



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



N. Mazinanian*, I. Odnevall Wallinder, Y. Hedberg

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

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ABSTRACT

To ensure the safety of metals and alloys intended for food contact, a new European test protocol (CoE protocol) using citric acid as a food simulant was published in 2013. This study investigated the influence of citric acid and exposure conditions on the metal release from an austenitic manganese stainless steel (AISI 201). Exposures in 5 g/L citric acid resulted in significantly lower metal releases compared with specific release limits set by the CoE protocol. 5 g/L (0.3 vol%) citric acid was more aggressive than 3 vol% acetic acid (Italian protocol) due to higher metal complexation. Studies on abraded surfaces revealed that most metals were released during the first 0.5 h of exposure due to surface passivation. Surface abrasion, increased temperature (40–100 °C), increased surface area to solution volume ratio (0.25–2 cm²/mL) and increased citric acid concentration (0–21 g/L) all resulted in increased released metal quantities.

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1. Introduction

Austenitic stainless steel grades, with a minimum of 16 wt% chromium and 6 wt% nickel, are typically used in a wide range of food contact applications such as cutlery, hollow-ware and kitchen utensils, as well as for food processing, storage and transport equipment (CoE, 2013). Based on the American Iron and Steel Institute (AISI) classification, austenitic stainless steel grades are designated by numbers in the 200 (Fe–Cr–Ni–Mn–N stainless steels with ≥2 wt% Mn) and 300 series (Fe–Cr–Ni stainless steels ≤2 wt% Mn) (Sedriks, 1996). Since 2000, there has been an increasing usage of the 200 series in food contact applications, where manganese (up to 8 wt%), often combined with nitrogen and copper, have been substituted for nickel (CoE, 2013). Besides those standardized grades, some non-standardized “new 200 series”, stainless steels of reduced chromium (≤15 wt%) and nickel (<1 wt%) content found an increasing use in food contact applications in e.g. Southeast Asia. Information of their proper use and their corrosion and metal release properties are totally lacking (ISSF, 2005).

Data on the release of alloy constituents from stainless steels used in food contact is reported in the literature (Accominotti

et al., 1998; Flint and Packirisamy, 1995, 1997; Herting et al., 2008a; Kamerud et al., 2013; Kuligowski and Halperin, 1992). Studies on different stainless steel grades of the 200 series (Mn: 1.5–9.7 wt%, Ni: 1–5 wt%) exist for citric acid containing media (Herting et al., 2008b).

Iron, chromium, and manganese are all classified as essential trace elements for humans. A deficiency syndrome can occur when their intake is too low. The metals are mainly responsible for the correct functioning of innumerable enzymatic and metabolic reactions. Depending on their chemical forms and concentrations they may, however, induce adverse health effects (Ernest, 1991). The optimal dose can vary (influenced by, for example, diseases and allergies) and literature on upper dietary intake levels suggests different thresholds (Alexander, 1995; ANSES, 2011; EFSA, 2010; EVM, 2003; Thyssen and Menné, 2010; WHO, 2011).

Metals (as ions or complexes) can be released from metals and alloys in food contact, which may unacceptably change the organoleptic characteristics of the food or pose a risk for consumers (CoE, 2013). Different regulations, restrictions and technical guidelines have therefore been implemented to ensure the suitability and safety of finished articles (CoE, 2013; Italian law text, 1973; Simoneau, 2009). For instance, based on the Italian Ministerial Decree of 21 March 1973 (Italian law text, 1973), stainless steel articles on the market must pass a metal release test in one or

* Corresponding author.

more specified simulating solvents such as distilled water, 3 vol% acetic acid or sunflower oil. A new technical guide (the CoE¹ protocol) has recently been implemented in the European Union (EU), with the main aim to ensure the safety and suitable quality of materials in food contact (CoE, 2013). Compared with previous test protocols (e.g., Italian law text), 5 g/L (0.3 vol%) citric acid is used as the food simulant and stipulated test conditions are application-specific. This means that the same material can generate different outcomes on safety and suitability. Citric acid is a strongly metal complexing agent. This means that it is able to form different metal complexes with metals in solution or metals of the surface oxide (iron preferentially). Depending on the strength of the formed complex and adjacent bonds, the complex may detach from the surface. Citric acid has a higher metal complexation capacity compared with acetic acid (Essington, 2004). This results in a faster passivation (chromium enrichment) of the surface oxide of stainless steel compared with non-complexing acids such as nitric acid (Kremer, 2004; Zhang et al., 1985).

The objectives of this study were to (i) compare the CoE protocol and the Italian law text by investigating metal release and surface changes for as-received AISI 201 stainless steel, (ii) elucidate differences between citric and acetic acid from a chemical and fundamental metal release perspective, (iii) evaluate the influence of key experimental parameters (surface finish, solution pH, solution buffer and complexation capacity, surface area to solution volume ratio, and temperature), and (iv) investigate effects of repeated usage on the metal release process and surface oxide composition.

2. Materials and methods

2.1. Materials

Austenitic manganese stainless steel grade sheets of AISI 201 (2D² surface finish) were supplied by the International Stainless Steel Forum (ISSF). The nominal bulk composition is given in Table 1.

2.2. Exposure and experimental conditions

Samples were prepared with an approximate size of $2 \times 1.5 \text{ cm}^2$ and a thickness of 1 mm (total surface area of approx. 6 cm^2). Both as-received and abraded (1200 grit SiC paper) surfaces were investigated. All cutting edges of both as-received and abraded samples were prior to exposure abraded using 1200 grit SiC paper, ultrasonically cleaned in ethanol and acetone for 5 min, respectively, dried with cold nitrogen gas, and aged for $24 \pm 1 \text{ h}$ in a desiccator (at room temperature). The surface area to solution volume ratio was kept constant at $1 \text{ cm}^2/\text{mL}$, if not stated differently. Triplicate samples and one blank sample (test solution only) were exposed in parallel for each time period and test solution. All exposures were conducted in the same furnace (Torrsterilisator, Termaks, Norway). All vessels were acid-cleaned in 10% HNO₃ for at least 24 h, rinsed four times in ultrapure water (18 M Ω cm, Millipore, Sweden) and dried in ambient laboratory air. All chemicals used were of analytical grade (p.a.) or puriss p.a. grade (in the case of nitric acid, used to acidify solution samples to a pH of <2 prior to total metal release measurements). The pH of all test solutions was measured before and after exposure (with pH changes <0.14 in all cases).

With exception of Section 2.2.1., experimental conditions were chosen to investigate the effect of single exposure parameters, and test conditions specified by the CoE protocol were therefore not always followed. For example, as-received surfaces should be investigated according to the CoE protocol, but this would disable

Table 1

Nominal bulk alloy composition of stainless steel grade AISI 201 based on supplier information (wt%).

Fe	Cr	Mn	Ni	Si	Mo	Cu	P	S	Nb	Sn	N
Balance	16.94	5.77	3.59	0.65	0.21	0.39	0.033	0.002	0.01	0.01	0.15

single parameter investigations due to unknown storage conditions.

2.2.1. Comparison between CoE protocol and Italian law

As-received 201 sheets were exposed in 3 vol% acetic acid (pH 2.4), the suggested test solution by the Italian law text for foods of a $\text{pH} \leq 5$ (Italian law text, 1973), and in 5 g/L (0.3 vol%) citric acid solution (pH 2.4), stipulated in the CoE protocol for acidic foods of a $\text{pH} \leq 4.5$ (CoE, 2013), respectively, for 10 days at 40 °C.

2.2.2. Comparison between abraded and as-received samples

Both as-received and abraded 201 samples were exposed in 5 g/L citric acid (pH 2.4) for 2 h at 70 °C. As-received surfaces (2D) were investigated due to their relevance for commercial food related products. It should be stressed though that the surface finish varies significantly between different products on the market. Abraded and aged surfaces were investigated to ensure reproducible and well-defined uniform surface oxides to enable mechanistic studies of metal release processes and to allow comparison with literature data.

