



Study of the migration phenomena of specific metals in canned tomato paste before and after opening. Validation of a new quality indicator for opened cans



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ARTICLE INFO

Article history:

Received 15 February 2014

Accepted 14 March 2014

Available online 26 March 2014

Keywords:

Tomato paste samples

Quality indicator

Metal migration

Uncertainty calculation

ETAAS

ABSTRACT

A method for the simultaneous determination of Cd–Pb, As–Cu, Cr–Ni and Fe–Mn in canned tomato paste samples by Electrothermal Atomic Absorption Spectrometry was developed and validated. The validation procedure was conducted according to the terms of the European regulation for the official control of contaminants in foods. The validated method was applied for the determination of these metals and metalloids in 13 different tomato paste samples and the results showed that Cd content was higher than the maximum permissible value of 0.050 mg kg⁻¹ as proposed in European Regulation (EC) No 1881/2006 concerning fresh fruits and vegetables. Furthermore, a new quality indicator was evaluated in order to provide information about tomato paste quality and the appropriate storage time of an opened canned tomato paste. Finally, a migration test was accomplished based on the calculation of mass balance and the comparison of the elemental content in canned tomato paste samples and in aseptic paper pack and it was proved that Fe and Pb were the main metals migrating in tomato paste samples.

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1. Introduction

Metals are widely spread to air, soil and water as their natural component but also as a consequence of anthropogenic activities, including the use of fertilizers, pesticides, runoffs from industries and mining operations (Cao et al., 2010). Non-essential toxic metals, such as Cd, Pb, can be transported to plants mainly by their roots but also by the atmosphere, enter plants cells through transport systems, and become extremely toxic for both humans and plants (Williams et al., 2000; Gallego et al., 2012). In addition, packaging materials are proved to be a significant source of toxic

metals that can migrate into food (Karakas, 2012). Thus, human consumes a variety of metals from their daily dietary, and in different concentrations that can induce a health risk due to the fact that toxic elements have long biological half-lives, are not biodegradable and can accumulate in all living organisms (Cao et al., 2010; Kirkillis et al., 2012).

Lead and cadmium are considered as human carcinogens by the International Agency for Research on Cancer, since lead can cause gastrointestinal or kidney cancer and cadmium cause cancers of the lung, the prostate, the pancreas, and the kidney, when they are excessively consumed (Waisberg et al., 2003). In lower doses, they can cause a number of diseases, especially cardiovascular, kidney, nervous system, blood as well as bone diseases (Zhuang et al., 2009). The recommended maximum permissible levels of lead and cadmium in vegetables and fruits are 0.10 and 0.050 mg kg⁻¹, respectively (European Commission Regulation, 2006), but to the best of our knowledge no maximum permissible level of these metals in canned tomato paste samples was established.

Arsenic is also toxic mainly in inorganic form. Its toxicity ranges from skin lesions to cancer of the brain, liver, kidney, and stomach. For an adult, a dose around 1–3 mg kg⁻¹ is estimated to be lethal (Hughes, 2002; Sharma and Sohn, 2009). FAO/WHO Expert Committee of Food Additives (2006) has established Provisional

Abbreviations: PTWI, Provisional Tolerable Weekly Intakes; THGA, Transversely-Heated Graphite Atomizer; EDL, Electrodeless Discharge Lamp; ETAAS, Electrothermal Atomic Absorption Spectrometry; LOD, limits of detection; LOQ, limit of quantification; RSD, relative standard deviation; ICQ, internal quality control chart; AA, analyte absorbance; C, concentration; E.C, European Commission; DGE, Deutsche Gesellschaft für Ernährung; OGE, Österreichische Gesellschaft für Ernährung; SGE, Schweizerische Gesellschaft für Ernährungsforschung; SVE, Schweizerische Vereinigung für Ernährung; FNB, Food and Nutrition Board; IOM, Institute of Medicine.

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Tolerable Weekly Intakes (PTWI) of toxic elements from food. For As in inorganic form, a PTWI of 0.015 mg kg^{-1} per body weight was established. On what concern the other trace elements that can be found in food, and are essential but also harmful at excessive levels national governments have established Tolerable Upper Intake Levels (Capar et al., 2007).

The last few years, studies about the metal content of tomatoes and their products have been increased since tomato is among world's most popular fruit. The concentrations of metals were determined by different methods, such as ICP-MS, and flame or graphite furnace Atomic Absorption Spectrometry (Zhuang et al., 2009; Demirbas, 2010; Karakaş, 2012).

