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ORIGINAL PAPER

A voltammetric approach to an estimate of metal release from tinplate promoted by ligands present in canned vegetables

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Abstract A linear sweep voltammetric (LSV) approach is proposed for achieving rapid information on metal release from tinned containers into preserved vegetables. Chopped tomato and pea preserves were chosen as prototypes for acid and nearly neutral canned food, respectively. Metal release in these vegetables tinned into both bare and lacquered containers was compared with that found in synthetic samples containing some organic complexing agents (acetic, ascorbic, citric, malic, oxalic, pyroglutamic acids) present in the vegetables considered, thus showing that some of these components affected markedly the metal release in bare cans. These ligands were concomitantly found to also affect LSV profiles recorded in parallel at Sn and Fe electrodes in synthetic samples, causing the starting potential for their oxidation to be lower, the higher the ligand activity of the species considered. The data indicated that metal release and starting potentials for metal discharge are strictly related, so that LSV is able to provide rapid and useful information on the nature of the protective effect (electrochemical or physical) of tin on the steel underlayer, as well as on the extent of Sn and Fe release.

Keywords Linear sweep voltammetry · Metal release · Tinned containers · Preserved vegetables

1 Introduction

Tinned containers are frequently employed for the storage of fruits and vegetables containing organic acids whose ligand properties can promote metal dissolution which is frequently associated to organoleptic changes and reduction of nutritive value, as well as to the release of disagreeable flavours [1–4].

Tinplate deterioration processes are complex because of the stratified structure and possible heterogeneity of the material used to assemble the containers. In fact, the material consists of a base layer of low carbon steel (giving mechanical strength), an intermediate layer of tin–steel alloy (resulting from flow-brightening, which protects steel from galvanic corrosion by oxidant species) and a final very thin tin layer (acting as sacrificial anode), together with possibly added Cr to prevent formation of iron oxide and sulphuration processes [4, 5]. To be really protective, tin must be anodic to steel and this has been verified for the majority of canned foods, mainly under anaerobic conditions [6, 7]. This notwithstanding, tin coupled to steel may even behave as the cathode if contacted by canned food containing species displaying so high ligand activity towards iron ions as to facilitate their formation from the oxidation of the parent metal. In fact, the lack of continuity of the tin layer, encountered for instance in the close neighbourhood of the can region involved in the lid welding to the cylindrical body, could allow can content and metals in the underlayer to interact, thus giving rise to redox events conditioned by the physical state of food containers. Consequently, both chemical composition of preserved food and micro-structural characteristics of the tinplate/foodstuff interphase (i.e. roughness and physical properties of both sample and passivation layer) can play an important role in metal release processes involved in canned food [4–8].

This is the reason why, in the last two decades, several investigations have focused on metal release from tinned containers, as well as on the formation of tinplate

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passivating films, which can be promoted by food-containing organic acids [9–19].

In the present investigation, metal release from polymer coated and uncoated tinned containers promoted by some real food samples was evaluated in view of verifying its possible connections with the electrochemical potentials for the oxidation of the main metal constituents in these samples. Thus, both metal release and potentials for metal oxidation were measured in a variety of media with the goal of checking whether a potential scale can be defined for inferring reliable expectations on tinplate corrosion caused by organic components more frequently encountered in canned vegetables. In particular, electroanalytical data achieved by linear sweep voltammetry (LSV) were compared with corrosion findings concerning metal release occurring in tinplates contacted for long times by either chopped tomato or pea preserves, which were chosen as prototypes for acid and nearly neutral food canned samples, respectively. Throughout this study, suitably prepared synthetic food simulating samples were also used extensively in order to achieve more reliable information under controlled conditions.

2 Experimental

2.1 Chemicals

All the chemicals employed were of analytical reagent-grade quality and were used as received. In all instances high purity deionised water (resistivity $\geq$18 MΩ cm), purified with an Elgastat® UHQ-PS System ("Elgastat water"), was used as the solvent and diluent.

Stock standard solutions containing different elements (Mg, Al, Cr, Mn, Fe, Ni, Zn, Cu, Mo, Cd, Sn, Sb, Ba, Pb and Bi) at controlled concentrations were prepared by suitably diluting the corresponding 1,000 mg L^{-1} standard solution for ICP (Merck) with Elgastat water added with ultrapure-grade 65% w/w HNO_3 (Merck), to achieve a final acid concentration of 0.5%.

The same procedure was also adopted to prepare stock standard solutions containing either Sn(II) or Fe(III) alone at different and known concentrations, the last also used for cathodic stripping voltammetric (CSV) measurements. A stock standard 1 M catechol solution, used in CSV analysis of iron, was prepared by dissolving in Elgastat water a weighed amount of the commercial product (Aldrich), preliminarily recrystallized from methanol as described in the literature [20].

Synthetic samples used to mimic both ligand composition and pH of real canned samples were prepared by dissolving in Elgastat water controlled amounts of the investigated organic constituents listed in Table 1. These aqueous solutions were not buffered to avoid the addition of high amounts of possible competitive ligands. Their pH was instead adjusted to the desired value by appropriate additions of 1 M NaOH or $HClO_4$ solutions.