2.2.3. Effect of metal complexation capacity

Abraded 201 samples were investigated in 5 different test solutions (with citric acid concentrations increasing from 0 to 20.8 g/L at given pH (4.5) and buffer capacity (BC = 0.07), c.f. Table 2, at 40 °C for 24 h. The theoretical background and calculations of solution composition of varying citric acid concentration, but of the same pH and BC, are given in Appendix A. Citric acid, C₆H₈O₇, is a weak triprotic organic acid with pK_a values of 3.12, 4.76, and 6.39 (Goldberg et al., 2002), and acetic acid, C₂H₄O₂, a weak monoprotic acid with a pK_a value of 4.75 (Goldberg et al., 2002; Lin et al., 1993). Both 3 vol% acetic acid and 0.3 vol% citric acid have a pH of 2.4 and a similar BC of approx. 0.01 (Figs. A.1 and A.2, Appendix A). However, at $\text{pH} < 3$ and $\text{pH} > 11$ is the BC independent of the presence or absence of complexing agents (Urbansky and Schock, 2000). In order to investigate the effect of complexation capacity of citric and acetic acid on the metal release process for grade 201, the investigated pH had to exceed 3. The pH largely influences the extent of metal complexation with complexing agents and shows the largest influence at pH values close to the pK_a values of the acid (Lin et al., 1993). A pH of 4.5 was therefore selected, which is close to pK_a values of both acetic and citric acid. 5 g/L citric acid is the stipulated food simulant concentration in the CoE protocol (CoE, 2013), whereas 20.8 g/L citric acid equals its amount in artificial lysosomal fluid (ALF, pH 4.5), a fluid that simulates intracellular inflammatory conditions in lung cells (de Meringo et al., 1994). The BC of the 20.8 g/L citric acid solution (at pH of 4.5) was kept constant (BC 0.07) for the other solutions of varying acetic acid and citric acid concentration. Acetic acid was in this study used to keep the BC constant and thereby enable a comparison between citric acid and acetic acid (molar concentration one third of that of citric acid) from a metal release perspective.

2.2.4. Effect of sample surface to solution volume ratio

Five different surface area to solution volume ratios (0.25, 0.5, 0.75, 1, and $2 \text{ cm}^2/\text{mL}$) were investigated from a metal release perspective for abraded 201 samples in 5 g/L citric acid (pH 2.4) at 70 °C for 2 h.

¹ Council of Europe.

² "Cold-rolled, annealed and pickled, not skin passed" (Aperam, 2014).

Table 2
Chemical composition of 5 test solutions, all of pH 4.5 and a buffer capacity of 0.07.

Solution name	Citric acid concentration (g/L)	Acetic acid concentration (g/L)	Added NaOH (g/L)
0CA	–	7.8	1.84
0.01CA	0.01	7.7	1.83
0.1CA	0.1	7.7	1.85
5CA	5	6.2	2.84
20.8CA	20.8	–	4.21

CA – citric acid.

2.2.5. Effect of temperature

Abraded 201 samples were exposed to 5 g/L citric acid (pH 2.4) for 2 and 26 h, respectively, at 40, 70, and 100 °C, respectively.

2.2.6. Effect of repeated exposure

Abraded 201 samples were exposed to 5 g/L citric acid (pH 2.4) and 3 vol% acetic acid (pH 2.4), respectively, for three consecutive 30 min exposure periods at 100 °C, as stipulated by the Italian law text (Italian law text, 1973). Metal release measurements were conducted after all three immersion periods and surface analyses after the complete exposure.

2.3. Metal analysis (atomic absorption spectroscopy) and presentation of data

Total concentrations of released iron, chromium, nickel and manganese in solution were determined for acidified samples (pH < 2) by means of graphite furnace atomic absorption spectroscopy, GF-AAS (Perkin Elmer AA800 analyser). The atomization temperature was 2400 °C (for iron and nickel), 2300 °C (for chromium), and 1900 °C (for manganese). All analyses were based on three replicate readings for each solution sample and a quality control sample of known concentration was analyzed every 8th sample. The limits of detection (LOD) for iron, chromium, nickel and manganese were 0.0004, 0.00007, 0.0002, and 0.0002 µg/cm², respectively. The limit of quantification (LOQ), above which a value has approximately <30% error, was estimated to ≤0.004 µg/cm² or ≤4 µg/L for all elements and test solutions. Calibration was conducted using a blank solution (ultrapure water) and three calibration standards, 10 µg/L, 30 µg/L, and 100 µg/L for chromium, nickel and manganese and, 50 µg/L, 100 µg/L, and 200 µg/L for iron. The solutions were diluted up to 20 times to ensure their concentrations to be in the calibration range.

Released metals are normalized to the exposed stainless steel surface area and solution volume in the unit µg/cm², calculated by multiplying the measured concentration (µg/L) times the solution volume (L) and divided by the exposed geometrical stainless steel surface area (cm²). 1 µg/cm² is for the standard surface area to solution volume ratio (loading) of 1 cm²/mL equivalent to 1000 µg/L or approximately 1 mg/kg, where kg is the mass of the food simulant (in this case the solution). For other loadings, the unit mg/kg can be calculated from the unit µg/cm² times the loading in cm²/mL. All release data is presented in the unit µg/cm² as the average value of three independent exposures, with the parallel blank exposure concentration, if >0, subtracted. Error bars show the standard deviation between these triplicate samples.

2.4. Chromium speciation

The oxidation state of released chromium was investigated of non-acidified samples of as-received 201 exposed in 5 g/L citric acid (pH 2.4) and in artificial tap water (DIN, 2011) for 2, 4, 8, 26, and 240 h, respectively, using differential pulse adsorptive

cathodic stripping voltammetry (DPAdCSV). A Metrohm 797 VA Computrace instrument with a hanging mercury drop working electrode, a Ag/AgCl (saturated KCl) reference electrode, and a platinum auxiliary electrode were used for measurement of samples (2 mL) in the supporting electrolyte (2.5 mL: 0.2 M sodium acetate, 0.05 M diethylenetriaminepentaacetate (DTPA), 2.5 M sodium nitrate) diluted by ultrapure water (8 mL, 18.2 MΩcm) to 10.5 mL solution and adjusted to a pH of 6.2 ± 0.1 with 30% ultrapure NaOH. The detailed procedure is described in (Hedberg et al., 2012a).

2.5. Surface analysis (X-ray photoelectron spectroscopy)

Compositional analysis of the outermost surface (5–10 nm) were performed by means of X-ray photoelectron spectroscopy, XPS (UltraDLD spectrometer, Kratos Analytical, Manchester, UK) using a monochromatic Al Kα X-ray source (150 W) on 2 separate surface areas approximately sized 700 × 300 µm². Elements of the outermost surface oxide were identified by running a wide spectrum and high resolution spectra (pass energy of 20 eV) for the main alloying elements; Fe 2p, Cr 2p, Ni 2p, Mn 2p, O 1s, and C 1s (as energy reference). The results are presented as the relative content of oxidized iron, chromium, nickel, and manganese in the outermost surface oxide, e.g. $[\text{Cr}_{\text{ox}}/(\text{Cr}_{\text{ox}} + \text{Fe}_{\text{ox}} + \text{Ni}_{\text{ox}} + \text{Mn}_{\text{ox}})]$. Peak overlap between Ni and Mn was accounted for. Relative changes in the surface oxide thickness (before and after exposure) were roughly assessed based on the absence or presence of non-oxidized metal peaks.

2.6. Electrochemical measurements (open circuit potential)

To investigate the effect of temperature and time on electrochemical surface processes, open circuit potential (OCP) measurements, using a Metrohm µ-Autolab type II potentiostat and Nova 1.5 software, were conducted in 5 g/L citric acid (pH 2.4, aerated) at 40 °C (1.5 h), 70 °C (3 h), and 100 °C (5 h), subsequently. The 201 stainless steel sheets were abraded and aged as described in Section 2.2. Approximately 6 cm² of the sample sheet was immersed, and an Ag/AgCl sat. KCl electrode was used as reference electrode.

2.7. Statistical evaluation

A student's *t*-test (for unpaired data with unequal variances) was employed to test the significance of a difference between two independent sample sets (triplicate samples, respectively). If the probability (*p*-value) was <0.05, the difference between two values was considered as significant (Livingston, 2004). In this study, *p*-values <0.05, <0.01, and <0.001 are identified by (*), (**), and (***) with higher significance for smaller *p*-values.

3. Results and discussion

3.1. The CoE protocol is more aggressive than the Italian law text from a metal release perspective

Fig. 1 illustrates the main experimental differences between the CoE protocol (CoE, 2013) and the Italian law text (Italian law text, 1973). While 3 vol% acetic acid (pH 2.4) was considered as the worst case test simulant for foods of a pH ≤ 5 in the Italian law text, the CoE protocol stipulates 5 g/L (0.3 vol%) citric acid (pH 2.4) for foods of a pH ≤ 4.5. Despite the same pH (2.4) and buffer capacity (approx. 0.01, Fig. A.1 in the supporting information), their abilities to complex metal ions are different (Goldberg et al., 2002). Since complexation has been shown to largely influence the release

