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New Ultrasound-Assisted Extraction Sample Preparation Procedure for the Fast Determination of Total Sn in Canned Tomatoes by HG-ICP OES

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Abstract: An analytical method with no need for laborious sample preparation before determining the total Sn in canned tomatoes by hydride generation (HG) coupled to inductively coupled plasma optical emission spectrometry (ICP OES) was developed. The ultrasound-assisted extraction with various reagents (acidic media: HCl, HNO_3, CH_3COOH or *aqua regia* and alkaline: TMAH) that could replace the traditional wet sample digestion in the presence of a concentrated HNO_3-H_2O_2 mixture was tested and compared. Tin hydride was generated directly from the prepared sample solution in the reaction with 1% $NaBH_4$ or via prior acidification with a 1 mol L^{-1} HCl. The effect of the sample pretreatment before HG-ICP OES measurements on the Sn signal was also examined. The best results were obtained with *aqua regia* as the extraction medium, followed by a simple two-fold dilution of the sample extract combined with the addition of L-cysteine. The developed method was characterized by a detection limit of Sn at 0.74 ng g^{-1}, a precision of better than 6%, and a trueness, verified by the analyte spike-and-recovery test, of 98.4–104%. Its usefulness was demonstrated by the determination of Sn in seven canned tomatoes.

Keywords: tin; canned tomatoes; sample preparation; hydride generation; ICP OES

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1. Introduction

Canning is a simple and inexpensive technology for preserving the freshness of foodstuffs [1–5]. Canned products have a long shelf life and do not require storage at low temperatures or any special treatment during their transport or distribution [2,3]. This is a food product enclosed mainly in metal cans. Its long shelf life is ensured by the pasteurization process and the hermetic tightness of the packaging, protecting against air, light, filth, microorganisms, and contamination [3,6]. In addition, such processing helps preserve the nutritional value and sensory properties of food [2]. One of the most known metallic materials for the production of cans is Sn; hence, the food packaging made of tinplate (tin-coated steel) has a wide application in the food industry for producing food cans [7]. Noteworthy, the tinplate has played an important role in preserving food for over a hundred years, likely because it combines the strength and formability of steel on the one side and the corrosion resistance and good appearance of Sn on the other [2,8]. Unfortunately, using the tinplate for food packaging results in partially contaminated food products with Sn. Apparently, due to the corrosion of unlacquered cans, some Sn dissolves into the food content, especially when plain uncoated internal surfaces are used [1,7]. The oxidation of the tinplate followed by the release of the Sn ions into the food is known as the "sacrificial anode effect", i.e., a physicochemical mechanism that protects the underlying steel from its corrosion [1]. Therefore, the resin/polymer coating (lacquering) of the inside of the tinplate of the can is now a common way to protect food from metal contact and to prevent corrosion, especially the subsequent release of Sn from cans and the contamination

of the canned food [2,9,10]. In practice, the tinplate deterioration processes are complex and different parameters affect the internal corrosion rate, e.g., thermal treatment, tinplate variables (impurities and surface defects), the acidity of food, the contact time between the food and the packaging, the food water content, the presence of additives or oxidizing reagents, the presence of air (oxygen) in the headspace, and the storage conditions (time and temperature) [6,10–13]. Despite these considerations, it can be said that human exposure to Sn has a dietary origin, particularly from the consumption of canned food [14,15]. Although inorganic Sn compounds have rather a low systematic toxicity due to their poor absorption from the gastrointestinal tract, the consumption of canned food highly contaminated with the soluble Sn compounds may be manifested in various symptoms such as gastric irritation, nausea, vomiting, abdominal cramps, headaches, or fever [8,14,15]. Due to the moderate toxicity, a maximum permissible level of 200 mg kg^{-1} of Sn in canned food has been set by the European Union [16]. Consequently, determining Sn in such products became important because it gives information about the contamination process and helps improve canned food quality and safety [1,5,12].

The determination of Sn in canned food concerns mainly vegetables and their products [5,6,8,10–15,17–27], fruits [1,5,10,14,15,18,28,29], mushrooms [21,30], meat [3,4,14,15,18,26,30,31], and fish [2–4,10,14,18,20,23–27,30–34]. Tomatoes are among the most popular vegetables cultivated worldwide for fresh consumption [11]. It is a warm-season crop that is sensitive to frost; therefore, to ensure year-round availability for humans, after harvesting, most of the crop (80%) is industrially processed, into, e.g., canned whole tomatoes, pastes, ketchups, or sauces [6,11]. Notably, processed tomatoes are considered one of the most aggressive products due to their ability to initiate corrosion when packaged in metal containers [6], which could increase the content of Sn in the canned product [6].

