm²/mL
The outcome of a comparison of release data with SRL levels largely depends on the sample loading.

As-received 304 (2B) 2 h at 70 °C 5 g/L Citric acid (pH 2.4) Surface to volume ratios: 0.25, 0.5, 0.75, 1, 1.3, and 2 cm²/mL

Loading of 1 cm²/mL

Corresponding SRL value (µg/cm²) decreases by increasing the loading

Example (Loading 1 cm²/mL): SRL of Ni 0.14 µg/cm²
Illustration of relevant loadings. 1 cm²/mL (standard loading of this study) is one of the worst cases.
Degrees of freedom in the CoE protocol.

- An increased temperature results generally in an increased amount of released metals, but can also contribute to improved surface passivity at specific conditions.
- Most metals are released during a short initial period of exposure. Pre-passivation or repeated tests result in reduced amounts of released metals.
- Surface conditions of the stainless steel surface prior to exposure influence the amount of released metal. As a consequence most metals are released during the first two hours of exposure for as-received or abraded surfaces. Repeated exposures, or defined surface preparation conditions in the CoE guideline are recommended.
- An increased surface area to solution volume ratio (loading) results in higher concentrations of released metals. A defined loading in the CoE guideline for general material testing or a defined range of possible loadings for application-specific testing are recommended.
The released amounts of metals for all stainless steel grades and test conditions investigated were all below their corresponding release limits (SRLs) stipulated in the CoE protocol.

Passivation and chromium enrichment of the surface oxide during exposure in citric acid resulted in reduced amounts of released metals with time. Most metals were released from as-received or abraded stainless steel during the very initial exposure period. As a consequence, subsequent exposures resulted in lower released amounts of metals per hour. The released metal fraction from passive stainless steel surfaces is therefore neither proportional to the bulk composition nor to the surface oxide composition.

Chromium was released in its trivalent form. No hexavalent chromium was released or detected in citric acid for the investigated grades (201 and 304).
• The amounts of released metals were reduced upon repeated use of stainless steel. The surface of the stainless steel passivates fast in citric acid after surface abrasion.

• The surface condition of the stainless steel prior to exposure influences the amount of released metals.

• An increased surface area to solution volume ratio (loading) resulted in higher concentrations of released metals. A loading of 1 cm²/mL was selected in this study to enable a comparison between different grades and representative for one of the worst cases (e.g. flat pans).
Appendix-1
Additional studies on abraded grade 201
The CoE protocol stipulates more aggressive conditions than the Italian law text from a metal release perspective.

Mazinanian N, Odnevall Wallinder I, Hedberg Y. Comparison of the influence of citric acid and acetic acid as simulant for acidic food on the release of alloy constituents from stainless steel AISI 201, J Food Eng 2015: 145: 51-63.
Abraded and as-received surfaces show similar release patterns and enrichment of chromium in the surface oxide upon exposure in citric acid.

Mazinanian N, Odnevall Wallinder I, Hedberg Y. Comparison of the influence of citric acid and acetic acid as simulant for acidic food on the release of alloy constituents from stainless steel AISI 201, J Food Eng 2015: 145: 51-63.
Citric acid as the food simulant is a more aggressive solution from a metal release perspective compared with acetic acid, primarily due to its higher metal binding ability.

Mazinanian N, Odnevall Wallinder I, Hedberg Y. Comparison of the influence of citric acid and acetic acid as simulant for acidic food on the release of alloy constituents from stainless steel AISI 201, J Food Eng 2015: 145: 51-63.
A relatively linear relation between released concentrations of alloy constituents from grade 201 and surface area to solution volumes between 0.25 and 1 cm²/mL.

Mazinanian N, Odnevall Wallinder I, Hedberg Y. Comparison of the influence of citric acid and acetic acid as simulant for acidic food on the release of alloy constituents from stainless steel AISI 201, J Food Eng 2015: 145: 51-63.
Exposures in solutions at 100 °C increase the amount of released metals compared with lower temperatures despite the enrichment of Cr in the surface oxide.

Mazinanian N, Odnevall Wallinder I, Hedberg Y. Comparison of the influence of citric acid and acetic acid as simulant for acidic food on the release of alloy constituents from stainless steel AISI 201, J Food Eng 2015: 145: 51-63.
Repeated immersion results in lower released amounts of metals and improved barrier properties of the surface oxide with time.