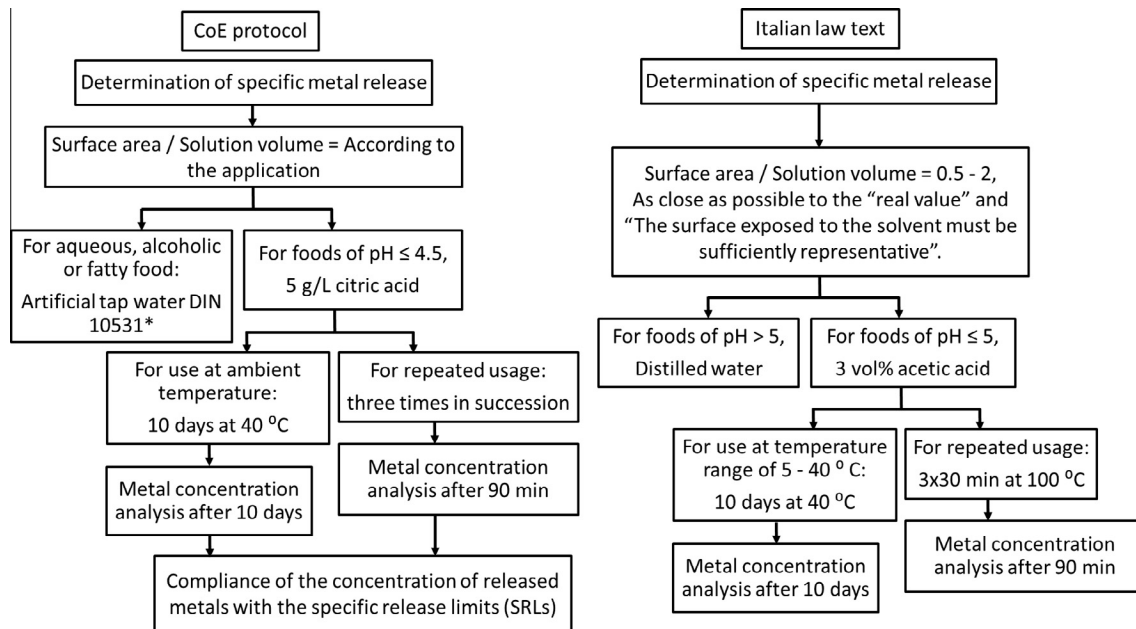


Fig. 1. Illustration of main experimental and analytical differences between the CoE protocol (CoE, 2013) and the Italian law text (Italian law text, 1973). For repeated usage (the duration should be chosen according to the application), the compliance test (CoE protocol) is done for the third exposure, and the sum of the first and second exposure concentrations should not exceed seven times the SRLs. *Chemical composition of the artificial tap water described in DIN 10531 (DIN, 2011).

of metals from e.g. stainless steel (Hedberg et al., 2011; Kocijan et al., 2003; Milošev, 2002), differences between the food simulants were investigated from a chemical and metal release perspective (Fig. 2).

Fig. 2 clearly illustrates that exposures in citric acid, the stipulated food simulant by the CoE protocol, resulted in higher amounts of released metals after 10 days (significantly for Mn, Cr, and Ni) compared with exposures in acetic acid, the suggested simulant of acidic food by the Italian law text. As will be discussed in Section 3.3, this is explained by a higher complexation capacity of citric acid compared with acetic acid.

Released metal concentrations for an application-specific surface area to solution volume ratio were compared to specific release values (SRLs) (CoE, 2013). The SRLs of relevance for this study (Fe, Cr, Ni, Mn) are shown in Table 3 together with literature data on a safe intake level of Fe (Alexander, 1995), Cr (EFSA, 2010; WHO, 1996), Mn (EVM, 2003), and Ni (WHO, 2011). SRL data is based on toxicological information (e.g., JECFA³, EFSA⁴ or national risk assessment bodies), relevant legislations that control the presence of metals in foodstuff, oral intake data of food and drinking water from several European countries, available release data, and/or the ALARA⁵ principle. Even though the surface area to solution volume ratio investigated in this study (1 cm²/mL) represents a worst case in terms of expected ratios for pots and pans (typically between 0.2 and 1 cm²/mL), the release of metals from grade 201 was significantly below corresponding SRL values for all test conditions according to the CoE protocol.

Chromium was released in its trivalent form, no hexavalent form (detection limit of 0.1 µg/L) was detected either in citric acid or in artificial tap water (DIN, 2011) up to 10 days of exposure, respectively (data not shown). These findings are in agreement with previous chromium speciation measurements for released chromium from chromium-containing alloys in synthetic biological

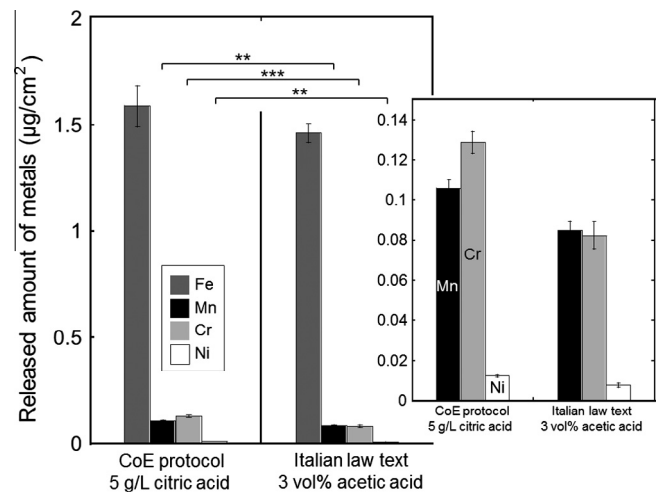


Fig. 2. Released amounts of Fe, Cr, Ni, and Mn (µg/cm²) from as-received austenitic stainless steel grade 201 (2D surface finish) after immersion into 5 g/L citric acid (pH 2.4, BC = 0.01) and 3 vol% acetic acid (pH 2.4, BC = 0.01) for 10 days at 40 °C, as stipulated by the CoE protocol and the Italian law text, respectively. Asterisks indicate significant differences between the CoE protocol and the Italian law text with $p < 0.05$ (*), $p < 0.01$ (**), and $p < 0.001$ (***). The magnified graph shows data with Fe excluded (no differences shown).

fluids (Flint et al., 2007; Hedberg et al., 2013; Hedberg and Odnevall Wallinder, 2014).

3.2. Abraded and as-received surfaces show similar release patterns and enrichment of chromium in the surface oxide upon exposure in citric acid

Compositional changes of the outermost surface oxide and extent of released metals in citric acid (pH 2.4) from abraded and as-received stainless steel grade 201 are shown in Fig. 3. Chromium was enriched with time in the outermost surface oxide for

³ Joint FAO/WHO Expert Committee on Food Additives.

⁴ European Food Safety Authority.

⁵ As Low As Reasonably Achievable.

Table 3

Safe upper intake of metals for an adult with an average body weight of 60 kg (consuming 1 kg/day of foodstuffs) (Alexander, 1995; CoE, 2013; EFSA, 2010; EVM, 2003; WHO, 1996, 2011), their corresponding SRL values, and data source (CoE, 2013). The unit mg/kg food is in this study equivalent to 1 $\mu\text{g}/\text{cm}^2$ for the standard surface area to solution volume ratio of 1 cm^2/mL .

Metal	Safe upper intake of the metal (mg/day)	SRL (mg/kg food)	SRL values based on:
Fe	10–15 (Alexander, 1995)	40	Available oral intake data The ALARA principle employed
Cr	0.25 (EFSA, 2010; WHO, 1996)	0.25	Available oral intake data
Mn	1–10 (EVM, 2003)	1.8	Toxicological reference values A fixed allowance of 20% employed
Ni	0.7 (WHO, 2011)	0.14	Toxicological reference values A fixed allowance of 20% employed

both surface finishes, more rapidly for abraded surfaces, Fig. 3 (left). The relative amount of oxidized chromium ($[\text{Cr}_{\text{ox}}/(\text{Cr}_{\text{ox}} + \text{Fe}_{\text{ox}} + \text{Ni}_{\text{ox}} + \text{Mn}_{\text{ox}})]$) increased from 37% to 55% for the as-received finish, and from 24% to 61% for the abraded surface, after 2 h of exposure. Similar oxidized/metallic peak ratios (data not shown) were observed for the unexposed abraded and as-received surfaces indicative of similar initial surface oxide thicknesses. Non-significant changes in this relative thickness were observed after exposure in citric acid.

Higher amounts of released metals were observed for abraded surfaces compared with as-received surfaces, significant for Fe (1.6 fold) and Mn (2.4 fold) but non-significant ($p > 0.05$) for Cr and Ni, Fig. 3 (right). Despite higher released amounts from the abraded surface, the trends were the same. Higher release for abraded/aged surfaces compared with as-received surfaces, and similar trends, are in agreement with previous studies on metal release from austenitic stainless steel grade 304 exposed into ALF at 37 °C (Herting et al., 2006) and from ferritic stainless steel grade 430 immersed into 3 vol% acetic acid (pH 2.4) for 10 days at 40 °C (Herting et al., 2008a). A preferential release of Fe and Mn, compared with Cr and Ni was observed for all exposures, independent of sample preparation, in agreement with literature findings on stainless steels (Galván et al., 2012; Hedberg et al., 2013; Herting et al., 2008b; Okazaki and Gotoh, 2005; Virtanen et al., 2008). Comparable released amounts of Cr from abraded compared with as-received surfaces, Fig. 3 (right), are explained by the passive surface oxide characteristics, rapidly enriched in chromium to similar levels for both surfaces upon exposure in citric acid.