To determine the concentration of Sn in canned foodstuffs, several analytical methods and techniques are used. These include spectrophotometry [24,35,36], fluorometry [37,38], electrochemometric techniques, such as stripping voltammetry [13,21,30], X-ray fluorescence [39], neutron activation analysis (NAA) [40], and atomic spectrometric techniques, namely flame (F-) [1,15,17,19] and electrothermal (ET-) [2,4,8,18,20,33] atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP OES) with the pneumatic nebulization (PN) [12,14,28,29,32,33], hydride generation (HG) [14,33,41] sample introduction, or inductively coupled plasma mass spectrometry (ICP-MS) [3,10,11,29,34]. It should be stated that the HG technique particularly allows for the increased sensitivity of the Sn measurements, the elimination of most of the matrix interferences, and the possibility of quantifying the traces of Sn [14,33,41]. Very recently, a new approach for determining metal ions was provided based on novel covalent organic frameworks (COFs) and fluorescence detection [31]. In the cited work [31], a kind of novel COFs, developed from 2,5-dimethoxy-1,4-dicarbaldehyde (DMTA) and tetra (4-aminophenyl) ethylene (ETTA) (COF-ETTA-DMTA), was designed and applied to detect traces of Sn(II) in canned food (luncheon pork, fish, red kidney beans). Similarly, Gouda and Amin [26] designed a unique optical sensor to determine Sn ions in environmental samples and foodstuffs, e.g., canned fish, tomatoes, and meat. In addition to determining the total Sn, speciation studies are of interest too. Accordingly, Fisera et al. [33] demonstrated methods for the separation of inorganic and organic Sn compounds using chromatographic techniques (ion exchange (EC) and high-performance liquid chromatography (HPLC)) with online spectrometric detection (ET-AAS and ICP OES). The proposed methods could be potentially used to analyze marine food samples, e.g., fish.

Atomic spectrometry methods require the total decomposition of the samples before their analysis, which is usually performed by the traditional wet digestion in the presence of concentrated reagents, mainly HNO_3 in different mixtures with H_2O_2 [1,2,6,10,12,14,18,19,22,28,29], H_2O [11], $HClO_4$ [4], or HCl [8,15,17,24,25]. Nitric acid alone is practiced as well [3,23,34,41]. Dry mineralization, though less common, is also used [4,26,30]. Because the determination of traces of Sn can still be challenging due to low analyte concentration, matrix effects, or insufficient sensitivities of detection methods, additional separation and preconcentration

techniques have attracted attention and are included in the sample preparation step. To date, several works have been reported, and a couple of separation/preconcentration extraction procedures are applicable for the determination of (ultra)traces of Sn in food samples. Accordingly, Amjadi et al. [17] developed an ultrasound-assisted (US) temperature-controlled ionic liquid (IL) microextraction (ME) combined with FAAS for determining Sn in various canned products, including canned peas and cheese. In another work [18], the procedure based on US-IL dispersive liquid-liquid (DLL) ME was proposed to determine Sn in several food samples (covering the canned ones like canned tuna, peas, and olive) by employing ETAAS was proposed. In the work of Ulusoy et al. [19], a cloud point extraction (CPE) procedure followed by the FAAS detection was applied for the simultaneous determination of Sn and Pb in canned foods such as juices, tomato paste, corn, and green peas. Similarly, Biata et al. [22] reported methodology based on US-CPE for preconcentration of Sb, Sn, and Tl in various natural samples, including canned beans and tomatoes, before their determination by ICP OES. The same extraction technique (US-CPE) was used by Altunay et al. [27] for the preconcentration of Sb and Sn as a prior step to their determinations with FAAS in beverages and selected (non)canned beverages and foods. In turn, Zounr et al. [25] develop a new solid-phase microextraction (SPμE) procedure for preconcentration and determination of Sn species in beverages and food samples (including canned products, i.e., peas, olives, corn, tuna fish) by ETAAS.

Although effective, traditional sample treatment is time-consuming and requires the use of hazardous reagents, special tools, and tedious procedures. Moreover, this long-lasting and laborious sample preparation method can lead to losses of Sn and other elements and/or the uncontrolled contamination of the pretreated samples. Therefore, alternative greener methodologies involving partial or no previous decompositions of the analyzed samples, which could avoid or minimize any inconveniences related to wet sample digestion, are of great interest.

