Compliance tests of stainless steel as a food contact material using the CoE test guideline

Yolanda Hedberg, Neda Mazinanian, Inger Odnevall Wallinder

KTH Royal Institute of Technology, School of Chemical Science and Engineering, Department of Chemistry, Division of Surface and Corrosion Science, Dr. Kristinas v. 51, 100 44 Stockholm, Sweden

yolanda@kth.se, nedam@kth.se, ingero@kth.se

Background

A new technical test guideline[1] has been implemented by the Council of Europe (CoE) to ensure the suitability and safety of finished articles of metals and alloys in food contact. The main differences to earlier tests employed, such as the Italian Ministerial Decree of 21 March 1973[2], are the use of citric acid as food simulant, and certain test procedures. Specific maximum metal release limits into the test medium have been defined for each alloying element (compliance test).

The use of citric acid in the new test guideline is relevant as it is commonly present in both acidic and alkaline food.

Studies described in this document show that:

- None of the constituent alloying elements of stainless steel are released in amounts exceeding their corresponding release limits (SRLs), stipulated in the CoE protocol.
- Metal release rates decrease with time due to a gradually improved passivation of the stainless steel surface.
- Amounts of released metals diminish upon repeated use.

[1]CoE (2013). Council of Europe, Metals and alloys used in food contact materials and articles, a practical guide for manufacturers and regulators. ISBN: 978-92-871-7703-2, European Directorate for the Quality of Medicines & HealthCare (EDQM).
[2]Italian Decree (1973). Decreto ministeriale 21/03/1973, hygienic conditions of packaging, containers and articles intended to come into contact with foodstuffs or with substances of human use.

Investigated stainless steel grades *(composition in weight-%) and surface preparation.*

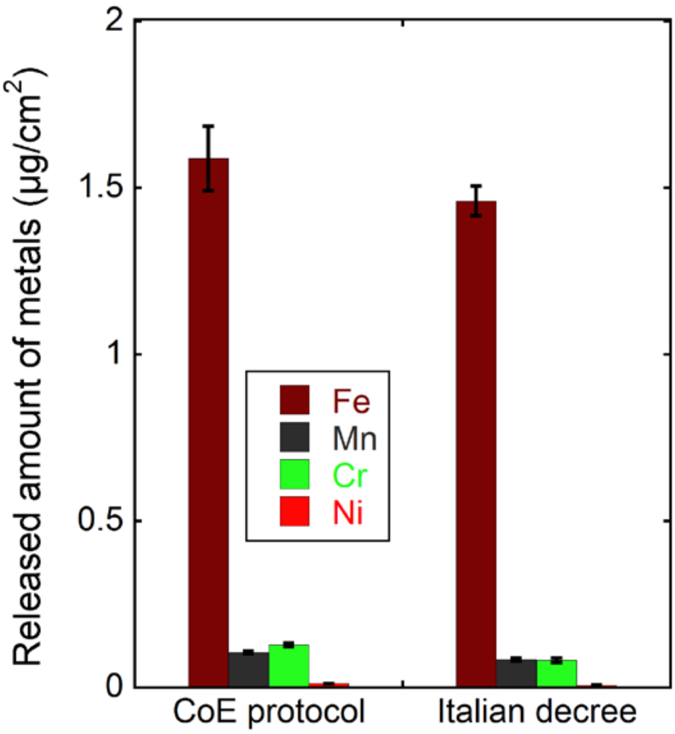
Name	UNS	EN	Micro-structure	Surface finish	Fe	Cr	Mn	Ni	Cu	Mo	N	C	S
EN1.4003	S40977	1.4003	Ferritic	2B[3]	Balance	11	1	< 1	-	-	-	-	-
430	S43000	1.4016	Ferritic	2B		16	0.3	0.1	0.04	0.02	0.03	0.03	0.002
204	S20431 (+Cu)	1.4597 (+Cu)	Austenitic	2B		16	9.1	1.1	1.6	0.15	0.19	0.1	0.004
201	S20100	1.4372	Austenitic	2D[4]		16.9	5.8	3.6	0.4	0.21	0.15	0.11	0.002
316L	S31603	1.4404	Austenitic	2B		17	1.3	10.2	0.5	2.04	0.05	0.02	-
304	S30400	1.4301	Austenitic	2B		17.9	1.2	9.0	0.4	0.36	0.04	0.04	0.003
LDX 2101	S32101	1.4162	Duplex	2B		21.4	4.8	1.6	0.3	0.28	0.22	0.02	0.001

- no data available; all stainless steel coupons were, prior to exposure, edge-ground (1200 SiC paper), ultrasonically cleaned (in ethanol and acetone for 5 min), dried with cold nitrogen gas, and aged for 24 ± 1 h in a desiccator (at room temperature). No classical passivation of the stainless steel samples by oxidizing acids was performed prior to testing.