3.3. Citric acid as the food simulant was the more aggressive solution from a metal release perspective compared with acetic acid, primarily due to its higher complexation capacity

Significantly more metals were released from grade 201 after exposure into the 20.8CA solution (only citric acid) compared with the OCA solution (only acetic acid), findings that suggest a higher complexation capacity of citric acid compared to acetic acid. Differences in complexation capacities between citric and acetic acid are most probably related to the fact that citrate, or the HCit^{-2} ion, is predominating at pH 4.5 and can form bi- or polydentate metal complexes, while acetate only can form monodentate complexes, and has therefore a lower stability constant for metals (Essington, 2004). From this follows that surface- or released metals are more likely to form stable complexes in the presence of citric acid compared with acetic acid.

Almost similar amounts of metals were released into the test solutions with citric acid concentrations ≥ 0.1 g/L (except for Cr, ≥ 5 g/L), Fig. 4. No significant differences in released amounts of metals were observed in 0.01 g/L citric acid compared with acetic acid only (OCA). This is in agreement with previous findings that did not reveal any significantly increased amounts of Fe, Ni, and Mn, but significantly for Cr, released from stainless steel particles when increasing the citric acid concentration (BC of 0.07, pH 4.5) above 1 g/L citric acid (BC of 0.003, pH 4.5) (Hedberg et al., 2011). This observation is most probably explained by a slower surface and/or solution complexation of trivalent Cr compared with the bivalent metal ions (Fe, Ni, Mn) (Essington, 2004).

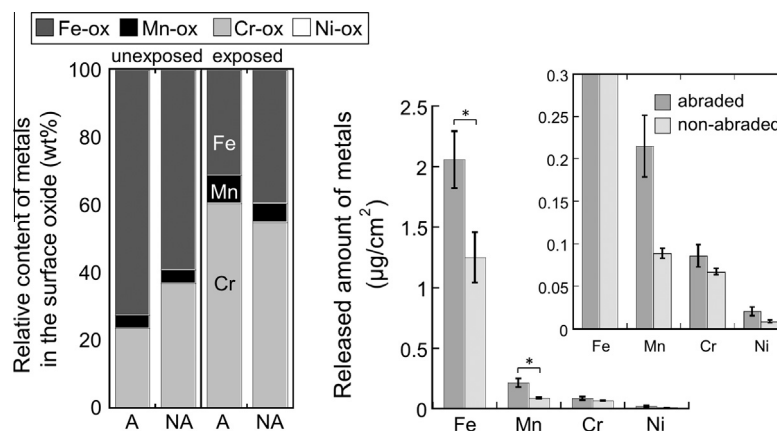


Fig. 3. Left: Relative content of metals in the surface oxides of abraded (A, 1200 grit SiC paper, 24 h aged) and non-abraded (NA, as-received 2D surface finish) austenitic stainless steel grade 201 before (unexposed) and after 2 h of exposure in citric acid (pH 2.4) at 70 °C (exposed). No oxidized Ni was observed. Right: Released amounts ($\mu\text{g}/\text{cm}^2$) of alloy constituents (Fe, Mn, Cr, and Ni) from abraded and non-abraded grade 201 after 2 h of exposure in citric acid (pH 2.4) at 70 °C. The inset graph shows the same data, but magnified. Asterisks indicate significant differences with $p < 0.05$ (*), $p < 0.01$ (**), and $p < 0.001$ (***).

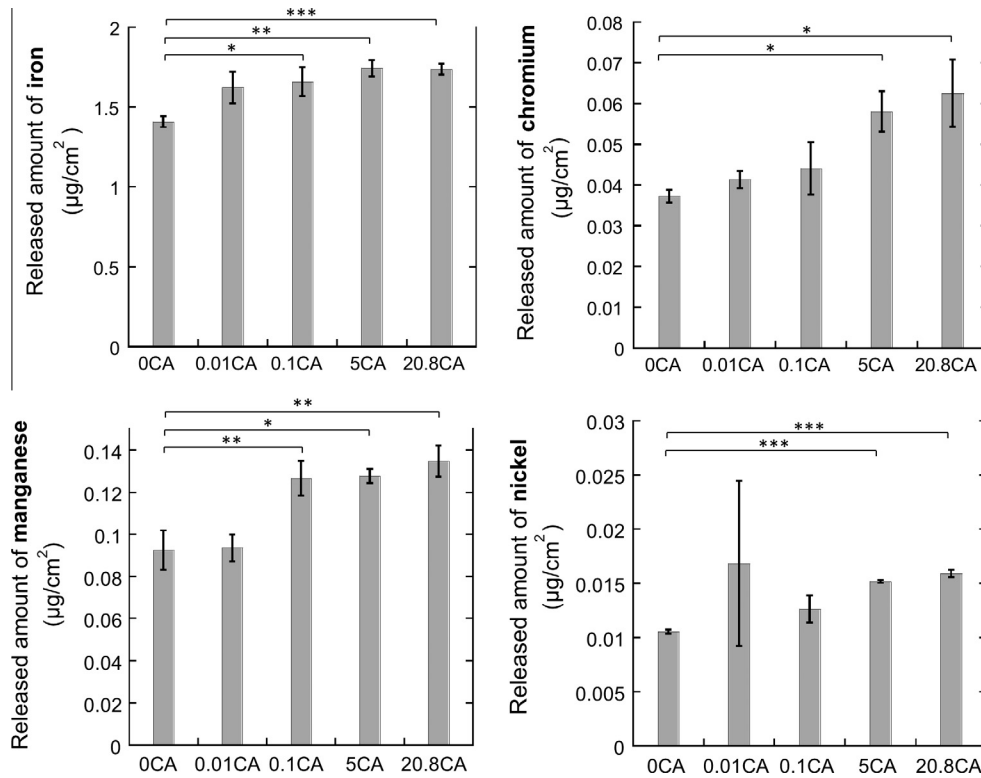


Fig. 4. Released amounts of Fe, Cr, Mn, and Ni ($\mu\text{g}/\text{cm}^2$) from abraded and 24 h aged austenitic stainless steel grade 201 after immersion into citric acid (CA) solutions of 0, 0.01, 0.1, 5, and 20.8 g/L (pH 4.5, BC = 0.07) for 24 h at 40 °C, respectively. Asterisks indicate significant differences between the citric acid containing solutions compared to the test solution containing only acetic acid (OCA), with $p < 0.05$ (*), $p < 0.01$ (**), and $p < 0.001$ (***).

Fig. 5 shows a comparison between released amounts of metals from abraded grade 201 after exposure in 5 g/L citric acid of pH 2.4 (BC = 0.01) for 26 h at 40 °C and 5 g/L citric acid of pH 4.5 (BC = 0.07) for 24 h at 40 °C, respectively. It can be concluded that the large difference in pH only resulted in slight differences in metal release (<1.2 times higher at pH 2.4 compared with pH 4.5 for all alloy constituents). It should be emphasized that the complexation capacity, the buffer capacity, and the pH of these two solutions are different, with predominant species of H_3Cit and H_2Cit^- at pH 2.4, and of HCit^{2-} at pH 4.5. The small difference in metal release may, beside the small time difference, hence be the

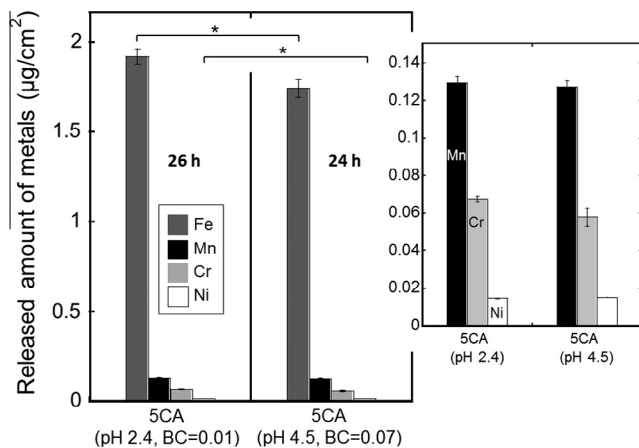


Fig. 5. Released amounts of Fe, Cr, Ni, and Mn ($\mu\text{g}/\text{cm}^2$) from abraded and 24 h aged austenitic stainless steel grade 201 after exposure in 5 g/L citric acid (pH 2.4, BC = 0.01) and in 5 g/L citric acid (pH 4.5, BC = 0.07) at 40 °C for 26 and 24 h, respectively. The right graph is magnified with Fe excluded. Asterisks indicate significant differences between released metals in the two test solutions, with $p < 0.05$ (*), $p < 0.01$ (**), and $p < 0.001$ (***).

combined result of higher amounts of released metals due to the lower pH (Hedberg and Odneval Wallinder, 2012; Okazaki and Gotoh, 2005; Virtanen et al., 2008) and reduced amounts due to lower complexation capacity at pH 2.4 compared with pH 4.5.