The literature survey indicates no works dealing with the determination of Sn in canned tomatoes using simplified sample preparation procedures, completely omitting wet digestion. So far, a very simple approach for the simultaneous determination of Sn(II) and Pb(II) in canned food (mushrooms, bamboo shoots) combined with electrochemical detection was presented in the work of Pungjunun et al. [21]. In the mentioned work, the sample portion was mixed with a low-concentrated HNO_3 solution (2%) for 5 min, then adjusted to proper pH (7) with NaOH solution. After that, the sample solution aliquot was diluted 2-fold with 0.1 mol L^{-1} oxalic acid and 0.1 mmol L^{-1} hexadecyltrimethylammonium bromide (CTAB) before further analysis. Finally, extraction induced by emulsion breaking (EIEB) was recently proposed, which aimed to replace acid-wet digestion before determining Sn in edible oils samples by ETAAS and ICP-MS [42]. The emulsion was obtained by vortex agitation of the sample (15 s) with extracting mixture (2% Triton X-114 in diluted HNO_3 (3%)). Then, the emulsion was heated up (90 °C, 60 min) for breaking, i.e., oil-aqueous phase separation. Measurements were performed directly from the lower aqueous phase (acid medium) with the extracted tin.

Recently [41], we developed an accurate method for determining Sn in a low concentration range in fresh and canned tomatoes by HG-ICP OES after the wet digestion of the representative samples. Since we supposed that it is possible to find an alternative sample preparation procedure based on the ultrasound-assisted solvent extraction (UAE) that allows to eliminate the labor wet digestion sample preparation prior to the measurements, we decided to continue our investigations. Hence, the present work aimed at developing and validating the HG-ICP OES-based method appropriate for accurately determining total Sn in canned tomatoes that is free from possible interferences from the sample matrix on the Sn signal at the same time. The suitability of various effortless UAE procedures with various extractants was examined and compared to this end. Finally, the developed method was applied to analyze the seven canned tomatoes commercialized in the Polish market.

2. Experimental

2.1. Instruments

A Milestone (Sorisole, Italy) high-pressure microwave digestion system (MLS-1200 MEGA) equipped with a rotor (model MDR 300/10) and Teflon vessels was used for the wet digestion of the CT samples in a closed system. The UAE of the CT samples with *aqua regia*, TMAH, and dilute acid solutions was performed with a Polsonic (Warsaw, Poland) ultrasonic bath (model Sonic 14) with controlled time and temperature. The separation of the solid residues from the CT sample solutions left after the UAE in given conditions was performed by centrifugation in a laboratory centrifuge, model MPW-350 (Med. Instruments, Warsaw, Poland).

All spectrometric measurements of Sn were done by a Jobin Yvon (Longjumeau, France)—JY-38S sequential ICP OES. The optimized working parameters for the HG-ICP OES hyphenated system are summarized in Table 1. The background-corrected intensities of the emission line of the Sn line (Sn_{net}) were used in all investigations.

Table 1. HG-ICP OES operating parameters.

ICP OES Detection	
Generator (MHz)	40.68
RF power (W)	1000
Injector i.d. (mm)	2.5
Observation zone	Radial, 12 mm above the load coil
Ar flow rate (L min^{-1})	Plasma: 13.0 Auxiliary: 0.20 Carrier gas: 0.35
Integration time (s)	0.10
Measurement replicates	3
Delay time [a] (s)	30
Wavelength (nm)	Sn I 283.9
HG	
Solutions flow rate (mL min^{-1})	Sample: 1.0 Additional acid [b]: 1.0 $NaBH_4$: 1.0
Reagents concentrations [b]	
$NaBH_4$ (%)	1.0 (in 0.1 mol L^{-1} NaOH)
HCl [b] (mol L^{-1})	1.0
AA [c] and LC [c]:	2.0% and 0.5%

I: atomic line. AA: ascorbic acid. LC: L-cysteine. [a] Time necessary to achieve a steady Sn response after merging the sample and $NaBH_4$ solutions in the Y-shaped connector. [b] For the procedure using TMAH as an extracting reagent (P6). [c] Final concentrations in analyzed sample solutions.