[3] 2B surface finish: bright cold rolled, annealed, pickled, and skin-passed
[4] 2D surface finish: Dull cold rolled, annealed and pickled

Citric acid as food simulant (CoE-protocol) is conservative from a metal release perspective towards stainless steel grades compared with acetic acid (Italian decree).

Studies on stainless steel grade 201 (surface finish 2D) revealed similar or higher amounts of metals released into citric acid, the food simulant of acidic food in the new CoE test guideline (5 g/L or 0.3 vol% citric acid), compared with 3 vol% acetic acid stipulated by the Italian decree. Despite a relatively large surface area to solution volume ratio (1 cm^2 in 1 mL test medium) Fe, Cr, Ni, and Mn were released at levels below their stipulated specific release limits in both tests after 10 days exposure at 40 °C.



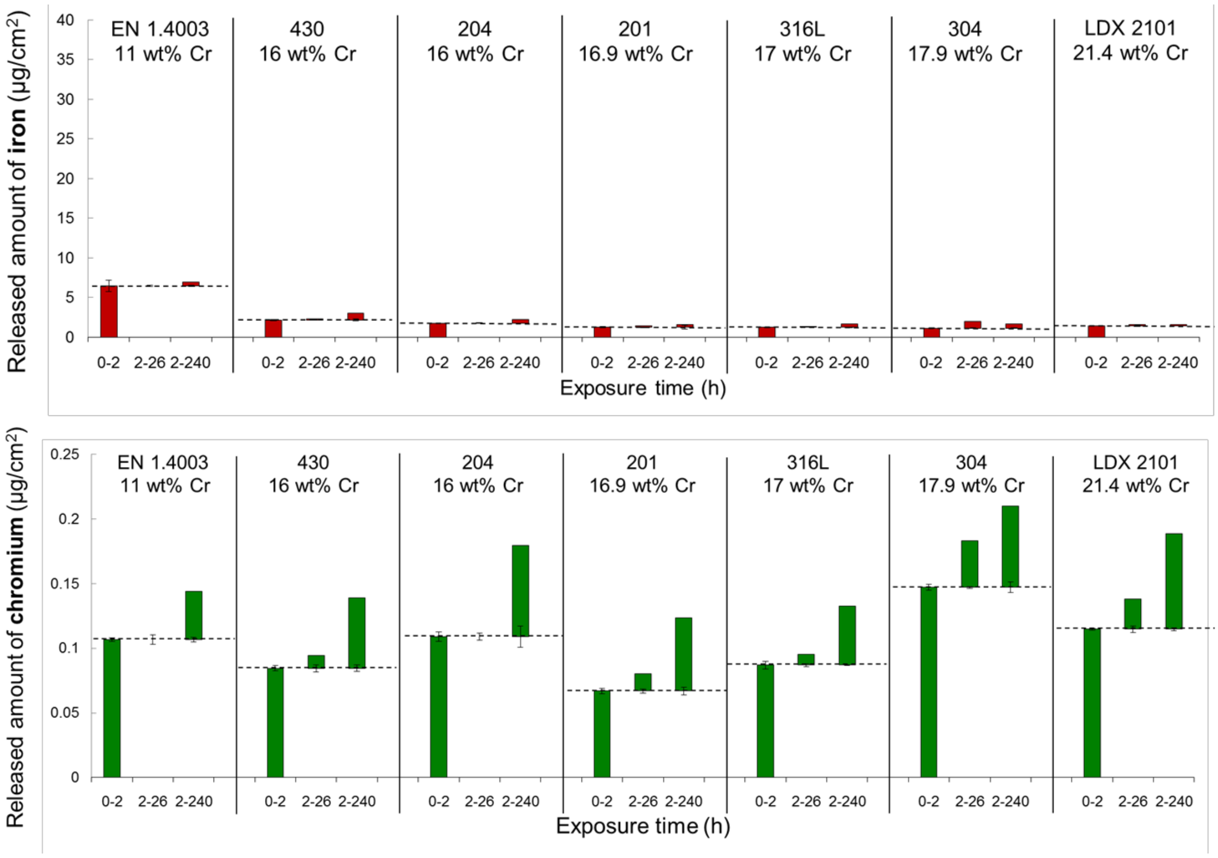
Test protocols. *Comparison between released amounts of metals from grade 201 when tested according to the CoE test protocol (citric acid, pH 2.4) and to the Italian decree guideline (acetic acid, pH 2.4), respectively, at 40 °C for 10 days[5]. All concentrations of released metals in solution were below stipulated specific release limits: 40 µg/cm² for Fe, 0.25 µg/cm² for Cr, 0.14 µg/cm² for Ni, and 1.8 µg/cm² for Mn (at the loading of 1 cm²/mL of this study).*