The stipulated CoE test solution with 5 g/L citric acid (pH 2.4) was hence found to be the more aggressive solution from a metal release perspective compared with 3 vol% acetic acid (pH 2.4), suggested by the Italian law text (Fig. 2), and more or equally aggressive when compared with citric acid solutions of similar or higher concentration and complexing capacity at pH 4.5, Figs. 4 and 5.

A significant enrichment of chromium in the outermost surface oxide (up to 67 wt% Cr compared with 24 wt% Cr for the unexposed surface) was evident upon exposure in citric acid of varying concentration at pH 4.5, Fig. 6 (left). No significant differences were observed between the different concentrations, or when compared with exposures in 5 g/L citric acid at pH 2.4, Fig. 6.

3.4. A relatively linear relationship exists between released concentrations of alloy constituents from grade 201 and surface area to solution volumes between 0.25 and 1 cm^2/mL

The CoE protocol stipulates an application-relevant ratio for testing without defining the surface area to solution volume ratio. A ratio between 0.5 and 2 (without specifying the unit) was suggested in the Italian law text (Italian law text, 1973). A linear correlation between the released concentration of a metal and the sample surface area to solution volume ratio would be expected if solution equilibrium would not be reached, suppressing the further release process. The influence of the surface area to solution volume ratio on the relative extent of metal release is presented in Fig. 7 (left) as the concentration of released metal compared with its estimated concentration, if assuming linearity when increasing the surface area to solution volume ratio from 0.25 to 0.5, 0.75, 1, and 2 cm^2/mL . The results show that the

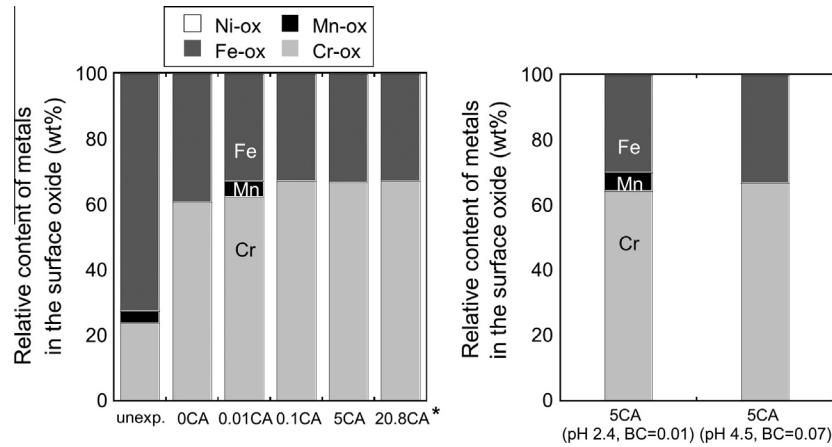


Fig. 6. Left: Relative content of oxidized metals (wt%) in the surface oxide of austenitic stainless steel grade 201 (abraded and 24 h aged) prior to (unexp.) and after exposure to five different test solutions of varying citric acid concentration from 0 to 20.8 g/L (pH 4.5, BC = 0.07) for 24 h at 40 °C, respectively. Data for 20.8 g/L citric acid (20.8CA) is based on a single sample, indicated by the asterisk (*). Right: Relative content of oxidized metals (wt%) in the surface oxide after exposure in 5 g/L citric acid (pH 2.4, BC = 0.01) and in 5 g/L citric acid (pH 4.5, BC = 0.07) at 40 °C for 26 and 24 h, respectively.

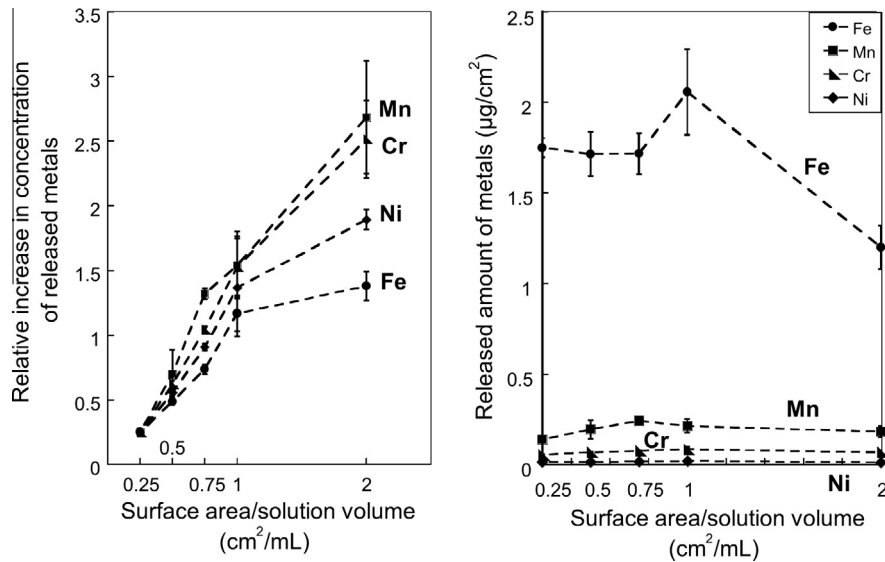


Fig. 7. Left: Relative changes in released concentrations of Fe, Mn, Cr, and Ni compared with expected concentrations if assuming linearity when increasing the surface area to solution volume ratio from 0.25 to 0.5, 0.75, 1, and 2 cm²/mL for abraded (24 h aged) austenitic stainless steel grade 201 after 2 h of exposure to citric acid (pH 2.4) at 70 °C, and, right: corresponding released amounts of metals normalized per surface area (µg/cm²).

concentrations of released metals (Fe, Cr, Mn, and Ni) increase with increased surface area to solution volume ratios. Released concentrations were 10, 8, and 6 times higher for Mn/Cr, Ni, and Fe, respectively, for an 8 times larger ratio (2 cm²/mL compared with 0.25 cm²/mL). These findings are in agreement with previous studies (Allen and Batley, 1997; Herting et al., 2008a). While there was a relatively linear correlation ($0.9 \leq R^2 \leq 1$) between released concentrations of all metals and the surface area to solution volume ratio between 0.25 and 1 cm²/mL (Fig. 7 (left)), the slope was reduced for Fe at ratios between 1 and 2 cm²/mL. Similar trends have also been reported for stainless steel grade 430 in 3 vol% acetic acid (Herting et al., 2008a).

The results clearly illustrate that if a linear relationship exists between the released concentration of a given metal and the surface area to solution volume ratio, release data can be normalized to the actual surface area of interest, i.e. a relatively constant released amount of metal per surface area independent on exposure conditions (surface area to solution volume). If non-linearity is observed, released concentrations of metals will be overestimated if predicted based on surface area. For grade 201 in citric acid, normalization with exposed surface area was only possible

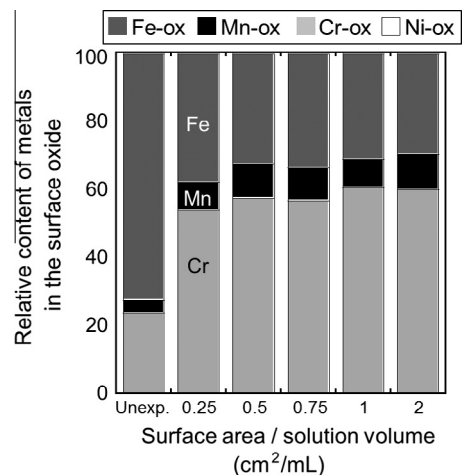


Fig. 8. Relative content of oxidized metals (wt%) in the surface oxide of austenitic stainless steel grade 201 (abraded and 24 h aged) prior to (unexp.) and after exposure (0.25, 0.5, 0.75, 1, and 2 cm²/mL) into citric acid (pH 2.4) for 2 h at 70 °C. No oxidized Ni was detected.