Microwave (MW) digestions were conducted in an acid oxidizing mixture consisting of nitric acid (65% w/w) plus hydrogen peroxide (30% w/w) in a volumetric ratio of 1:1.

All CSV measurements were performed in solutions buffered at pH = 6.9 with 0.1 M (*N*-2-hydroxyethyl) piperazine-*N*′-2-ethanesulfonic acid (HEPES, Fluka), which acted as the supporting electrolyte too.

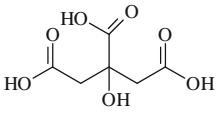
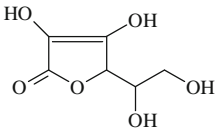
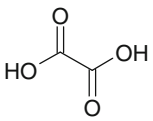
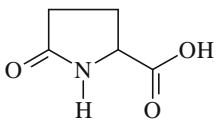
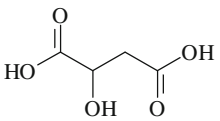
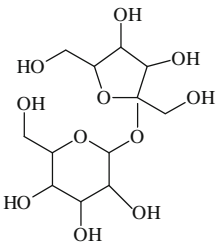
2.2 Real and synthetic samples

In order to estimate the role played by complexing agents frequently encountered in canned vegetables in the promotion of tinplate corrosion, we used chopped tomatoes and pea preserves as prototypes of acid and neutral real food samples, respectively. For the sake of comparison, metal ions present in these real samples were determined both before and after their canning, both in bare (E4/1) and in epoxyphenolic lacquered (E1/1) 400 mL tinplate cans. The internal tin coating was 11.2 and 2.8 g m^{-2} in E4/1 and E1/1 cans, respectively. Synthetic samples consisting of stock model solutions were also analysed prior to and after their tinning, once again both in E4/1 and E1/1 400 mL tinplate cans. They were prepared by adding to Elgastat water controlled amounts of either each of the main ligands present in the mentioned real samples or all these ligands together (in both cases to achieve the concentrations reported in the last two columns of Table 1).

Both fresh tomatoes (*Solanum Lycopersicon*) and recently harvested green peas (*Pisum Sativum*) were purchased in June 2007 from local supermarkets. Fresh tomatoes were first diced into ca. 2 cm cubes and peas were podded manually. A portion of both tomato and pea batches (about 70 kg each) was analysed for metals, while the remainders were canned at the Experimental Station for the Preserving Industry (SSICA) of Parma (Italy), following a standard procedure which can be summarized as follows.

Chopped tomatoes and peas were preliminarily cooked at 80 °C and then transferred into both E4/1 and E1/1 400 mL tinplate containers, by minimizing the head space and adding a brine (1.7% NaCl and 3.0% sucrose aqueous solution) to the sole pea cans. These containers, each containing an average of either 400 g of tomato (including its serum released spontaneously) or 270 g of peas plus 150 mL of brine, were then sealed and sterilized in autoclave at either 98 °C for 20 min (tomato samples) or 121 °C for 60 min (peas samples). The same procedure was also adopted for canning synthetic model solutions. All synthetic and real canned samples were stored at room

Table 1 Compounds employed to prepare synthetic samples suitable for mimicking concentration and pH of real canned chopped tomato or pea preserves

Compound	Formula	pK_a	Synthetic sample composition (mM)	
			Tomato simulating samples (pH = 4.0)	Pea simulating samples (pH = 6.3)
Citric acid		$pK_1 = 3.1$ $pK_2 = 4.8$ $pK_3 = 6.4$	26.0	3.1
L-Ascorbic acid		$pK_1 = 4.1$ $pK_2 = 11.6$	1.7	0.7
Oxalic acid		$pK_1 = 1.3$ $pK_2 = 4.3$	1.3	8.9
(*S*)-Pyroglutamic acid		$pK = 3.3$	9.3	–
Malic acid		$pK_1 = 3.4$ $pK_2 = 5.0$	18.6	13.3
Acetic acid		$pK = 4.8$	6.7	–
Sucrose		–	–	87.6
Sodium chloride	NaCl	–	–	291.0

temperature (20 ± 0.1 °C), until a scheduled number of them was opened at programmed times for metal ion analysis performed after microwave digestion. This preliminary mineralization step was preceded by (i) a homogenisation by a PBI-International (Milan) Sterilmixer for tomato samples; (ii) a separation of brine from solid by

filtration and subsequent homogenisation of the solid phase by a PBI-International Sterilmixer for pea samples; (iii) no pre-treatment for synthetic samples.

2.3 Microwave digestion

All microwave digestions were run on a Milestone MLS-1200 MEGA (FKV, Bergamo-I) equipped with an EM-45 exhauster of nitric acid fumes, a control panel and a MDR-1000/6/100/110 rotor, this last being a turntable operating with a maximum of six digestion vessels. Each digestion vessel consisted of a tetrafluoromethoxyl polymer (TFM) sample holder inserted in a hollow polyether-ether-ketone copolymer (PEEK) container. At the top of each vessel, a PEEK relief-valve was placed, aimed at allowing vapour release for pressure values exceeding 110 bar.