[5] *c.f.* reference 2 (free available online) for detailed description of similarities and differences of both protocols.

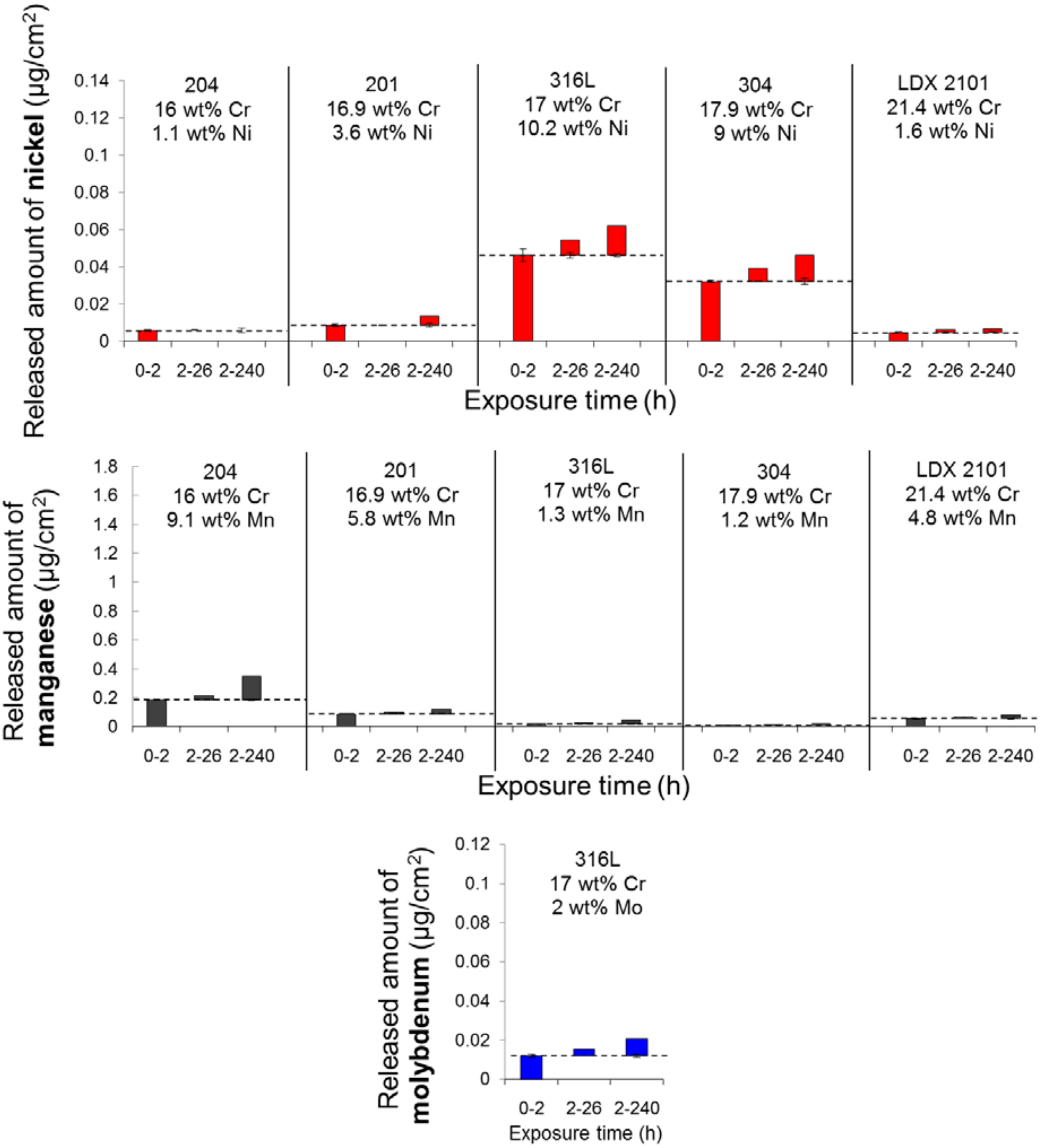
All stainless steel grades tested according to the CoE protocol released lower amounts of metals compared with specific release limits.