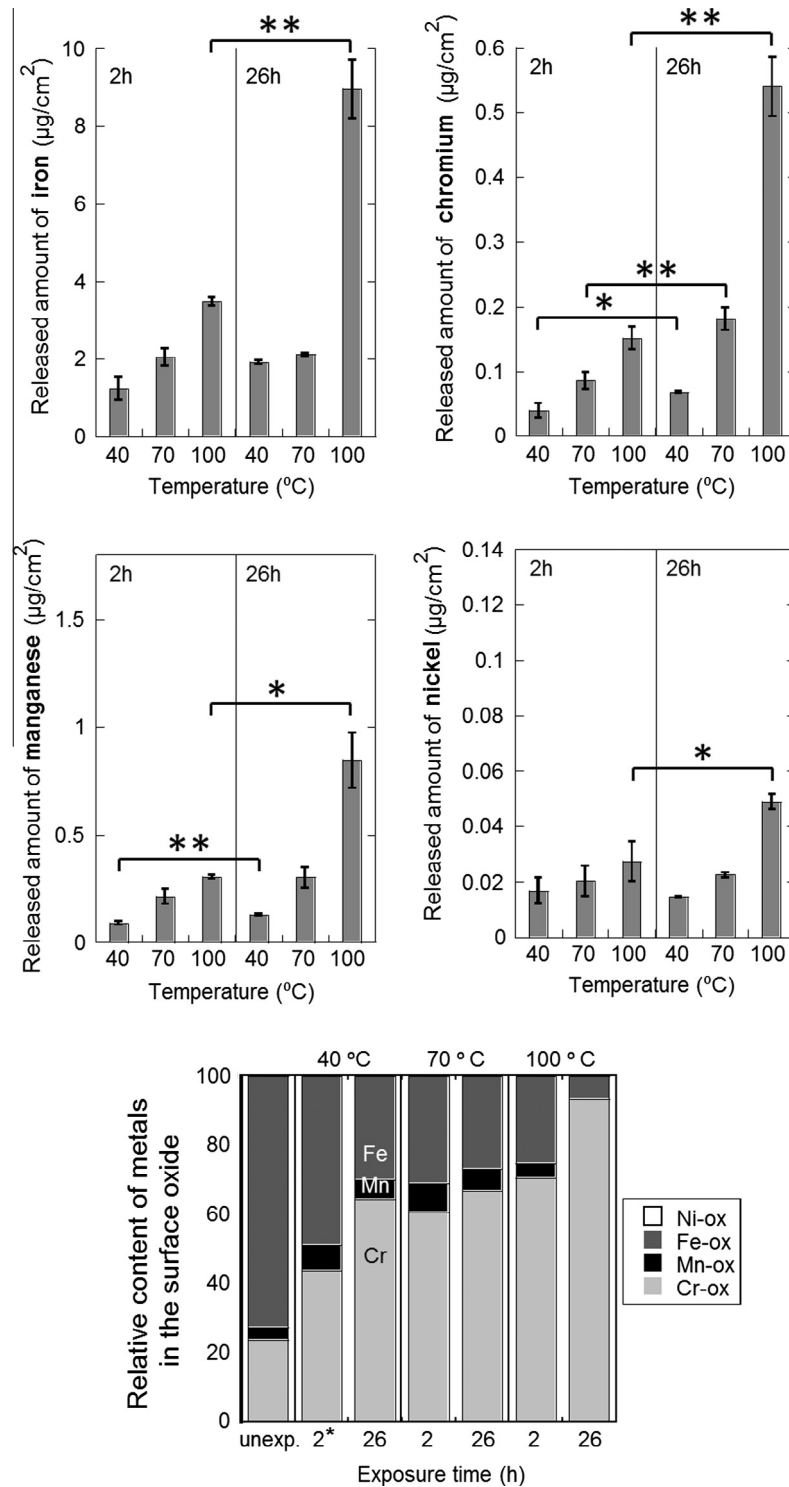


Fig. 9. Released amounts of Fe, Cr, Ni, and Mn ($\mu\text{g}/\text{cm}^2$) from abraded and 24 h aged austenitic stainless steel grade 201 after exposures to citric acid (pH 2.4) for 2 and 26 h at 40, 70, and 100 $^{\circ}\text{C}$, respectively. Asterisks indicate significant differences between released amounts of metals after different exposure times at a given test temperature, with $p < 0.05$ (*), $p < 0.01$ (**), and $p < 0.001$ (***). Bottom: Relative content of oxidized metals (wt%) in the surface oxide of austenitic stainless steel grade 201 (abraded and 24 h aged) prior to (unexp.) and after exposure in citric acid (pH 2.4) for 2 and 26 h at 40, 70, and 100 $^{\circ}\text{C}$, respectively. Data for 2 h at 40 $^{\circ}\text{C}$ is based on a single sample, indicated by the asterisk (*).

for ratios varying between 0.25 and 1 cm^2/mL , Fig. 7 (right), ratios relevant for most commercially available pots and pans.

Differences in surface area to solution volume did not significantly influence the composition of the surface oxide as depicted from XPS compositional analysis, Fig. 8.

Since the surface area to solution volume ratio is not clearly defined in the CoE protocol and is application-specific, it can be speculated that the same material tested at a low ratio may pass the compliance test and SRL values (concentrations), but possibly not if tested at a significantly higher ratio. The surface area to solu-

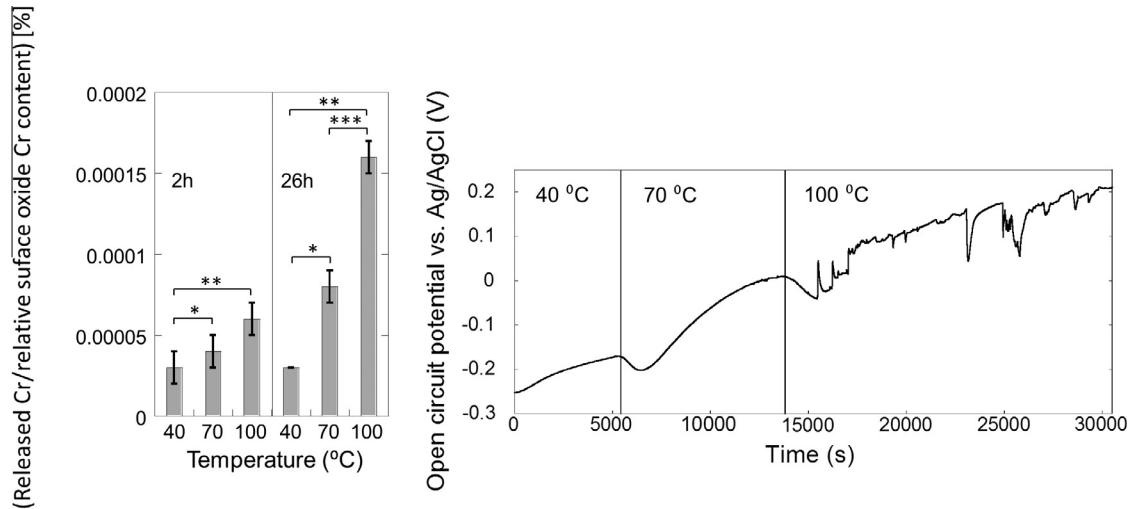


Fig. 10. Left: Released amounts of Cr normalized to the stainless steel sheet mass and its relative mass content in the surface oxide (in%) for abraded and 24 h aged austenitic stainless steel grade 201 after exposure in citric acid (pH 2.4) for 2 and 26 h at 40, 70, and 100 °C, respectively. Asterisks indicate significant differences between the released amounts of metal at different exposure times at the same test temperature, with $p < 0.05$ (*), $p < 0.01$ (**), and $p < 0.001$ (***). Right: Change in open circuit potential over time for abraded and 24 h aged grade 201 stainless steel exposed in 5 g/L citric acid solution of pH 2.4 at varying exposure temperatures (40, 70, and 100 °C).

tion volume ratio is hence the single most important parameter influencing the outcome of a compliance test with the SRL values.

3.5. An increased temperature of 100 °C increases the amount of released metals, despite a significant Cr enrichment of the surface oxide

An increased solution temperature resulted in significantly increased released amounts of all metals, Fig. 9. The largest amount of released metals per surface area was observed after 26 h at 100 °C, despite a substantial enrichment of Cr in the surface oxide

(94%) during the same period, Fig. 9 (bottom). Similar findings were evident when normalized to the Cr content in the surface oxide, exemplified for Cr in Fig. 10 (left).

All metals revealed reduced release rates with time in the acidic solutions (data not shown), which correlated with the enrichment of Cr in the surface oxide, Fig. 9 (bottom). The relative Cr content increased from approximately 24% to 43% after 2 h in 5 g/L (0.3 vol%) citric acid (pH 2.4) at 40 °C and up to approximately 94% (26 h at 100 °C) with time and/or increased temperature. The highest temperature (100 °C) resulted in a significant thickening of the surface oxide, suggested by a significant reduction and/or