In a previous study, the level of tin in canned tomato paste was determined, in order to estimate the migration from the coating material of the can (Pasiás et al., 2012). The purpose of this study was to continue the study of migration phenomena of other selected metals and metalloids, of the coating material from cans before and after opening and under refrigerating at 4°C (in-home storage conditions), for 7, 28, 35 and 41 days. Thus, the concentrations of Cd, Pb, Cr, Ni, Cu, As, Fe and Mn were determined, using the developed and validated method, in eleven samples of canned tomato paste that were selected from the local market (Athens, Greece) and two tomato paste samples packed in aseptic paper pack. From the results obtained, a new quality indicator based on the fraction of Fe content to the total determined elemental content has been established. Finally, different migration tests were performed in order to exploit the percentage of elemental migration from the package coating material into the tomato paste.

2. Materials and methods

2.1. Instrumentation

A Perkin–Elmer SIMAA-6000 simultaneous multielement atomic absorption spectrometer with a longitudinal Zeeman-effect background correction system, equipped with a Transversely-Heated Graphite Atomizer (THGA), and an AS-72 autosampler were used. Electrodeless Discharge Lamps (EDL) were used for As, Pb, Cd and hollow cathode lamps were used for Cu, Fe, Mn, Ni, and Cr (Perkin Elmer, California, USA). Atomic signals were measured in peak area mode. The digestions were performed on a MARS X-Press microwave oven (CEM Corporation, Matthews, USA).

2.2. Reagents and analytical solutions

Ultra pure water ($18.2 \text{ M}\Omega \text{ cm}$ at 25°C) from a Millipore Direct-Q-UV water purifier (Millipore) obtained using a Milli-Q system (Millipore). All solutions were prepared with Suprapur grade nitric acid (Merck, Darmstadt, Germany). The argon was of 99.999% purity. The standard solutions containing $50 \mu\text{g L}^{-1}$ of Pb, Fe, Mn, Ni, As, and Cu $25.0 \mu\text{g L}^{-1}$ of Cr, and $5.0 \mu\text{g L}^{-1}$ of Cd were prepared by appropriate dilution of 1000 mg L^{-1} Pb, Fe, Mn, Ni, As, Cu, Cr and Cd stock standard solutions (Merck) and acidified with 1% (v/v) Suprapur grade nitric acid. The working solutions were prepared automatically by the autosampler. The palladium/magnesium modifier solution was prepared by appropriate dilution of 10 g L^{-1} Pd (Merck) in HNO_3 and 1 g L^{-1} Mg in 1% (v/v) HNO_3 (High Purity Standards, Charleston, SC). For quality assurance two different certified reference materials (NIST 1573a, tomato leaves and ERM-BC084a, tomato paste) were also analyzed.

2.3. Analytical procedure

All glassware and polypropylene bottles were cleaned with acidified ultra pure water. Eleven different canned tomato paste samples and two different packed in aseptic paper pack, under different brand names, were purchased from the local markets in Athens, Greece during December 2012. The expiration dates of all samples were December of 2015. The samples were transferred in the laboratory and were coded as S1 to S13 (meaning Sample 1 to Sample 13). Samples S1, S2, S5, S7, S8 and S11 had the internal surface fully coated with plastic layer, while samples S3, S4, S6 had no plastic layer on the side lids and samples S9, S10 had the internal surface coated with plastic film layer apart from bottom and top lids, respectively. S12 and S13 were also double concentrated tomato paste samples packed in aseptic paper pack and under the same brand name with S7 and S8 samples, respectively.

Samples were milled and homogenized in a food processor and 0.5000 g of the homogenized tomato paste sample were weighted into the Teflon vessels and 5 mL of $65\% \text{ HNO}_3$ and 1 mL $36\% \text{ H}_2\text{O}_2$ were added. The samples were digested with MARS X-Press (CEM Corporation) microwave oven with a preselected program (first stage; 1600 W , 2 min ramp time, 165°C , 0 min hold time, second stage; 1600 W , 3 min ramp time, 175°C , 5 min hold time) and then diluted to a final volume of 20 mL with ultrapure water. For some metals, a further dilution was needed.

In order to investigate the effect of the storage time at 4°C the samples were left in their packages in the refrigerator and were re-homogenized and re-digested after 7, 28, 35, and 41 days. Furthermore, two different migration tests were accomplished using washed packages from the same canned tomato paste samples which were filled (a) with acidified ultra pure water ($\text{pH} = 4$) and (b) with tomato paste of known metal and metalloid content. Samples were stored for 4 days at 4°C . The tomato paste of known metal content was a tomato paste sample packed in aseptic paper (control sample) and which was put in a washed canned package under the same brand name test sample₁ (TS₁) under the condition described before. In order to provide comparable results a same second control sample (TS₂) was left opened under the same conditions with the test sample₁. The whole procedure was performed twice and the (%) Enhancement was calculated based on Eq. (1). Theoretically, if no migration took place during storage the (%) Enhancement₁ in TS₁ should be equal to the (%) Enhancement₂ in TS₂.

$$(\%) \text{ Enhancement}_x = \frac{([\text{TS}_x] - [\text{control sample}]) \times 100}{[\text{control sample}]} \quad (1)$$

where [TS_x] the content in mg kg^{-1} of trace elements in test samples, [control sample] the content in mg kg^{-1} of trace elements in control sample.