Digestions were conducted on 3.0–3.5 g of real samples, pretreated as mentioned above, or on 5–8 mL of model solutions, added in both cases with the mineralising mixture consisting of 1 mL of nitric acid (65% w/w) plus 1 mL of hydrogen peroxide (30% w/w). The five-step power program adopted for the microwave digestion was as follows: (i) 2 min with an irradiation power of 250 W; (ii) 2 min with 0 W; (iii) 5 min once again with 250 W; (iv) 2 min with 400 W; (v) 5 min with 650 W. Both power program and composition of the digestion mixture were optimised, as described elsewhere [21, 22], with the aim of achieving a total mineralization of real matrices, also in the view of minimising interferences in their subsequent electroanalysis arising from adsorption at the electrode surface of residual traces of biological material.

2.4 Induced coupled plasma-mass spectrometric measurements

Induced coupled plasma-mass spectrometric (ICP-MS) measurements on microwave digested samples were performed by a Spectromass 2000 Type MSDIA10B (Spectro Analytical Instruments, D) under the operating conditions listed in Table 2. They were optimised, as reported previously [21, 23, 24], to maximise, on one hand, the signal with respect to the background noise for all *m/z* values explored and on the other hand to minimise the suppression effect on ICP-MS signals caused by the high salt content [25–27]. Pure argon (transistor quality) was used for all determinations. The nebulization system consisted of a conventional concentric-flow pneumatic nebulizer (Spectro, Meinhard type) fed with a nebulizer flow of argon of 1.1 L min^{-1} which led to a nebulizer gas pressure of 2.8 bar.

All signals collected for the metal isotopes considered (counts s^{-1}) were normalized to the signal of the internal standard ($^{115}In^{+}$), whose content was kept carefully constant (0.1 ppm) in order to correct for non-spectral interferences and for signal instability. Unless otherwise stated, mean values and standard deviations are always relative to ten replicate measurements.

Table 2 ICP-MS operating conditions

Plasma conditions	
Frequency	27.12 MHz
Rf power	1,350 W
Auxiliary gas flow	1.2 l min^{-1}
Coolant gas flow	18 l min^{-1}
Sampler	Nickel (HMC), 1.0 mm diameter orifice
Skimmer	Nickel (HMC), 0.8 mm diameter orifice
Vacuum parameters	
Interface	2.04 mbar
Quadruple	8.9×10^{-6} mbar
Turbo voltage	10 V
Mass spectrometer settings	
Secondary electron multiplier	−1,950 V
Peak resolution	0.75 amu
Pause calibration factor	3.0
Ion optic ensemble	
Extraction lens (LO)	−450 V
Optic lens A (LA)	−70 V
Photon stop lens (LB)	0 V
Optic lens C (LC)	−100 V
Quadruple entrance lens (LD)	−80 V
Field axis (FA)	5 V
Deflection	
In	−500 V
Out	−190 V

HMC High matrix content

Stock standard solutions mentioned above were used to construct calibration plots for all elements investigated. From the sensitivities drawn as angular coefficients of these plots, the detection limits (DL) reported in Table 3 were evaluated for a signal-to-noise ratio of 3. Noise was calculated from the standard deviation of 10 replicate measurements of the background intensity recorded at the same *m/z* ratio used to generate the specific calibration curve. The absence in the diluent (Elgastat water added with 0.5% ultrapure 65% w/w HNO_3) of the investigated elements at concentrations higher than their DL was first checked by preliminary ICP-MS measurements.

2.5 Electroanalytical measurements

Linear sweep (LSV) and cathodic stripping (CSV) voltammetric measurements were performed at 20 ± 0.1 °C in undivided three-electrode cells by using a voltammetric

Table 3 Detection limits and relevant correlation coefficients (R) found in ICP-MS determinations for the elements considered

Element	Isotope (amu)	DL (ppb)	R
Magnesium	24	5.32 ± 0.16	0.999
Aluminium	27	2.34 ± 0.07	0.999
Chromium	52	1.35 ± 0.04	0.999
Manganese	55	0.78 ± 0.02	0.999
Iron	56	82.9 ± 0.17	0.960
Nickel	60	5.70 ± 0.11	0.999
Zinc	64	3.79 ± 0.09	0.999
Copper	65	4.12 ± 0.08	0.999
Molybdenum	98	0.57 ± 0.01	0.999
Cadmium	112	0.86 ± 0.01	1.000
Tin	118	0.76 ± 0.01	0.998
Antimony	121	0.26 ± 0.01	0.999
Barium	138	0.49 ± 0.01	0.999
Lead	208	1.06 ± 0.01	1.000
Bismuth	209	8.27 ± 0.04	0.999

unit consisting of a PGSTAT 30 (Ecochemie, Twente) potentiostat driven by Ecochemie GPES 3.2 software installed on a Pentium III personal computer. In all cases, the counter electrode was a 1 cm^2 platinum sheet, while the reference electrode was a $Ag/AgCl, Cl^-_{sat}$ electrode connected to the cell by a salt bridge containing the medium also employed in the test solutions.