2.2. Reagents

All chemicals were of at least analytical grade. A commercial 1000 mg L^{-1} ICP standard stock solution of Sn(IV) from Merck (Merck, Darmstadt, Germany) was used. Working standard solutions for the calibration and the test studies were prepared daily by stepwise dilutions of the stock standard and acidified to a concentration of 0.1 mol L^{-1} HCl. For the wet digestion of samples, carried out only for comparative purposes, 65% (m/v) HNO_3 (Merck) and 30% (m/v) H_2O_2 (Avantor Performance Reagents, Gliwice, Poland) were used. In the case of the UAE of the samples, a 25% (m/v) aqueous solution of tetramethylammonium hydroxide (TMAH) (Sigma-Aldrich, St. Louis, MO, USA) and a concentrated *aqua regia* solution, as well as diluted solutions (1 mol L^{-1}) of HNO_3, HCl, and CH_3COOH, were applied. *aqua regia* was prepared just before use by mixing 37% (m/v) HCl (Merck) and 65% (m/v) HNO_3 solutions in a volume ratio of 3:1 (v/v). 1 mol L^{-1} (v/v) HNO_3, HCl, and CH_3COOH solutions were prepared by diluting their concentrated solutions (Merck). Tin hydride was generated in the reaction with a 1.0% (m/v) $NaBH_4$ solution and stabilized with 0.1 mol L^{-1} NaOH. The reducing agent solution was freshly prepared

by dissolving its appropriate amount (Sigma-Aldrich) in a 0.1 mol L^{-1} solution of NaOH (Avantor Performance Reagents) and filtering before use through a hard filter paper (type: 3H, Ahlstrom & Munktell, Germany). To enhance the HG reaction of Sn(IV), L-cysteine (LC) (Sigma) and L(+)-ascorbic acid (AA) were used. The 5.0% (*m*/*v*) solutions of both reagents were prepared by dissolving them in water. Deionized water (18.3 MΩ cm^{-1}) from an EASYpure RF purification system (Barnstead™, USA, model D7033) was used throughout.

2.3. Samples

Seven (n = 7) samples of canned peeled tomatoes (abbreviated "CT") of different brands were analyzed and coded from CT1 to CT7. Importantly, they differed in the type of can. Accordingly, 5 lacquered (CT1–CT5) and 2 unlacquered (CT6, CT7) cans were examined. After opening the cans, the tomatoes were separated from the brine, drained of the juice, and ground to a pulp using a mortar and pestle. The homogenized pulp was placed in polyethylene containers and refrigerated until the analysis.

2.4. Experimental Procedures

The applicability of six different sample preparation procedures (P1–P6) of the CT samples prior to their analysis by HG-ICP OES on the total content of Sn was tested. These were: (i) digestive, i.e., the closed-vessel microwave-assisted wet digestion (MAD) with a mixture of concentrated HNO_3-H_2O_2 (P1), and (ii) non-digestive, i.e., based on the UAE (P2–P6) with *aqua regia* (P2), diluted (1 mol L^{-1}) solutions of HCl (P3), HNO_3 (P4), and CH_3COOH (P5) as well as 25% TMAH (P6). The MAD procedure (P1), enabling us to fully decompose the CT samples matrix followed by the HG-ICP OES measurements, was used as the reference.

P1: MAD (reference procedure): 2.0 g portions of the CT samples were decomposed with a mixture of concentrated HNO_3 and H_2O_2 reagents (6.0 and 1.0 mL, respectively), employing a 9-step microwave-assisted heating program with a maximum power of 600 W for 45 min. The resulting sample digests were quantitatively transferred into 30-mL polypropylene screw-capped containers (Equimed, Poland), made up with water to 25.0 g, and stored in a refrigerator until measurements (4 °C).

P2: UAE with aqua regia: 2.0 g portions of the CT samples were weighed into polypropylene centrifuge tubes with screw caps and poured with 2.0 mL of freshly prepared *aqua regia*. The tubes were then capped and immersed in an ultrasonic bath for the ultrasonication treatment for 15 min at room temperature. The resulting sample suspensions were then made up to 25.0 g with water and centrifuged (12,000 rpm/10 min). The obtained CT sample extracts were filtered into containers and refrigerated until measurements (4 °C).

P3–P5: UAE with low concentrated (1 mol L^{-1}) acids: 2.0 g portions of the CT samples were weighed into polypropylene centrifuge tubes and treated with 25.0 g of 1 mol L^{-1} HCl (P3), HNO_3 (P4) or CH_3COOH (P5) solutions. The tubes were wrapped with parafilm and then immersed into an ultrasonic bath for ultrasonication treatment for 30 min at 60 °C. After cooling, the contents of the tubes were centrifuged (12,000 rpm/10 min). Finally, the resulting CT sample extracts were filtered into containers and refrigerated (4 °C).

P6: UAE with TMAH: 2.0 g portions of the CT samples were weighed into polypropylene centrifuge tubes, and 2.0 mL of a 25% TMAH solution was poured in. The tubes were wrapped with parafilm and then immersed into an ultrasonic bath for the ultrasonication treatment for 30 min at 60 °C. They were allowed to cool down, and the resulting CT sample suspensions were brought up with deionized water to 25.0 g. Next, the contents of the tubes were centrifuged (12,000 rpm/10 min), and the resulting CT sample extracts were filtered into containers. They were kept in a refrigerator (4 °C) before measurements.