Pd ($1.25 \mu\text{g}$) was used as the optimal chemical modifier for the simultaneous determination of Cd–Pb and As–Cu. Pd–Mg ($1.25\text{--}5.0 \mu\text{g}$) was used as the appropriate chemical modifier for the simultaneous determination of Fe–Mn, and no chemical modifier was used for the simultaneous determination of Cr–Ni. The pyrolysis and atomization temperature curves were obtained for all the pairs tested by spiking $20 \mu\text{L}$ of a digested sample solution and $20 \mu\text{L}$ of the mixed standard solution in order to investigate the electrothermal behaviour of those elements. It should be mentioned that in simultaneous multi-element Electrothermal Atomic Absorption Spectrometry (ETAAS) analysis furnace temperatures have to be compromised related to the group of analytes to be determined. The graphite furnace programmes followed are summarized in Table 1.

Quantification was performed with calibration curves constructed from integrated absorbance measurements and prepared automatically by the autosampler by spiking $20 \mu\text{L}$ of a digested sample solution with $20 \mu\text{L}$ of 5 different standard solutions in the range of $0.0\text{--}50.0 \mu\text{g L}^{-1}$ for the determination of Cu–As and Fe–Mn; $0.0\text{--}5.00 \mu\text{g}_{\text{Cd}} \text{ L}^{-1}$ and $0.0\text{--}50.0 \mu\text{g}_{\text{Pb}} \text{ L}^{-1}$ for the determination of Cd and Pb; $0.0\text{--}50.0 \mu\text{g}_{\text{Ni}} \text{ L}^{-1}$ and $0.0\text{--}25.0 \mu\text{g}_{\text{Cr}} \text{ L}^{-1}$ for the determination of Ni and Cr. $5 \mu\text{L}$ of the appropriate chemical modifier was also injected into the graphite tube. The instrumental limits of detection, LOD ($\mu\text{g L}^{-1}$) and of quantification (LOQ) were calculated from the equations $\text{LOD}_{\text{inst}} = 3.3 \times S_{\text{BL}}/b$ and $\text{LOQ}_{\text{inst}} = 10 \times S_{\text{BL}}/b$, respectively, where S_{BL} was the standard deviation of ten blank determinations and b the slope of the curve. The method' LODs were calculated from the equation $\text{LOD}_{\text{meth}} (\text{ng g}^{-1}) = \text{LOD}_{\text{instr}} (\text{ng mL}^{-1}) \times V_{\text{dilution}} (\text{mL}) \times m (\text{g})^{-1}$. According to Commission Regulation 333/2007/EC the $\text{LOD}_{\text{S}_{\text{meth}}}$ and $\text{LOQ}_{\text{S}_{\text{meth}}}$ for Cd and Pb should be less than one tenth and less than one fifth, respectively, of the maximum level in Regulation (EC) No 1881/2006.

Precision under repeatability and reproducibility conditions were also estimated from the calibration curves using samples with various concentration levels matrix spiked solutions. As method's precision performance criteria were used the HORRAT_r, meaning the observed relative standard deviation (%RSD_r) under repeatability conditions divided by the RSD_r value estimated from the Horwitz equation (Thompson, 2000) using the assumption $r = 0.66R$ and HORRAT_r values, meaning the observed RSD_r value under reproducibility divided by the RSD_r value calculated from the Horwitz equation. According to Commission Regulation 333/2007/EC the HORRAT_r and HORRAT_R values should be less than 2. Furthermore, the trueness of measurements was also assessed through recovery of additions of known amounts of the element to the unknown samples. Finally, two different certified reference materials (NIST 1573a and ERM-BC084a) were analyzed in order to check the accuracy of the method. Recovery data are only acceptable when they are within $\pm 20\%$ of the target value (European Commission, 2002, 2007).

Internal quality control charts (IQCs) were also constructed in order to decide whether results are reliable enough to be released. ICQ is the main criterion for an analyst to check continuously the accuracy of the analytical data obtained from day to day in the laboratory. In the IQCs measured values of twenty repeated analyses of the digested certified reference material NIST 1573a were plotted against the run number. Based on these continuous measurements a control chart was constructed by drawing horizontal lines on the chart: \bar{x} (mean value), $\bar{x} + s$ (mean value + standard deviation) and $\bar{x} + 2s$ (upper warning limit) and $\bar{x} - 2s$ (lower warning limit), $\bar{x} + 3s$ (upper action or control limit) and $\bar{x} - 3s$ (lower action or control limit). Afterwards, the certified reference material was re-digested when a new analysis was performed place and the calculated content of the trace elements was placed in the control chart as a new mark. The method was defined as an 'analytical system under control' if no more than 5% of the measured values exceed the warning limits and none of them the action or control limits (Taverniers et al., 2004).

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