The amount of released metals from all stainless steel grades investigated were below the CoE stipulated specific release limits (SRLs) for all metals in both citric acid and in artificial tap water. Released amounts of metals in artificial tap water were below findings in citric acid, and close to limits of detection, and hence not presented.

Release of metals from the investigated as-received stainless steel coupons in citric acid predominantly occurred during the first 2 hours, followed by diminished released amounts.



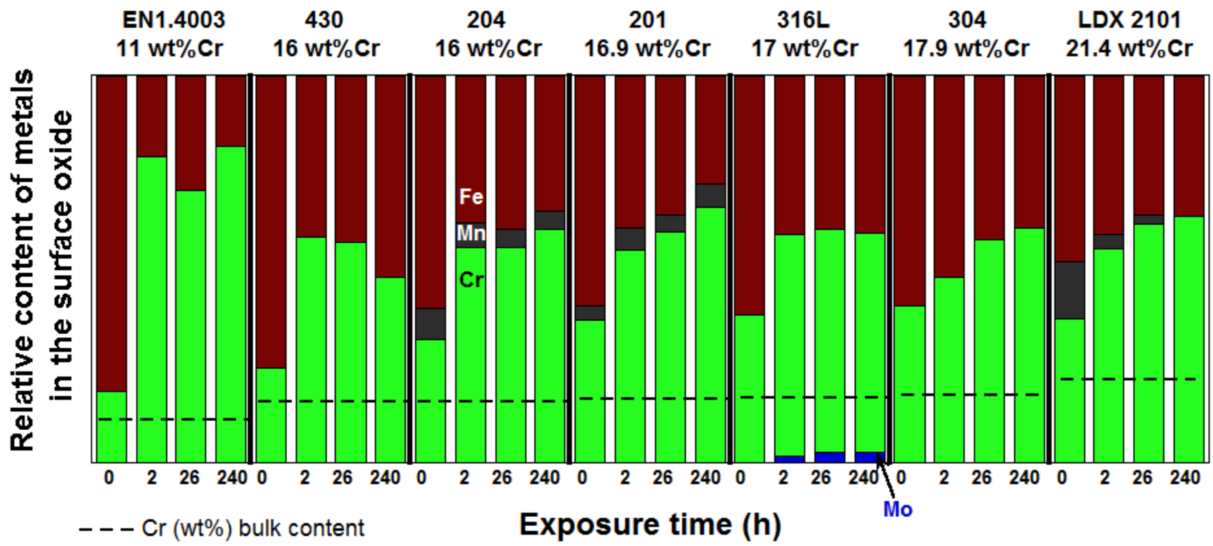
Stainless steel grades. *Released amounts of Fe and Cr from different stainless steel grades into 5 g/L citric acid (pH 2.4) after exposure for 2 h at 70 °C followed by 24 and 238 h at 40°C. Observed data is to be compared with the specific release limits (SRLs) of 40 µg/cm² for Fe, and 0.25 µg/cm² for Cr (at the loading of 1 cm²/mL of this study). The dotted lines show the released amount after 2 hours of exposure. If an additional amount is released after 2 hours, it is indicated above the dotted line for the time intervals 2-26 hours and 2-240 hours.*