In LSV measurements the working electrode was either a tin (99.999%, from Aldrich) or an iron (99.95%, from Aldrich) wire inserted into a Teflon tube, so that only a metallic disc with a geometric area of about 0.125 mm^2 was exposed to the analysed solutions, which always contained 0.05 M sodium perchlorate as the supporting electrolyte and with small amounts of either a 1 M NaOH or $HClO_4$ solution to adjust the pH to the desired value. Before use, these working electrodes were polished with wet emery cloth with progressively decreasing grain sizes (from 60 to 600 grit), washed with Elgastat water and then inserted, after drying, into the voltammetric cell. These measurements were performed with a sweep rate of 20 mV s^{-1} to minimize both double-layer charging currents caused by surface processes involved in these investigations (see below) and the effect of the irreversible character displayed by the relevant charge-transfer reactions.

Determinations of total iron ions ($Fe^{3+} + Fe^{2+}$) were performed by CSV in order to achieve a DL (0.1 ppb) lower than that offered by ICP-MS for this element (see Table 3). These CSV analyses were performed in 15 mL of 0.01 M HEPES buffer solutions (pH = 6.9) which were added with both 10–1000 μL aliquots of the MW digested real or synthetic samples and 30 μL of a 1 M catechol solution. This diphenol was added because its iron complexes are known to be accumulated by adsorption at a hanging mercury drop electrode (HMDE) [20] which was used as the working electrode (Metrohm 663VA, area about 0.52 mm^2). The potential waveform involved the application to the HMDE of a preconcentration potential of −0.1 V for 60 s, during which the solution was stirred at 2,500 rpm. Subsequently, after an equilibration time of 10 s under static conditions, the electrode potential was cathodically scanned from −0.1 to −0.8 V with a sweep rate of 20 mV s^{-1}. Quantitative results were achieved from cathodic stripping currents by using the standard addition method.

Unless otherwise stated, all electroanalytical measurements were run in nitrogen deaerated solutions.

3 Results and discussion

3.1 Metal release into canned food samples

To achieve a correct evaluation of metal release from both E4/1 and E1/1 containers into real samples, some tomato and pea batches were analysed for their metal content prior to and after tinning. The analysis of fresh tomatoes and peas showed that as many as 8 (Mg, Cr, Ni, Cd, Sn, Sb, Pb and Bi) of the 15 elements considered were below the corresponding DL. Zn was the sole element found in the 7% NaCl + 3.0% sucrose aqueous solution used as the brine for canned peas, even though at very low levels (ca. 0.4 ppm). A higher content (ca. 11 ppm) for Zn was found in fresh peas, while its concentration in fresh tomatoes was comparatively lower (ca. 1.4 ppm). Ba was present in fresh peas alone in small concentration (ca. 1.8 ppm), while a moderate content, ranging roughly from 0.2 to 2.0 ppm, was found in both fresh vegetables for 4 of the elements considered (Al, Mn, Cu and Mo). Finally, significant concentrations of the sole Fe were found in both fresh matrices (ca. 8 ppm in peas and 4 ppm in tomatoes).

Subsequently, the content of all the mentioned elements was monitored with time on pea and tomato samples canned in both E4/1 and E1/1 containers. No appreciable concentration change was observed for all these elements in both types of preserves tinned in E1/1 containers, even after canning times of 200 days, thus showing unambiguously that the protective effect provided by the epoxyphenolic layer was very effective. In pea and tomato samples tinned into bare E4/1 containers, an appreciable concentration increase with canning time was found for Fe and Sn alone, as illustrated in Fig. 1. In particular, Fig. 1a shows that iron release in canned pea samples (nearly neutral medium) was significant, while the release of Sn was comparatively much lower. Conversely, Fig. 1b shows