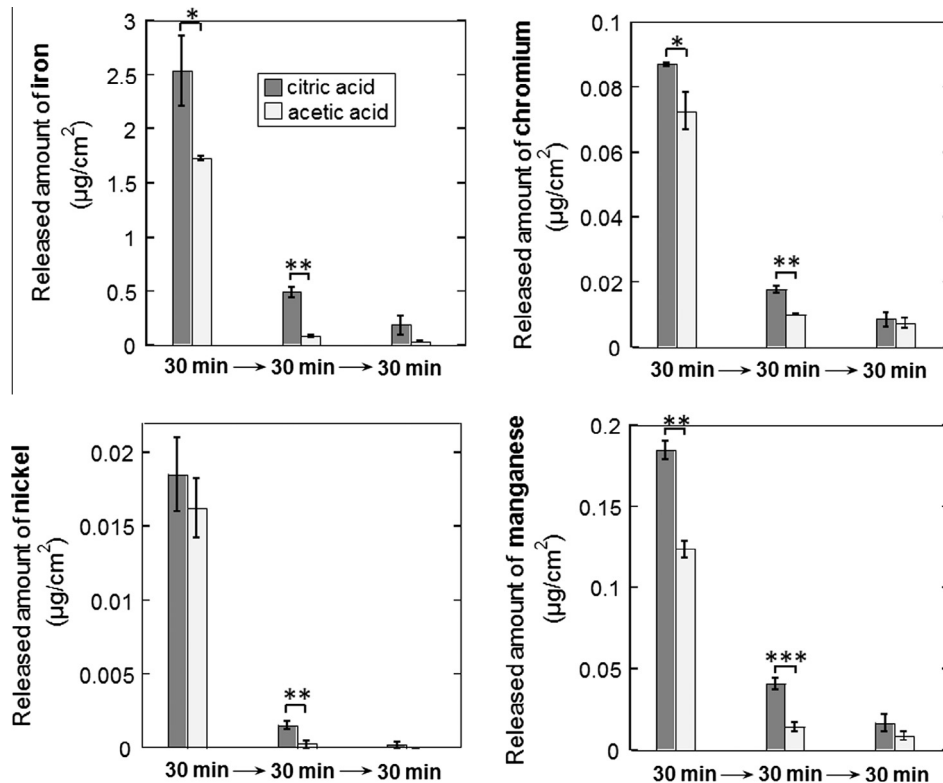


Fig. 11. Released amounts of Fe, Cr, Ni, and Mn ($\mu\text{g}/\text{cm}^2$) from abraded and 24 h aged austenitic stainless steel grade 201 after three consecutive (each 30 min) exposures in 5 g/L citric acid (pH 2.4) and 3% acetic acid (pH 2.4) at 100 °C, respectively. Asterisks indicate significant differences between released amounts of metals in the two test solutions, with $p < 0.05$ (*), $p < 0.01$ (**), and $p < 0.001$ (***).

absence of peaks assigned to Fe, Cr, Mn, and Ni in their metallic form after 2 and 26 h (data not shown). Reduced metal release rates with time are expected for stainless steel due to the passive surface oxide properties (Hedberg et al., 2013; Herting et al., 2008a; Jensen et al., 2003; Karimi et al., 2012). However, this effect may be less significant at elevated temperatures due to altered oxide properties (Neville and Hodgkiess, 1996) and increased tendency toward pitting (Sedriks, 1996), increased ligand-induced metal release (Essington, 2004), and/or changed chemical equilibrium. For example, while there was a 10-fold reduction in the release rate of Mn after 26 h exposure in citric acid (pH 2.4) at both 40 °C and 70 °C compared with the release rate of Mn after 2 h, it was only twice as low (5 fold) at 100 °C. A typical passive surface oxide on stainless steel is 1–3 nm thick (Olsson and Landolt, 2003). From observed released metal quantities and the assumption that released metals originate solely from the outermost surface oxide follows a calculated reduction in surface oxide thickness of approx. 4.5, 5.6, and 22 nm after 26 h at 40, 70, and 100 °C, respectively, which means that the metal released at elevated temperatures cannot solely originate from the initially formed surface oxide.

Open circuit potential measurements (OCP) were performed to further elucidate the mechanism of metal release from grade 201 at increased temperature, Fig. 10 (right). A generally increased passivity was observed with increased temperature, indicated by more positive OCP values. No evidence for any metastable pitting events or other electrochemical surface processes was observed at 40 or 70 °C. Metastable pitting events were though taking place at 100 °C, observed by sudden drops in OCP followed by re-passivation to original OCP levels (Hedberg et al., 2012b), and the initial occurrence of sudden ennoblement events, possibly caused by the formation of oxidizing surface species, such as MnO₂ (Hedberg et al., 2012b). The latter possibility with repeated formation and dissolution of oxidizing manganese oxides at the surface is supported by XPS findings, Fig. 9 (bottom). No oxidized manganese was observed in the outermost surface oxide after 26 h exposure in citric acid at 100 °C, whereas it was present after the shorter exposure periods (2 h) and when exposed at the lower temperatures (40 and 70 °C).

These observations suggest a combined metal release mechanism with an increased tendency for metastable pitting and ligand-induced metal release (chemical or electrochemical surface oxide dissolution) at 100 °C.

3.6. Repeated immersion results in significantly reduced released amounts of metals and improved barrier properties of the surface oxide with time

Repeated immersion of the abraded grade 201 in citric acid at 100 °C, Fig. 11, showed significantly reduced released amounts of metals in both acetic and citric acid, respectively. The sum of the first and second exposure concentrations was significantly lower compared with seven times the SRLs, the limit stipulated by the CoE protocol for repeated tests (CoE, 2013). The third exposure was significantly lower compared with the SRLs, despite the fact that the surfaces were abraded (and 24 h aged) prior to the first exposure. Significantly more metals were released during the first and second exposure period (30 min) when exposed in 5 g/L citric acid (pH 2.4) compared with 3 vol% acetic acid (pH 2.4). This is believed to be an effect of the higher complexation capacity of citric acid compared with acetic acid at that pH, previously discussed in Section 3.3. No differences were observed after the third immersion. Repeated exposure resulted in a strong enrichment of Cr in the surface oxide for both acids (from 24% to 78 and 68 wt% for citric acid and acetic acid, respectively). The major reduction in metal release upon repeated exposure is explained by the fact that most metals were released during the first immersion period and that a

more stable passive surface oxide formed with time, indicated by the Cr enrichment of the surface oxide (Herting et al., 2008a).

4. Conclusions

To ensure the safety of metals and alloys intended for food contact, a new European food application test protocol (CoE protocol) was published as a Technical Guide in September 2013, substituting earlier versions. The objectives of this study were to investigate the influence of (i) citric acid⁶ compared with acetic acid⁷, (ii) other exposure conditions on the extent of metal release, and (iii) changes in surface oxide composition of austenitic manganese stainless steel (AISI 201) commonly used in food contact applications upon different exposure conditions and repeated usage. An additional objective was to determine if, when tested in accordance with the conditions stipulated by the CoE protocol, the release of metals from 201 stainless steel was well below the specific release limits (SRLs) for all released elements. The following main conclusions were drawn:

- (1) The release of metals from 201 stainless steel was well below SRLs for all released elements (as-received, 5 g/L citric acid, pH 2.4, 40 °C, 10 days of exposure).
- (2) 5 g/L (0.3 vol%) citric acid (buffer capacity, BC, of 0.01, pH 2.4), the stipulated food simulant by the CoE protocol for acidic food, was a more aggressive test solution (increased metal release) compared with 3 vol% acetic acid (BC 0.01, pH 2.4), suggested by the Italian law text and almost equally aggressive when compared with citric acid solutions of higher BC and pH (BC 0.07, pH 4.5).
- (3) Chromium was released in the trivalent form (no hexavalent Cr could be detected).
- (4) Exposures of abraded and aged grade 201 in citric acid resulted in higher amounts of released metals compared with acetic acid at a given pH (4.5) and BC (0.07) most probably due to the strong complexation capacity of citric acid.
- (5) Released concentrations of alloy constituents from grade 201 (Fe, Cr, Mn, and Ni) increased linearly when increasing the surface area to solution volume ratio from 0.25 cm²/mL to 1 cm²/mL (typical loadings for pots and pans), and non-linearly (suppressed) between 1 and 2 cm²/mL for Fe. As the surface area to solution volume ratio should be chosen as application-specific as possible and is not further defined by the CoE protocol, it is essential to define this parameter when comparing release data with stipulated specific release limits.
- (6) The release of metal constituents from grade 201 increased with increasing temperature. Most metals were released at the highest investigated temperature, 100 °C, due to a higher tendency for metastable pitting events (pits that re-passivate) and complexation/ligand-induced metal release, compared with 40 and 70 °C.
- (7) Repeated exposures (3 × 3 min) in test solutions of 3 vol% acetic acid (pH 2.4) and 5 g/L citric acid (pH 2.4) at 100 °C, respectively, resulted in significantly reduced amounts of released metals due to improved barrier properties of the surface oxide (Cr enrichment, passivation of surface oxide).

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⁶ The stipulated food simulant in the CoE protocol.

⁷ Used as a recommended simulant at acidic conditions (pH ≤ 5) in the Italian Ministerial Decree of 21 March 1973.