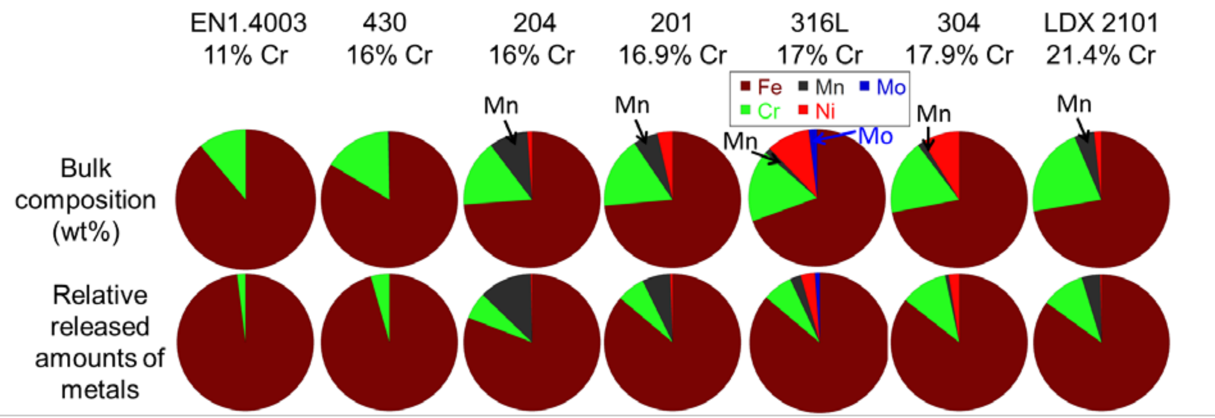
Stainless steel grades. *Released amounts of Ni, Mn, and Mo from different stainless steel grades into 5 g/L citric acid (pH 2.4) after exposure for 2 h at 70 °C followed by 24 and 238 h at 40°C. Observed data is to be compared with the specific release limits (SRLs) of 0.14 µg/cm² for Ni, 1.8 µg/cm² for Mn, and 0.12 µg/cm² for Mo (at the loading of 1 cm²/mL of this study). The dotted lines show the released amount after 2 hours of exposure. If an additional amount is released after 2 hours, it is indicated above the dotted line for the time intervals 2-26 hours and 2-240 hours.*

All investigated stainless steel grades revealed improved surface passivation with time in citric acid and hence reduced released amounts of metals.

All stainless steel surfaces gained in passivity with time upon exposure in citric acid due to an increased chromium content in the surface oxide. For example, the bulk chromium content of grade 204 is 16 wt-% and its surface oxide chromium content is 32 wt-% for the as-received surface due to a chromium enrichment (passivation). When exposed to citric acid (pH 2.4), the surface oxide is further enriched in chromium (already 56 wt-% after 2 hours of exposure) due to surface passivation and a preferential release of iron. Main changes occurred during the first 2 hours of immersion in citric acid. No active corrosion was evident at given exposure conditions. Very low amounts of metals were released into solution during 10 days of exposure at pH 2.4. These quantities correspond to an alloy mass loss being less than 0.000025 %. Iron and manganese were the preferentially released metals, while nickel was released to the lowest extent when compared to its bulk alloy content. Most metals were released during the first 2 hours of exposure, with lower amounts released during subsequent exposure periods up to 10 days. Observed release rates (released amounts of metals per surface area and time unit) were consequently reduced with time.