Each time, three parallel samples (n = 3) were prepared for analysis. Importantly, all sample solutions were prepared by weight (to avoid differences in density). Canned tomatoes CT1 was selected and used for all optimization studies. With each set of the mineralized and extracted samples, appropriate blanks were also prepared and included in the final results. They were also used as diluents of the matrix-matched standard

solutions to match the effects of the reagents on the HG reaction of Sn. This is because the final acidity is a key parameter affecting the response of Sn during the HG process. The concentration of HNO_3 (P1), *aqua regia* (P2), and TMAH (P6) in resulting procedural blank solutions was ~3.4 mol L^{-1}, 1.0 mol L^{-1}, and 2.0%, respectively. Except for CT6 and CT7, the concentration of Sn was determined in undiluted sample solutions. In the case of these two samples, due to a high Sn content, the prepared sample solutions had to be diluted five times to match the concentration range used for the calibration of HG-ICP OES. To keep the acidity of these sample solutions unchanged, they were diluted using the respective procedural blanks as a diluent.

2.5. Sample Pretreatment before HG

Before measurements by HG-ICP OES, the CT samples solutions were pretreated, which included their 2-fold dilution with the simultaneous addition of the AA and LC solutions (the case of P1 and P2) or the LC solution alone (the case of P3–P6). The final concentrations of these reagents in the resulting sample solutions were 2.0% (AA) and 0.5% (LC). In the case of procedures P1 and P2, adequate aliquots of prepared samples solutions (2.0 g) were transferred to 12-mL screw-capped polypropylene tubes into which the appropriate aliquots of the concentrated solutions of AA (1.6 g) (firstly) and LC (0.4 g) (secondly) were added. Then, the tubes were capped, mixed, and left to react at room temperature for at least 30 min before measurements. For the remaining procedures (P3–P6), adequate aliquots of the prepared samples solutions (2.0 g) were transferred to 12-mL screw-capped polypropylene tubes into which the appropriate aliquot of the concentrated LC solution (0.6 g) was added, followed by the addition of a proper aliquot of water (1.4 g). Importantly, the respective blanks and the Sn matrix-matched standard solutions for each sample preparation procedure were pretreated analogously to the sample solutions.

2.6. Tin HG

A continuous flow system with a gas-liquid phase separation directly hyphenated with the ICP OES spectrometer was applied for the tin hydride generation [43]. The HG system contained a modified cyclonic spray chamber, a parallel nebulizer (Burgener type), two Y-shaped polypropylene connectors, delivery PVC pump tubings, the PTFE capillary tubings, and two peristaltic pumps. In this system, all solutions (sample, HCl, and $NaBH_4$) were simultaneously pumped in the separate streams by one peristaltic pump. Two combinations were tested for comparison, i.e., with three (1) and two (2) streams of the reagents. In the (1) case, the sample/standard solution was mixed in the first Y-connector with the HCl solution, after which the acidified sample/standard solution was mixed with the $NaBH_4$ solution in the second Y-connector. The resulting reaction mixture was introduced through the reaction coil to the spray chamber (acted as a phase separator). Tin hydride was transported directly to the ICP torch in an Ar carrier stream which was introduced through the gas inlet of the nebulizer. The post-reaction waste solution was drained from the chamber with the aid of the second peristaltic pump. Considering the (2) combination, a stream of the HCl solution was excluded; hence only one Y-connector was used. In this case, the sample/standard and $NaBH_4$ solutions were mixed in the Y-connector, followed by introducing the resulting reaction mixture (through the reaction coil) into the chamber.

In general, Sn hydride was generated directly from the prepared sample solutions by merging them with the $NaBH_4$ solution in one single Y-connector, i.e., using the 2nd combination. Only in procedure P6 (the UAE with TMAH) was the 1-st combination used. Accordingly, Sn hydride was generated by the prior acidification, i.e., mixing the sample solution with a 1 mol L^{-1} HCl solution and then with the $NaBH_4$ solution.

2.7. Spike-and-Recovery Experiments

Since we did not have access to the appropriate certified reference material (CRM), the validity of the results obtained for the reference procedure was verified by a recovery test.

The standard addition method was used for this aim. Accordingly, the samples of CT1 were spiked with proper amounts of a Sn(IV) standard to achieve the concentration of 20 and 40 ng g^{-1} in the measured samples solutions, then subjected to the MAD procedure (P1) and the pretreatment procedure before the HG reaction, and finally analyzed for recoveries using the HG-ICP OES method.