Mazinanian N, Odnevall Wallinder I, Hedberg Y. Comparison of the influence of citric acid and acetic acid as simulant for acidic food on the release of alloy constituents from stainless steel AISI 201, J Food Eng 2015: 145: 51-63.
Appendix-2

Metal release from different grades of stainless steel in food-relevant solutions. Influence of solution, test protocol, surface finish, and repeated exposure - a comparison with previous KTH data.
**Investigated materials.**

<table>
<thead>
<tr>
<th>Surface finish</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2B</td>
<td>Cold rolling, heat treatment, pickling and skin passing</td>
</tr>
<tr>
<td>2D</td>
<td>Cold rolling, heat treatment, pickling</td>
</tr>
<tr>
<td>2R</td>
<td>Cold rolling and bright annealing</td>
</tr>
<tr>
<td>Shot-blasted</td>
<td>Cold rolling, heat treatment, pickling and skin passing, shot blasted with steel grit and then pickled</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>From ref. 1</th>
<th>grade</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
<th>Mo</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>N</th>
<th>Surface finish</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2205</td>
<td>0.022</td>
<td>22.5</td>
<td>5.6</td>
<td>1.7</td>
<td>3.1</td>
<td>0.31</td>
<td>0.020</td>
<td>0.001</td>
<td>0.15</td>
<td>2B</td>
</tr>
<tr>
<td></td>
<td>201</td>
<td>0.034</td>
<td>17.6</td>
<td>4.2</td>
<td>6.5</td>
<td>0.41</td>
<td>0.42</td>
<td>0.026</td>
<td>0.001</td>
<td>-</td>
<td>Shot-blasted</td>
</tr>
<tr>
<td></td>
<td>304</td>
<td>0.047</td>
<td>18.1</td>
<td>9.0</td>
<td>1.1</td>
<td>0.31</td>
<td>0.33</td>
<td>0.026</td>
<td>0.001</td>
<td>-</td>
<td>2B</td>
</tr>
<tr>
<td></td>
<td>310</td>
<td>0.056</td>
<td>24.2</td>
<td>19.1</td>
<td>0.9</td>
<td>0.23</td>
<td>0.37</td>
<td>0.019</td>
<td>0.001</td>
<td>-</td>
<td>2B</td>
</tr>
<tr>
<td></td>
<td>316L</td>
<td>0.032</td>
<td>16.6</td>
<td>10.6</td>
<td>1.0</td>
<td>2.1</td>
<td>0.40</td>
<td>0.024</td>
<td>0.001</td>
<td>-</td>
<td>2B</td>
</tr>
<tr>
<td></td>
<td>409</td>
<td>0.015</td>
<td>11.4</td>
<td>0.11</td>
<td>0.30</td>
<td>-</td>
<td>0.43</td>
<td>0.016</td>
<td>0.002</td>
<td>-</td>
<td>2B</td>
</tr>
<tr>
<td></td>
<td>430</td>
<td>0.040</td>
<td>16.0</td>
<td>0.22</td>
<td>0.48</td>
<td>0.064</td>
<td>0.27</td>
<td>0.017</td>
<td>0.002</td>
<td>-</td>
<td>2B</td>
</tr>
</tbody>
</table>

**Generally decreasing surface roughness:** 2D > 2B > 2R

Synthetic fluids and exposure conditions.

Exposures at 8 and 26 h (70 (2h) / 40 °C), CoE protocol

- **Citric acid, pH 2.4 (CA 2.4)**
  - 5 g/L citric acid

- **Citric acid, pH 4.5 (CA 4.5)**
  - 20.8 g/L citric acid + 6 g/L NaOH (pH 4.5)

- **Artificial tap water, pH 7.5 (TW)**
  - 0.12 g/L NaHCO₃, 0.07 g/L MgSO₄·7H₂O, 0.12 g/L CaCl₂·2H₂O

Exposure at 37 °C [1]

- **Artificial lysosomal fluid, pH 4.5 (ALF)**
  - 20.8 g/L citric acid, 6 g/L NaOH, etc.

Exposure at 40 and 100 °C [2]

- **Acetic acid, pH 2.4 (Italian law)**

---


Higher release of Fe from grades 304 and 201 in citric acid (pH 2.4, 70/40 °C, CoE protocol) compared with ALF (pH 4.5, 37 °C).