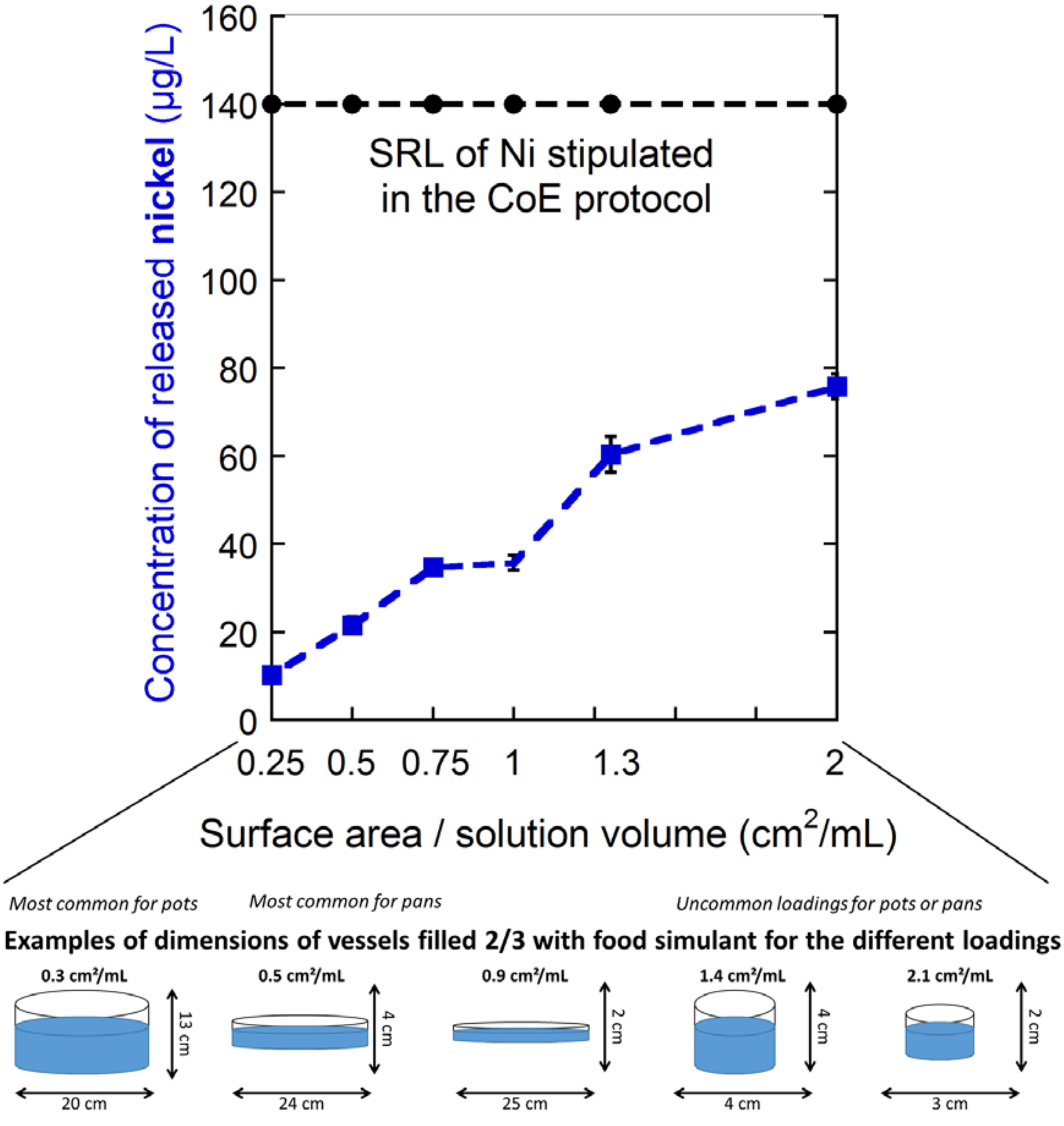
Chromium enrichment in the surface oxide with time. *Oxidized metal content of the outermost surface oxide (2-5 nm) of as-received stainless steel surfaces (0), and after different exposure periods (up to 10 days) in 5 g/L citric acid (2 h at 70 °C followed by exposure at 40 °C for another 24 or 238 h).*



Preferential release of Fe and/or Mn. *Nominal bulk composition (wt%) of all grades compared with the corresponding proportion of released metals after 240 h exposure (2 h at 70 °C, followed by 238 h at 40 °C) in 5 g/L citric acid (pH 2.4).*

The application-specific surface area to solution volume ratio influences the outcome of the compliance test.