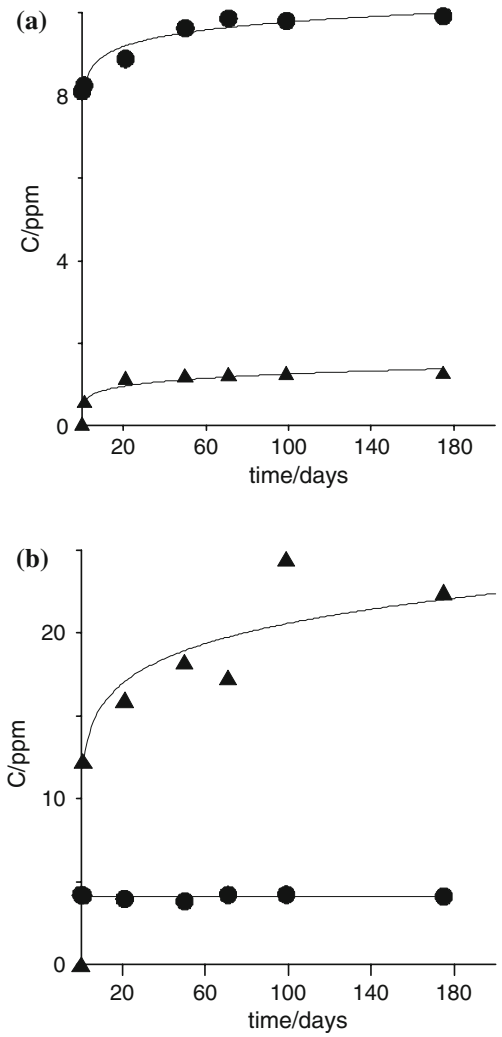


Fig. 1 Fe (●) and Sn (▲) release from bare E4/1 cans containing: pea (**a**) and tomato (**b**) samples. All concentrations reported are mean values of four replicate measurements. The relative standard deviation, calculated accordingly, ranged in all cases from 7 to 13%

that Sn release was significant in tinned tomato samples (acid medium), while Fe release was concomitantly inappreciable. In both preserves, Sn and Fe concentrations attained a limiting value which was approached after a time ranging from ca. 50 days (Sn and Fe in pea samples) to ca. 100 days (Sn in tomato samples). The existence of this limiting value seems to disagree with the occurrence of the continuous metal dissolution expected in view of the large availability of ligands in the analysed samples. Nevertheless, it must be taken into account that tinplate corrosion leads to insoluble oxide-hydroxide layers displaying a buffering effect on metal-solution concentrations, since saturation conditions are progressively attained. Thus, the progress of the corrosion process is not accompanied by a parallel increase of Sn and Fe concentrations in the solutions.

3.2 Metal release into canned synthetic samples

In order to verify whether metal release from tinned containers is promoted by ligands present in food matrices, attention was paid to its occurrence in cans filled with synthetic solutions prepared by adding some of the main components encountered in the tinned food considered. They were chosen among the organic acids (able to act as metal complexing agents) which are known to be present in these vegetables [28–32], together with sucrose and sodium chloride generally added in large amounts to preserving liquids. These components are listed in Table 1 where their solution concentration and pH (adjusted by suitable addition of $HClO_4$ or NaOH) are also reported.

Thus, a series of solutions in Elgastat water containing either one of these components alone or all them together were canned in both E4/1 and E1/1 400 mL tinplates (by the standard procedure above) and analysed for their metal content prior to and after tinning.

By monitoring synthetic samples sealed into E1/1 tins at increasing times, no appreciable release from the containers was observed. Conversely, analyses conducted at increasing times on different synthetic samples canned in E4/1 tins highlighted a significant release of Fe and Sn, accompanied by the release of very minor amounts (ranging from 0.03 to 0.40 ppm) of other elements (Ba, Cr, Cu, Zn).

The increase with time displayed by Fe and Sn in each of the synthetic samples considered is depicted in Figs. 2 and 3, showing that a satisfactory constant limiting value is in all cases attained after about 20–40 days. In fact, no further significant increase was found even up to 200 days.

In fairly good agreement with the results for canned food samples, the comparison of these Figures with each other allows the following remarks to be made: (i) Sn release is always, as an average, higher than the corresponding Fe release; (ii) the release of Sn is more significant in acid media, while a higher release of Fe is found in neutral media. The first finding is conceivably caused by the large difference between Sn and Fe surface contacted by the canned medium, in that a ratio of at least 100:1 is expected even in the worst hypothesis of deteriorated cans displaying several detinned sites. As to the pH effect on the release of these metals, it can be accounted for by considering that neutral media facilitate the formation of protective Sn oxide layers preventing the tin surface from being permeated by ligands. At the same time, Fe oxide layers are formed which are known to be easily permeated by tinned media, whose neutral pH makes the ligands available in their unprotonated forms which display a more effective complexing activity.

When these release measurements were repeated using synthetic samples prepared with higher or lower contents of ligands displaying the most significant effects (citric,