As-received 304 and 201
ALF 24 h at 37 °C
Citric acid solutions 26 h at (70/40 °C)

ALF – artificial lysosomal fluid (pH 4.5)

G. Herting, I. Odnevall Wallinder, C. Leygraf (2007), Metal release from various grades of stainless steel exposed to synthetic body fluids, Corrosion Science 49: 103–111
Higher or comparable release of Cr from grades 304 and 201 in citric acid (pH 2.4, 70/40 °C, CoE protocol) compared with ALF (pH 4.5, 37 °C).

As-received 304 and 201
ALF 24 h at 37 °C
Citric acid solutions 26 h at (70/40 °C)

ALF – artificial lysosomal fluid (pH 4.5)

G. Herting, I. Odnevall Wallinder, C. Leygraf (2007), Metal release from various grades of stainless steel exposed to synthetic body fluids, Corrosion Science 49: 103–111
Higher or comparable release of Ni from grades 304 and 201 in citric acid (pH 2.4, 70/40 °C, CoE protocol) compared with ALF (pH 4.5, 37 °C).

As-received 304 and 201
ALF 24 h at 37 °C
Citric acid solutions 26 h at (70/40 °C)

ALF – artificial lysosomal fluid (pH 4.5)

The release of Fe from grades 304 and 201 was lower compared with the ferritic grades but comparable with the duplex and austenitic grades (except 310).

409 > 430 > 2205 ≥ 201 ≈ 316 ≈ 304 >> 310

G. Herting, I. Odnevall Wallinder, C. Leygraf (2007), Metal release from various grades of stainless steel exposed to synthetic body fluids, Corrosion Science 49: 103–111
Low released amounts of Cr from grades 304 and 201, but comparable with the ferritic, duplex and austenitic grades (except 310).

As-received
37 °C
ALF (pH 4.5)
24 h
ALF – artificial lysosomal fluid

G. Herting, I. Odnevall Wallinder, C. Leygraf (2007), Metal release from various grades of stainless steel exposed to synthetic body fluids, Corrosion Science 49: 103–111
Very low amounts of released Ni from grade 201 and lower compared with the duplex and other austenitic grades.

![Graph showing nickel release from various stainless steel grades.](image)

- As-received
- 37 °C
- ALF (pH 4.5)
- 24 h

ALF – artificial lysosomal fluid
More Fe released from abraded surfaces compared with as-received surfaces, independent of grade.

37 °C
ALF (pH 4.5)
168 h

ALF – artificial lysosomal fluid

Released amount of iron (µg/cm²)
Higher or similar amounts of released Cr from abraded surfaces compared with as-received surfaces.

37 °C
ALF (pH 4.5)
168 h
ALF – artificial lysosomal fluid

G. Herting, I. Odnevall Wallinder, C. Leygraf (2007), Metal release from various grades of stainless steel exposed to synthetic body fluids, Corrosion Science 49: 103–111
More Ni released from abraded surfaces compared with as-received surfaces, independent of grade.

37 °C ALF (pH 4.5) 168 h

ALF – artificial lysosomal fluid

Released amount of nickel (µg/cm²)

G. Herting, I. Odnevall Wallinder, C. Leygraf (2007), Metal release from various grades of stainless steel exposed to synthetic body fluids, Corrosion Science 49: 103–111
The release of metals depends on the surface finish. The release of Fe from grade 304 decreased according to: abraded > 2D > 2B ≈ 2R.

G. Herting, I. Odnevall Wallinder, C. Leygraf (2007), Metal release from various grades of stainless steel exposed to synthetic body fluids, Corrosion Science 49: 103–111
The release of metals depends on prevailing experimental set-up. The release of Fe from grade 430 in acetic acid (pH 2.4) reduced upon repeated exposure to fresh solution at 100 °C.

G. Herting et al. 2008, Corrosion-induced release of chromium and iron from ferritic stainless steel grade AISI 430 in simulated food contact, J. Food Engineering 87: 291–300
The release of metals depends on the solution characteristics. More Fe released from grade 430 in the solution of ALF (pH 4.5) compared with acetic acid of lower pH (2.4).


The solution aggressivity governs to a large extent the metal release process.

**KEY MESSAGES**

Citric acid (5 g/L, pH 2.4) the most aggressive solution. CoE protocol more aggressive compared with Italian law.