3. Results and Discussion

3.1. Effect of the Extraction Reagent on the Sn HG Activity

As shown previously [41], when using strong inorganic acids, Sn hydride is generated only in a narrow, low acidity range, giving a sharp maximum at the so-called critical value (CV) point. At this point, the amount of $NaBH_4$ and NaOH is stoichiometrically equal to the amount of acid introduced into the system, and the maximum analyte signal is expected to be achieved [44]. The latter phenomenon was also checked in the present work, and the acidity curve for HCl (0.05–2.0 mol L^{-1}) actually showed the highest Sn response at ~0.28 mol L^{-1} HCl. Past this point, the Sn signal began to decrease, reaching a negligible level at an HCl concentration of 2.0 mol L^{-1}. These results showed that the reaction media and their concentration indeed play a crucial role in the HG of Sn. Since the concentration of the reagents in the resulting samples solutions is usually ≥1 mol L^{-1}, which is far from the optimal range for the HG of Sn, the effect of the sample preparation procedures tested in the present work (P1–P6) on the response of Sn during the HG process was verified in details. The appropriate Sn (50 ng g^{-1}) matrix-matched standard solutions were used for that, which were prepared using the respective procedural blanks obtained for these sample preparation procedures (P1–P6). The HG reaction was carried out by directly mixing these matrix-matched standards solutions with the $NaBH_4$ solution. The results (see Figure 1) were expressed as the signals (in a.u.), being the mean blank-corrected (netto) intensities of the Sn analytical line for three independently repeated measurements along with the respective SDs. The response for the simple aqueous Sn(IV) standard, recorded at the CV point, was taken as a reference and included in this figure.

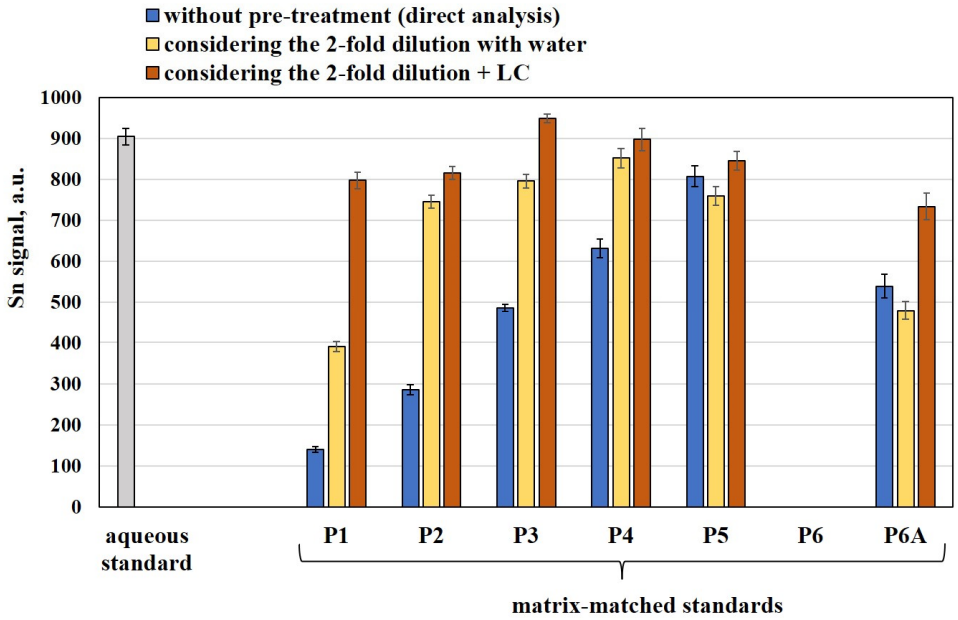

Figure 1. The effects of the reagents used in the compared sample preparation procedures and the sample pretreatments before HG on the measured response of Sn in HG-ICP OES acquired for the matrix-matched standard solutions (procedural blanks were used). P1: MAD in concentrated HNO_3-H_2O_2. P2: UAE with *aqua regia*. P3: UAE with 1 mol L^{-1} HCl. P4: UAE with 1 mol L^{-1} HNO_3. P5: UAE with 1 mol L^{-1} CH_3COOH. P6 and P6A: UAE with 25% TMAH without (P6) and with (P6A) an additional stream of 1 mol L^{-1} HCl for the HG. Standards: Sn(IV) at 50 ng g^{-1}. LC: L-cysteine.