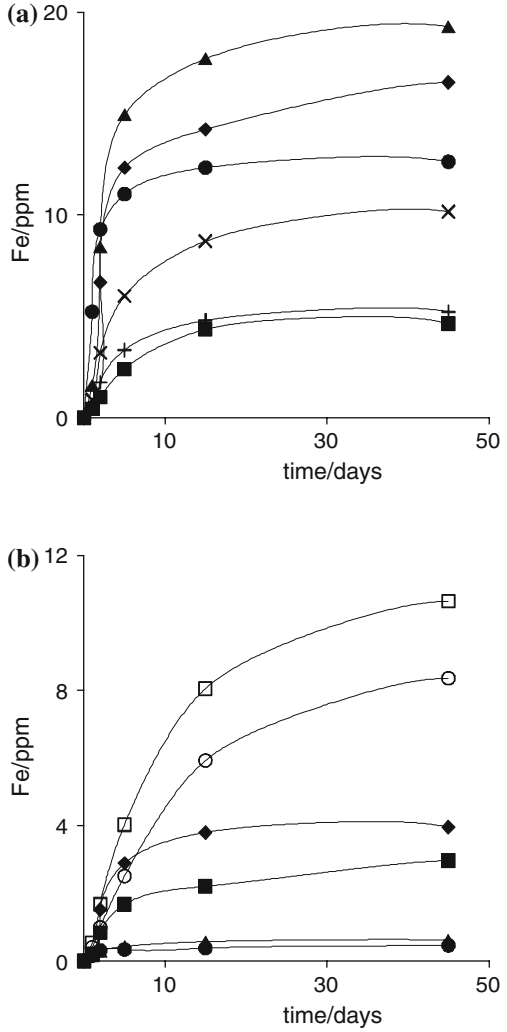


Fig. 2 Iron release from E4/1 cans into synthetic samples at pH 4.0 (**a**) and 6.3 (**b**) containing: acetic acid (□); pyroglutamic acid (○); citric acid (◆); malic acid (●); oxalic acid (■); ascorbic acid (▲); sucrose (✚); sodium chloride (×) at the concentrations reported in Table 1. All concentrations reported are mean values of four replicate measurements. The relative standard deviation, calculated accordingly, ranged in all cases from 6 to 15%

malic and oxalic acids), higher or lower constant limiting values, respectively, for both Sn and Fe releases were attained after about 20–40 days, thus suggesting the existence of a roughly linear dependence on the ligand concentration. On the other hand, just these ligands, among those considered, are known to give the more stable complexes with Sn ions, in that they are all characterized by formation constants (β_1 and β_2) whose logarithm is of the order of about 6–7 and 12–14, respectively [33–35]. These arguments strongly suggest that Sn release is markedly affected by the ligands present in the medium contacting the can surface.

Similar arguments can also be suggested to account for Fe release, because its limiting values agree quite well in this case with the sequence of stability constants of iron complexes with the majority of the ligands considered [36–38]. The sole exceptions are the exceedingly low Fe releases found at pH = 4.0 in the presence of citric and malic acids (see Fig. 2a) which give rather stable iron complexes. On the other hand, the high stability of iron complexes with the mentioned ligands is confirmed by findings at pH = 6.3 (see Fig. 2b). This anomalous behaviour may, however, be due to the fact that the corresponding tin complexes are comparatively more stable, so as to make tin anodic to iron (see below).

It must be pointed out, however, that limiting values shown in Figs. 2 and 3 are conditioned by the different concentrations adopted for the ligands. Consequently, in view of the dependence of metal release on the ligand concentrations, a more effective comparison should be based on comparable contents of these food components. Thus, for instance at pH = 6.3, higher limiting values for Fe release would be achieved in the presence of ascorbic acid, citric acid and oxalic acid contents comparable with that of malic acid (see Table 1).

Finally, it must be emphasized that Fe and Sn release observed in real samples is significantly lower than the corresponding release found in synthetic samples, but this is only an apparent disagreement. In fact, our synthetic samples were prepared by dissolving ligand contents comparable with those known to be available in the corresponding real samples, where they are, however, not present as freely diffusing solution species but as species partitioned between the solid vegetable matrix and the corresponding brine. Consequently, only a fraction of each ligand present in real samples is expected to be really available in the aqueous phase and hence in real contact with inner can surfaces.

3.3 Relation between LSV data and metal release

In order to gain direct evidence of the ability of the different food-simulating compounds to affect the electrochemical potential for Sn and Fe oxidation, a series of linear sweep voltammograms was recorded in different solutions, each containing a single species ligand (see Table 1), using either tin or iron working electrodes. All the experiments were conducted in aqueous solutions containing 0.05 M $NaClO_4$ as the supporting electrolyte, because perchlorate anions are known to display no ligand activity towards the tested metals.

Irrespective of the pH, in the absence of added ligands tin oxidation started at potentials very close to −0.3 V (−0.26 V at pH = 4.0 and −0.28 V at pH = 6.3), where tin(II) oxides/hydroxide layers passivating the electrode surface are formed, thus preventing the extension of the anodic process to longer times. Conversely, iron oxidation