CA 2.4 (T=70 °C+40 °C) > CA 4.5 (T=70 °C+40 °C) > ALF 4.5 (T=37 °C)
> acetic acid 2.4 (T=40 °C) >> TW 7.5 (T=70 °C+40 °C)

CA – Citric acid
ALF – Artificial lysosomal fluid
TW – Artificial tap water
Appendix-3
Detection limits and recovery of Fe, Cr, Mn, Ni, and Mo in artificial tap water (pH 7.5) and citric acid (pH 2.4) using Graphite Furnace Atomic Absorption Spectroscopy.
Limits of detection (LOD)* for Fe, Cr, Mn, Ni, and Mo in artificial tap water (pH 7.5) and citric acid (pH 2.4).

<table>
<thead>
<tr>
<th>elements</th>
<th>LOD in artificial tap water (pH 7.5) [µg/cm²]</th>
<th>LOD in citric acid (pH 2.4) [µg/cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.0002</td>
<td>0.0004</td>
</tr>
<tr>
<td>Ni</td>
<td>0.0004</td>
<td>0.0002</td>
</tr>
<tr>
<td>Cr</td>
<td>0.00004</td>
<td>0.00007</td>
</tr>
<tr>
<td>Mn</td>
<td>0.0001</td>
<td>0.0002</td>
</tr>
<tr>
<td>Mo</td>
<td>0.0002</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

1 µg/cm² corresponds to 1000 µg/L at the standard loading of this study (1 cm²/mL)

*calculated as 3 x average standard deviations of blank sample

The limit of quantification (LOQ), above which a value has approximately < 30% error, is estimated to be 10 times the LOD. It is hence ≤ 0.004 µg/cm² or ≤ 4 µg/L for all elements and solutions.
Recovery tests for Cr in both citric acid (pH 2.4) and artificial tap water (pH 7.5).

<table>
<thead>
<tr>
<th>Test solutions and concentrations</th>
<th>Recovery (%)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>citric acid solution (pH 2.4)</td>
<td>90.7</td>
</tr>
<tr>
<td>5 µg/L Cr in citric acid (pH 2.4)</td>
<td>99.9</td>
</tr>
<tr>
<td>10 µg/L Cr in citric acid (pH 2.4)</td>
<td>96.0</td>
</tr>
<tr>
<td>15 µg/L Cr in citric acid (pH 2.4)</td>
<td>101.3</td>
</tr>
<tr>
<td>30 µg/L Cr in citric acid (pH 2.4)</td>
<td>104.6</td>
</tr>
<tr>
<td>50 µg/L Cr in citric acid (pH 2.4)</td>
<td>111.5</td>
</tr>
<tr>
<td>60 µg/L Cr in citric acid (pH 2.4)</td>
<td>104.5</td>
</tr>
<tr>
<td>100 µg/L Cr in citric acid (pH 2.4)</td>
<td>113.4</td>
</tr>
<tr>
<td>Artificial tap water solution (pH 7.5)</td>
<td>96.2</td>
</tr>
<tr>
<td>20 µg/L Cr in artificial tap water (pH 7.5)</td>
<td>96.1</td>
</tr>
<tr>
<td>60 µg/L Cr in artificial tap water (pH 7.5)</td>
<td>91.8</td>
</tr>
</tbody>
</table>

* Recovery (%) must be in the range of 85-115 %
Recovery tests for Fe, Mn, and Ni in citric acid (pH 2.4).

<table>
<thead>
<tr>
<th>Test solutions and concentrations</th>
<th>Recovery (%)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 µg/L Fe in citric acid (pH 2.4)</td>
<td>97</td>
</tr>
<tr>
<td>100 µg/L Fe in citric acid (pH 2.4)</td>
<td>94.1</td>
</tr>
<tr>
<td>150 µg/L Fe in citric acid (pH 2.4)</td>
<td>107.4</td>
</tr>
<tr>
<td>200 µg/L Fe in citric acid (pH 2.4)</td>
<td>96.1</td>
</tr>
<tr>
<td>10 µg/L Mn in citric acid (pH 2.4)</td>
<td>100.3</td>
</tr>
<tr>
<td>15 µg/L Mn in citric acid (pH 2.4)</td>
<td>102.9</td>
</tr>
<tr>
<td>30 µg/L Mn in citric acid (pH 2.4)</td>
<td>100.2</td>
</tr>
<tr>
<td>60 µg/L Mn in citric acid (pH 2.4)</td>
<td>91.4</td>
</tr>
<tr>
<td>10 µg/L Ni in citric acid (pH 2.4)</td>
<td>101</td>
</tr>
<tr>
<td>15 µg/L Ni in citric acid (pH 2.4)</td>
<td>90.3</td>
</tr>
<tr>
<td>30 µg/L Ni in citric acid (pH 2.4)</td>
<td>100.8</td>
</tr>
<tr>
<td>60 µg/L Ni in citric acid (pH 2.4)</td>
<td>105</td>
</tr>
<tr>
<td>100 µg/L Ni in citric acid (pH 2.4)</td>
<td>106.9</td>
</tr>
</tbody>
</table>