It was observed that the composition of the sample solution indeed affected the formation of Sn hydride. In the case of the HG directly carried out from the matrix-matched standard solutions, the Sn signals differed, which can be described as follows: P5 > P4 > P3 > P6A > P3 > P2 > P1 >> P6. The highest response was obtained in the presence of 1 mol L^{-1} CH_3COOH (P5). Moreover, the latter signal was only slightly lower (~10%) than the reference signal. A reduction in Sn signal (~30%) was obtained for 1 mol L^{-1} HNO_3 (P4). In the presence of 1 mol L^{-1} HCl (P3), the suppression of the Sn signal was greater (~50%). A significant lowering of the Sn signals was observed in the case of *aqua regia* (~1 mol L^{-1}) (P2) and when the MAD procedure was applied (HNO_3/H_2O_2, ~3.4 mol L^{-1}) (P1), i.e., by 3- and 6.5-fold, respectively, as compared to the reference signal. It must be commented that in the case of procedure P6, the generation of Sn hydride directly from the 2% TMAH solution resulted in the blank-level signal of Sn. This meant no activity of Sn(IV) in the reaction with $NaBH_4$ under these conditions, probably due to the too-high alkalinity of the standard solution. The problem was solved by introducing an additional stream of 1 mol L^{-1} HCl before mixing the standard/sample solution with the reducing agent (P6A). Satisfactorily, this allowed us to obtain an Sn signal close to the one obtained for 1 mol L^{-1} HCl (P3).

3.2. Effect of L-Cysteine

To improve the derivatization process for the individual sample preparation procedures (P1–P6) tested here, the Sn (50 ng g^{-1}) matrix-matched standard solutions were additionally pre-pretreated before the measurements by HG-ICP OES. It was related to their 2-fold dilution (to lower the acid concentration) using the AA and/or LC solutions. The role of AA was to neutralize the residual acid after the MAD procedure (P1) [45]. The addition of LC directly to the standard/sample solution was intentional as it allowed the HG of Sn to shift to elevated acidities (up to 0.5 mol L^{-1} HCl or 1.0 mol L^{-1} HNO_3) and enhanced its signal by nearly 50% compared to that obtained under optimal acid conditions, i.e., recorded at CV point, in the absence of LC [44]. A simple 1:1 dilution of the matrix-matched standard solutions with water only was also analyzed for comparison. The responses for the undiluted Sn (50 ng g^{-1}) matrix-matched standard solutions were taken as a reference. The obtained results are graphically presented in Figure 1 (see Section 3.1).

In the case of the MAD procedure (P1), the simple 1:1 dilution with water allowed for an almost 2.8-fold increase of the Sn signal. The same dilution but with added AA (to final concentrations between 0.5–2%) led to a further increase of the Sn response by about 20–30%. As 2.0% AA gave the best results, it was selected as optimal. In the presence of 0.5% LC and 2% AA, the increase of the Sn signal was even more significant. Accordingly, the ~5.7 times higher Sn signal was reached as compared to this acquired when the standard solution was directly analyzed.

A similar behavior to that described above was observed in the case of the standard solution containing *aqua regia* (~1 mol L^{-1}, P2). The 1:1 dilution with water allowed for a ~2.6-fold increase of the Sn signal, which was further enhanced in the presence of 0.5% LC and 2% AA (~3-fold increase) when comparing it to the one obtained for the undiluted solution. The influence of AA and its mixture with LC on the Sn signal was also verified. It was additionally found that AA alone, independent of its concentration (0.5–2%), did not affect the measured Sn signal. However, it was noticed that in its presence (especially at the highest concentration, i.e., 2%), the course of the HG reaction in the chamber was less violent and turbulent. Therefore, for this procedure (P2), both the AA and LC solutions were added to the standard/sample solution before the measurements by HG-ICP OES.

In the case of 1 mol L^{-1} HCl (P3) and 1.0 mol L^{-1} HNO_3 (P4), the 1:1 dilution of standards prepared in these acids with water allowed to obtain the Sn responses by about 35–63% higher compared to the undiluted standards. Moreover, these Sn responses were close to the Sn signal recorded for the undiluted standard prepared in 1.0 mol L^{-1} CH_3COOH (P5), which was the highest. This confirms that the best conditions for producing Sn hydride in the media of inorganic acids occur at their lower concentrations [41]. On

the other hand, in the medium of the organic acid, the HG process for Sn was less dependent on the acid concentration since the 1:1 dilution of the standard solution prepared in 1 mol L^{-1} CH_3COOH with water practically did not change the Sn signal (difference within 5%). Accordingly, tin hydride could be effectively generated in both 0.5 and 1.0 mol L^{-1} CH_3COOH. The presence of 0.5% LC slightly increased the Sn signal for 1 mol L^{-1} HNO_3 (P4) and 1 mol L^{-1} CH_3COOH (P5), i.e., by less than 11% compared to these standards without the addition of LC, and only 1:1 diluted. A visible increase of the Sn signal was noted for 1 mol L^{-1} HCl (P3), i.e., by about 20%. As a result, the 2-fold dilution of the standard solution prepared in this acid with the simultaneous addition of the LC solution was responsible for up to a ~2-fold increase of the Sn signal compared to the undiluted standard solution. In addition, among the standard solutions prepared in 1 mol L^{-1} acids and pretreated with LC before HG, for HCl (P3), the highest Sn signal was obtained.