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Appendix A

Buffer capacity (BC) of citric acid, as a tricarboxylic acid, can be calculated by Eq. (A.1) (Urbansky and Schock, 2000) and is plotted for 5 g/L citric acid solution (chosen based on the CoE protocol (CoE, 2013)) in Fig. A.1:

$$BC = \ln 10 \left(\frac{K_w}{[H^+]} + [H^+] + \frac{C_{CA}[H^+](\beta_1 + 4\beta_2[H^+] + (\beta_1\beta_2 + 9\beta_3)[H^+]^2 + 4\beta_1\beta_3[H^+]^3 + \beta_2\beta_3[H^+]^4)}{(1 + \beta_1[H^+] + \beta_2[H^+]^2 + \beta_3[H^+]^3)^2} \right) \tag{A.1}$$

In which $K_w = 10^{-14}$, $[H^+] = 10^{-pH}$, C_{CA} = Molar concentration of citric acid, $\beta_1 = 10^{pKa3} = 10^{6.396}$, $\beta_2 = 10^{(pKa3 + pKa2)} = 10^{(6.396 + 4.761)}$, and $\beta_3 = 10^{(pKa3 + pKa2 + pKa1)} = 10^{(6.396 + 4.761 + 3.128)}$.

This formula is derived from:

$$\text{Mass balance : } C_{CA} = [H_3Cit] + [H_2Cit^{-1}] + [HCit^{-2}] + [Cit^{-3}],$$

$$(H_3Cit = C_6H_8O_7)$$

$$\text{Charge balance : } [H^+] + [Na^+] = [OH^-] + 1[H_2Cit^{-1}] + 2[HCit^{-2}] + 3[Cit^{-3}]$$

And the formal definition of buffer capacity: $dC_b/d(pH)$, where $C_b = [Na^+]$.

Buffer capacity of acetic acid, as a monocarboxylic acid, can be calculated by Eq. (A.2) (Urbansky and Schock, 2000) and is plotted for 3 vol% acetic acid solution (chosen based on the Italian law text (Italian law text, 1973)) in Fig. A.1:

$$BC = \ln 10 \left(\frac{K_w}{[H^+]} + [H^+] + \frac{C_{AA}K_a[H^+]}{(K_a + [H^+])^2} \right) \tag{A.2}$$

where $K_w = 10^{-14}$, $[H^+] = 10^{-pH}$, C_{AA} = Molar concentration of acetic acid, and $K_a = 10^{-pKa} = 10^{-4.757}$. This formula is derived from:

$$\text{Mass balance : } C_{AA} = [HAc] + [Ac^-], \quad (HAc = C_2H_4O_2)$$

$$\text{Charge balance : } [H^+] + [Na^+] = [OH^-] + 1[Ac^-]$$

And the formal definition of buffer capacity: $dC_b/d(pH)$, where $C_b = [Na^+]$.

Generally, buffer capacity of an aqueous solution is defined as the concentration of acid or base that must be added to influence the pH, with the mathematical formula presented in Eq. (A.3) (Powers et al., 2005; Urbansky and Schock, 2000):

$$BC = dC_b/d(pH) = -dC_a/d(pH) \tag{A.3}$$

where C_b and C_a are the molar concentration of added base and acid, respectively.

Buffer capacities measurements and formulas of aqueous solutions containing only one of the monoprotic weak acids (e.g. acetic acid), diprotic weak acids (e.g. sulfuric acid) or triprotic weak acids (e.g. citric acid) can be found in different studies (Lambert, 1990; Powers et al., 2005; Urbansky and Schock, 2000). In aqueous solutions containing a mixture of different acids, buffer capacity calculations and their derivation are more complicated. By considering the mass balance and charge balance and employing Eq. (A.3), it is possible to obtain the formula of buffer capacity for any aqueous solution containing one or a mixture of different kinds of acids.

Buffer capacity for the aqueous solutions containing a mixture of acetic acid and citric acid was calculated in this study as Eq. (A.4) and plotted in Fig. A.2:

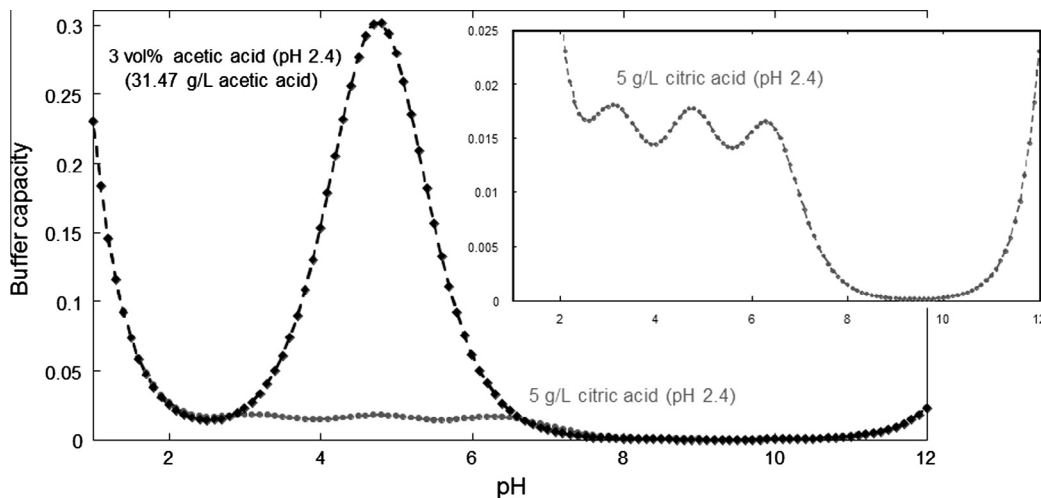


Fig. A.1. pH-dependency of buffer capacity for 5 g/L citric acid (pH 2.4, chosen based on the CoE protocol (CoE, 2013), based on Eq. (A.1) and 3 vol% acetic acid solution (pH 2.4, chosen based on the Italian law text (Italian law text, 1973), based on Eq.(A.2)).

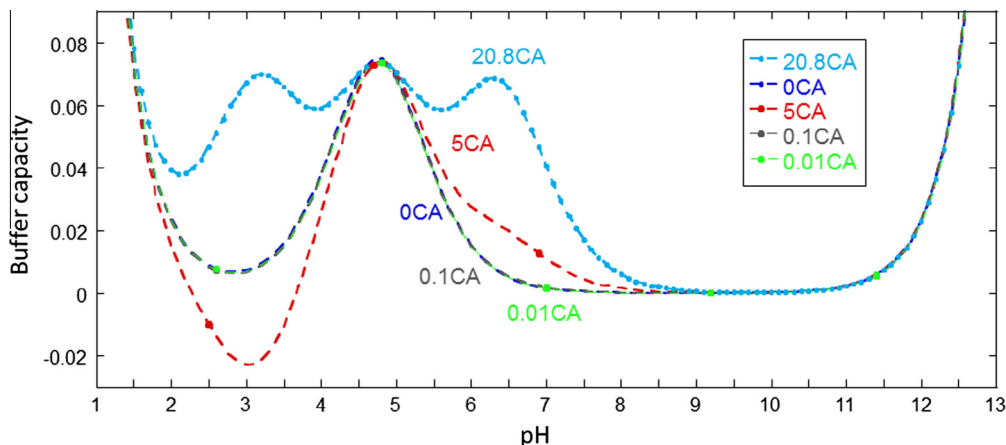


Fig. A.2. pH-dependency of buffer capacity for the 5 different test solutions (pH 2.4, and BC = 0.07) containing different concentrations of citric acid varying in the range of 0–20.8 g/L (by considering Eqs. (A.1), (A.2) and (A.4)).

$$BC = \ln 10 \cdot [H^+] \left(\frac{K_w}{[H^+]^2} + \frac{C_{AA} \cdot K_{AA}}{([H^+] + K_{AA})^2} + \frac{C_{CA} \cdot (2\beta_1[H^+] + \beta_2[H^+]^2 + 3) \cdot (\beta_1 + 2\beta_2[H^+] + 3\beta_3[H^+]^3)}{(\beta_1[H^+] + \beta_2[H^+]^2 + \beta_3[H^+]^3 + 1)^2} - \frac{C_{CA} \cdot (2\beta_1 + 2\beta_2[H^+])}{(\beta_1[H^+] + \beta_2[H^+]^2 + \beta_3[H^+]^3 + 1)} + 1 \right) \quad (A.4)$$

where $K_w = 10^{-14}$, $[H^+] = 10^{-pH}$, C_{AA} = Molar concentration of acetic acid, $K_{AA} = 10^{-4.757}$, C_{CA} = Molar concentration of citric acid, $\beta_1 = 10^{pKa3} = 10^{6.396}$, $\beta_2 = 10^{(pKa3 + pKa2)} = 10^{(6.396 + 4.761)}$, $\beta_3 = 10^{(pKa3 + pKa2 + pKa1)} = 10^{(6.396 + 4.761 + 3.128)}$.

This formula is calculated by:

$$\text{Mass balance: } C_{CA} + C_{AA} = [HAC] + [Ac^-] + [H_3Cit] + [H_2Cit^{-1}] + [HCit^{-2}] + [Cit^{-3}]$$

$$\text{Charge balance: } [H^+] + [Na^+] = [OH^-] + 1[Ac^-] + 1[H_2Cit^{-1}] + 2[HCit^{-2}] + 3[Cit^{-3}]$$

And the formal definition of buffer capacity: $dC_b/d(pH)$, where $C_b = [Na^+]$.

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