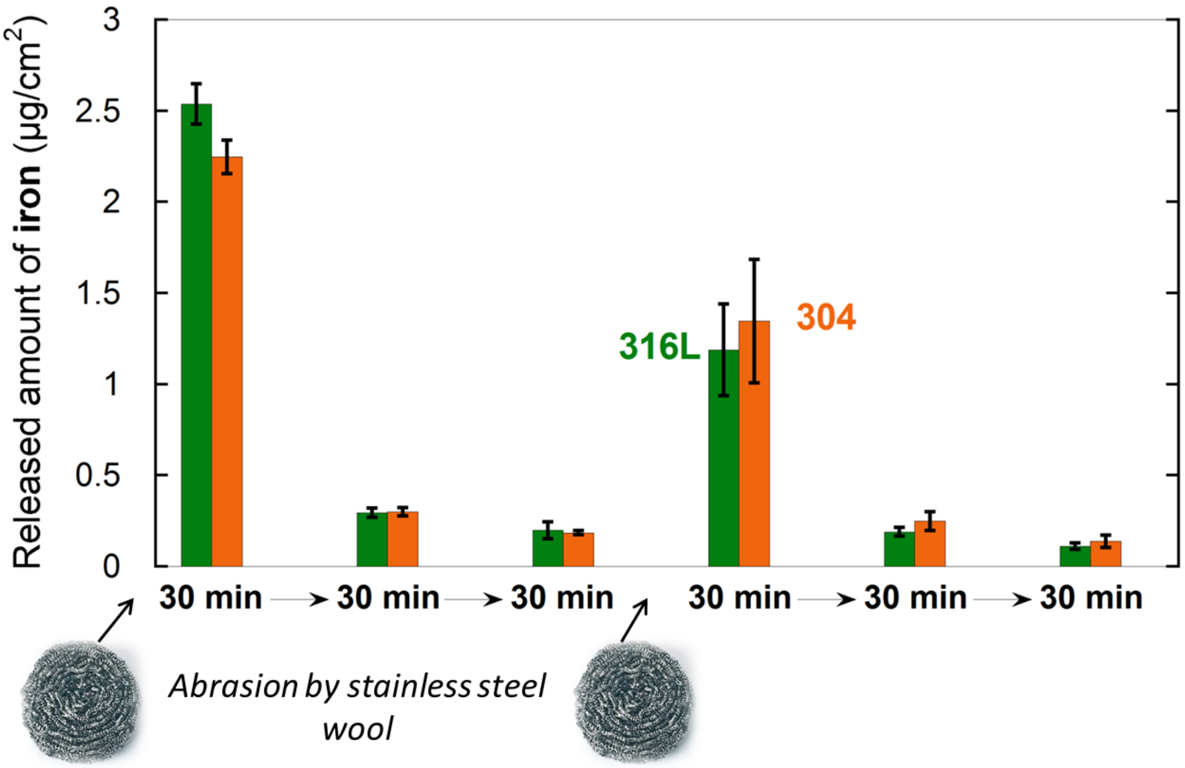
The surface area to solution volume ratio (loading) varies depending on the food contact application. A higher loading will hence result in higher metal concentrations in solution, although the amount of released metals from the same surface area in both cases is the same. A standard loading of 1 cm²/mL was selected in this study, which is higher compared with loadings for pots but representative for flat pans.



Surface area to solution volume ratio. *The influence of the surface area to solution volume ratio (loading) on the concentration of released metals illustrated for Ni, released from 304 (2B) after 2 h at 70°C in 5 g/L citric acid (pH 2.4). Typical loadings for pots and pans range between 0.25 and 0.50 cm²/mL, examples illustrated in the lower part of the figure. The CoE protocol does not specify the loading, whereas it is stipulated in the Italian decree test to vary between 0.5 and 2 (no unit given).*

Repeated exposure of stainless steel in citric acid results in lower released amounts of metals.

The investigated stainless steels showed reduced amounts of released metals upon repeated exposure in citric acid at 100 °C due to the enrichment of chromium in the surface oxide with time (surface passivation). Despite abraded surfaces and a relatively high surface area to solution volume ratio (1 cm^2/mL) all released amounts of metals were still lower than stipulated release limits.



Repeated exposure. *Released amounts of Fe upon repeated exposure of stainless steels 304 and 316L for 30 min at 100 °C in 5 g/L citric acid (pH 2.4). All samples were abraded with stainless steel wool, ultrasonically cleaned (in ethanol and acetone for 5 min), dried, and aged for 24 h (room temperature, in a desiccator) before the first and the fourth step of the exposure sequence.*

Degrees of freedom within the CoE protocol

Stipulated exposure conditions of the CoE protocol comprise some degrees of freedom to enable adjustments to a wide range of applications. The influence of selected parameters on the amount of released metals is summarized below:

- 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.

Key messages

- 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 cm^2/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).

Selected references

1. N. Mazinanian, I. Odnevall Wallinder, Y. Hedberg, *'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'*, technical report, commissioned by Team Stainless, December 2014.
2. N. Mazinanian, I. Odnevall Wallinder, Y. Hedberg. *'Comparison of the influence of citric acid and acetic acid as simulant for acidic food on the release of alloy constituents from manganese stainless steel.'* **Journal of Food Engineering**, 145(C), 51-63, 2015.
3. Y. Hedberg, M.-E. Karlsson, E. Blomberg, I. Odnevall Wallinder, J. Hedberg, *'Correlation between surface physicochemical properties and the release of iron from stainless steel AISI 304 in biological media.'* **Colloids and Surfaces B: Biointerfaces**, 122: 216-222, 2014.
4. Y. Hedberg, N. Mazinanian, I. Odnevall Wallinder, *'Metal release from stainless steel powders and massive sheet – comparison and implication for risk assessment of alloys'*, **Environmental Science: Processes and impacts** 15(2): 381-392, 2013.