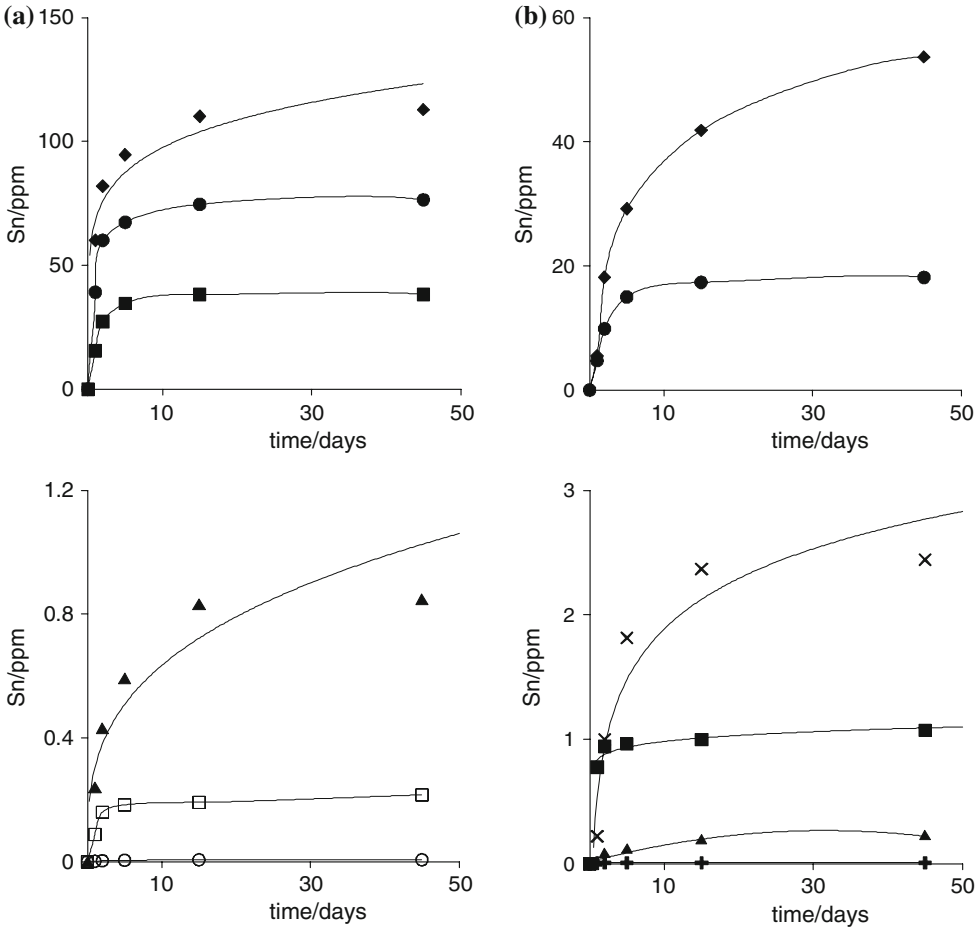


Fig. 3 Tin release from E4/1 cans into synthetic samples at pH 4.0 (**a**) and 6.3 (**b**) containing: acetic acid (□); pyroglutamic acid (○); citric acid (◆); malic acid (●); oxalic acid (■); ascorbic acid (▲); sucrose (✚); sodium chloride (×) at the concentrations reported in Table 1. All concentrations reported are mean values of four replicate measurements. The relative standard deviation, calculated accordingly, ranged in all cases from 5 to 17%

in the absence of added ligands occurs very close to −0.5 V (−0.55 V at pH = 4.0 and −0.54 V at pH = 6.3) and leads to the corresponding oxide/hydroxide species being unable to passivate the electrode surface, so that its anodic reaction continues with time. Consequently, under these conditions steel is anodic to tin, so that the superficial Sn layer in tinned containers acts only as a mere outward protective layer for the steel underlayer.

When these LSV were recorded in 0.05 M $NaClO_4$ aqueous solutions with one of the ligands considered at the concentration levels reported in Table 1, the oxidation of Sn and Fe electrodes was greater, as shown for the sake of illustration in Fig. 4, which refers to the behavior of tin at pH = 4.0 in the presence of some significant ligands.

From these voltammograms, the starting potential (E_s) for electrochemical oxidation of Sn and Fe in the presence of the different ligands was evaluated. The E_s values, collected in Table 4, were in all cases estimated as the potentials for metal discharge providing current signals equal to ten times the corresponding background currents recorded in the absence of the ligand at the same potentials.

In the reasonable hypothesis that these starting oxidation potentials are affected by comparable overvoltages in the presence of the different ligands assayed, their rank provides fairly reliable information about the ability of different tinned media to promote corrosion of can containers.

The data at pH = 4.0 show that Fe oxidation occurs more easily than Sn oxidation, except for the cases in which citric and malic acids are involved. In these last cases, tin is anodic to steel, so that it shows an electrochemical protective effect on iron, whose oxidation is consequently expected to become markedly depressed. This conclusion, drawn from voltammetric data, agrees well with Fe release found in the presence of these ligands. In fact, Fig. 2a shows that in the presence of these ligands a release of Fe approaching zero is achieved even at longer times, in spite of stability constants for the corresponding complexes being higher than those relative to other ligands considered. At the same time, Fig. 3a shows that just the presence of citric and malic acids causes the highest Sn release.