* Recovery (%) must be in the range of 85-115 %
Appendix-4

Typical loadings in food applications.
How is “surface area / solution volume ratio” calculated?

Based on **the CoE protocol**, for articles that can be filled, the test condition is defined as:

”The article should be filled with the simulant to approximately ⅔ total capacity and then suitably covered to reduce evaporation.”¹

Therefore, “surface area / solution volume ratio” is:
the total exposed surface area (to $\frac{2}{3}$ volume) / $\frac{2}{3}$ volume

For a cylinder without considering its upper circle (the lid of pot in our case), then we have:
”surface area / solution volume ratio” = \[\left(\frac{\frac{4}{3} \pi rh + \pi r^2}{\frac{2}{3} (\pi r^2h)}\right)\]

---

¹ CoE protocol (2013). Metals and alloys used in food contact materials and articles, a practical guide for manufacturers and regulators (first ed). European Directorate for the Quality of Medicines & HealthCare (EDQM), France, Chapter 3, page 182
### Example 1

<table>
<thead>
<tr>
<th>Dimensions*</th>
<th>“surface area / solution volume ratio” (1/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (2r): 15 cm Height (h) : 7 cm</td>
<td>0.48</td>
</tr>
</tbody>
</table>


### Example 2

<table>
<thead>
<tr>
<th>Dimensions*</th>
<th>“surface area / solution volume ratio” (1/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (2r): 20 cm Height (h) : 13 cm</td>
<td>0.32</td>
</tr>
</tbody>
</table>

### Example 3

<table>
<thead>
<tr>
<th>Dimensions*</th>
<th>“surface area / solution volume ratio” (1/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (2r): 23 cm Height (h) : 10.5 cm</td>
<td>0.32</td>
</tr>
</tbody>
</table>


### Example 4

<table>
<thead>
<tr>
<th>Dimensions*</th>
<th>“surface area / solution volume ratio” (1/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (2r): 19 cm Height (h) : 13 cm</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Example 5

<table>
<thead>
<tr>
<th>Dimensions*</th>
<th>“surface area / solution volume ratio” (1/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (2r): 25 cm Height (h) : 2 cm</td>
<td>0.91</td>
</tr>
</tbody>
</table>


Example 6

<table>
<thead>
<tr>
<th>Dimensions*</th>
<th>“surface area / solution volume ratio” (1/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (2r): 24 cm Height (h) : 4 cm</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Example 7

<table>
<thead>
<tr>
<th>Dimensions*</th>
<th>“surface area / solution volume ratio” (1/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (2r): 4 cm</td>
<td>1.4</td>
</tr>
<tr>
<td>Height (h): 4 cm</td>
<td></td>
</tr>
</tbody>
</table>

* http://www.ikea.com/se/sv/catalog/products/70208129/
** http://www.ikea.com/se/sv/catalog/products/00133038/
### Example 8

<table>
<thead>
<tr>
<th>Dimensions</th>
<th>“surface area / solution volume ratio” (1/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (2r): 2 cm</td>
<td></td>
</tr>
<tr>
<td>Height (h) : 2 cm</td>
<td>2.75</td>
</tr>
</tbody>
</table>

### Example 9

<table>
<thead>
<tr>
<th>Dimensions</th>
<th>“surface area / solution volume ratio” (1/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (2r): 3 cm</td>
<td></td>
</tr>
<tr>
<td>Height (h) : 2 cm</td>
<td>2.1</td>
</tr>
</tbody>
</table>
Based on the Italian law text, “adopt a surface-to-volume ratios as close as possible to the real value and in any case between 2 and 0.5.”

In reality, “surface area/ solution volume ratio” < 0.5 (1/cm) is also common and possible!

Therefore, “surface area/ solution volume ratio” range of 0.25 to 2 (1/cm) was chosen in the loading experiments.