In contrast, in the presence of other ligands (acetic, ascorbic, oxalic and pyroglutamic acids) tin acts simply as a mere outward protective layer for the steel underlayer, as underlined above in the absence of ligands. Under these pH conditions and in the presence of these ligands, tin release (but also iron release, even though on a minor scale) is

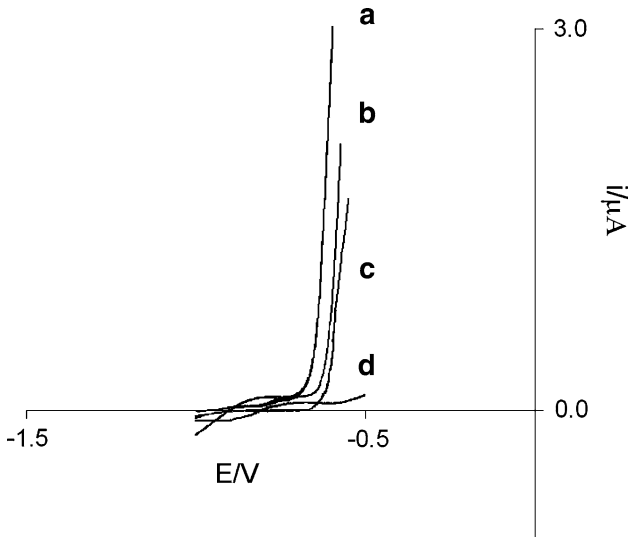


Fig. 4 Linear sweep voltammograms recorded at a Sn electrode with a scan rate of 20 mV s^{-1} in 0.05 M $NaClO_4$ aqueous solutions whose pH was adjusted at 4.0 by $HClO_4$ and added with: **a** 26.0 mM citric acid; **b** 1.3 mM oxalic acid; **c** 8.6 mM malic acid; **d** no ligand. Potentials are referred to an aqueous $Ag/AgCl/Cl^-_{sat}$ electrode

strictly related to its starting oxidation potential. At this acid pH, a release of Sn higher than that of Fe is found, in spite of expectations based on E_s values, because iron can be contacted by the ligands only in the few detinned sites present inside the can. Figure 2a shows that only moderate Fe amounts are released, on average, while Fig. 3a shows a more marked Sn release. It can be concluded that under these pH conditions both tin and iron release is strictly related to their starting oxidation potentials, as well as to their mutual position.

Similar arguments can be advanced to account for metal release found at pH = 6.3. Voltammetric data collected at this pH suggest that iron is anodic to tin in the presence of the majority of ligands (ascorbic and citric acids, sodium chloride and sucrose), so that no electrochemical steel protection takes place and tin again acts only as a outward protective layer for the steel underlayer. In contrast, tin is anodic to steel in the presence of oxalic and (even though only a little) malic acids. This notwithstanding, at this pH iron oxidation promoted by these species does not become markedly depressed, as can be seen by inspection of Fig. 2b where anything but negligible Fe releases are shown in the presence of oxalic and, especially, malic acids. Such an apparent disagreement may be accounted for by considering that E_s values inferred for these ligands are scarcely reliable, owing to the observed extensive passivation of the electrode surface which also led to poorly reproducible LSV profiles.

4 Conclusions

Simple recording of LSV profiles in the presence of food components displaying more or less ligand activity towards the constituents of can containers provides an effective approach for gaining rapid information on metal release processes involved in canned food.

The approach does not permit quantitative data on metal release to be acquired, but it contributes to understanding of thermodynamic conditions controlling a specific tinplate deterioration process. This allows discrimination of the cases in which tin is anodic to iron (so that it displays a real electrochemical protective effect on the steel underlayer) from those implying that tin is cathodic and acts as a simple coating layer physically protecting the steel. In the former case no significant Fe release is expected, while in the latter, significant amounts of iron can be released with time, especially for cans displaying several detinned sites, so that epoxyphenolic lacquered tinplates should be employed.

Table 4 Effect of pH and nature of the food-simulating ligand on the starting potential (E_s) for the oxidation of Sn and Fe electrodes dipped into 0.05 M $NaClO_4$ solutions added with 1 mM of the listed ligands

Food-simulating ligand	pH = 4.0		pH = 6.3	
	E_s (Sn) (V)	E_s(Fe) (V)	E_s (Sn) (V)	E_s(Fe) (V)
None	−0.26 ± 0.01	−0.55 ± 0.01	−0.28 ± 0.01	−0.54 ± 0.01
Sodium chloride	–	–	−0.32 ± 0.01	−0.55 ± 0.03
Sucrose	–	–	−0.28 ± 0.01	−0.55 ± 0.01
Pyroglutamic acid	−0.32 ± 0.01	−0.66 ± 0.01	–	–
Acetic acid	−0.34 ± 0.03	−0.63 ± 0.01	–	–
Ascorbic acid	−0.32 ± 0.01	−0.63 ± 0.07	−0.30 ± 0.01	−0.65 ± 0.01
Malic acid	−0.62 ± 0.01	−0.58 ± 0.05	−0.59 ± 0.09[a]	−0.60 ± 0.04
Citric acid	−0.66 ± 0.01	−0.60 ± 0.01	−0.62 ± 0.01	−0.66 ± 0.03
Oxalic acid	−0.63 ± 0.01	−0.69 ± 0.02	−0.71 ± 0.10[a]	−0.57 ± 0.08[a]

[a] Poorly reproducible data due to a rapid and extensive passivation of the electrode surface

The location of E_s on the potential scale can be exploited to estimate on one hand the expected degree of metal release and on the other hand the occurrence or not of extensive passivation processes at the electrode surface caused by these species.

Finally, the analytical data can be obtained rapidly and with low-cost instrumentation.

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