For the standard solution containing 2% TMAH (P6), the 2-fold dilution of this solution with water slightly lowered the Sn signal (the 11% decrease). On the other hand, the 1:1 dilution and the presence of 0.5% LC allowed for an almost 36% increase in the Sn response, comparing it with this obtained for the undiluted standard solution. Such a positive effect could be involved with the buffering capacity of LC and the formation of Sn-LC complexes, which appears to be useful for the stabilization of tin solution at a given acidity value [46].

Satisfactorily, it was observed that the proposed sample pretreatment before the HG (the 1:1 dilution using AA and/or LC solutions) resulted, independently of the procedure applied, in quite similar Sn signals and greater than those obtained in the absence of LC. Furthermore, except for the extraction with TMAH (P6), the Sn responses were close to this for the aqueous Sn standard attained at CV point (see Figure 1 in Section 3.1 Effect of the extraction reagent on the Sn HG activity); differences within 1–13% were noted. In the case of the TMAH (P6) extraction, the Sn signal was about 25% lower compared to that observed at the CV point.

3.3. Analytical Performance of the HG-ICP OES Method in Combination with Various Sample Preparation Procedures

Next, considering the proposed sample pretreatment before HG, the analytical performance of the HG-ICP OES method combined with different sample preparation procedures for determining Sn was assessed using the matrix-matched standard solutions. The following validation parameters were considered: (i) the slope of the calibration curve (a), (ii) the linear dynamic range (LDR), (iii) the determination coefficient (R^2), (iv) the limit of detection (LOD) of Sn, and (v) the precision of the replicate (n = 3) measurements of the Sn signal at 20 ng g^{-1} (expressed by the relative standard deviation, %RSD). Five-point calibration curves spanning the 0–0.100 ng g^{-1} concentration range of Sn were recorded. Respective LODs were calculated based on the 3σ criterium, considering the calibration slopes and measuring the SDs of the procedural blanks (σ). The obtained results are collected in Table 2.

As can be seen, the calibration curves for Sn were, independently of the sample preparation procedure applied (P1–P6), linear in the whole concentration range, showing high correlation coefficients (R^2 > 0.999). Similarly, a precision of better than 5% was obtained. The respective RSDs were very good and varied from 1.4% (P3) to 5.0% (P6). In the case of procedures P1, P2, and P3, the RSDs did not even exceed 3%. The comparison of the sensitivities, referred to the slopes of the calibration curves, showed that their values, except those obtained for procedures P1 and P6, were similar; the differences between them were within 9%. For these two procedures, the sensitivity was slightly lower, i.e., by about 13–16%. Satisfactorily, these results were consistent with the previous outcomes (see Figure 1 in Section 3.1) and proved that the procedural reagents present in variously prepared standard solutions did not affect the HG of Sn under the experimental conditions selected. In contrast, the LOD values of Sn differed and changed in the range between 0.74–3.2 ng g^{-1}, depending on the sample preparation procedure used. These differences

were mainly caused by the values of the reagent blank and the SD of the background in these conditions. The best LOD of Sn was achieved when *aqua regia* was used (P2). This LOD was about 2 times better than those assessed when HNO_3/H_2O_2 (P1), HCl (P3), or HNO_3 (P4) were employed and even 4 times better as compared to the ones achievable when using CH_3COOH (P5) or TMAH (P6).

Table 2. Analytical figures of merit for the Sn determined by HG-ICP OES under the optimized sample pretreatment and HG reaction conditions using matrix-matched standard solutions.

Procedure	a [a], a. u./(ng g^{-1})	Range [b], ng g^{-1}	R^2 [c], -	LOD [d], ng g^{-1}	RSD [e], %
P1	17.3	0–100	0.9991	1.2	2.9
P2	18.3	0–100	0.9992	0.74	2.1
P3	19.6	0–100	0.9999	1.6	1.4
P4	19.0	0–100	0.9972	1.9	3.3
P5	18.3	0–100	0.9995	2.9	3.7
P6	16.9	0–100	0.9999	3.2	5.0

P1: MAD in concentrated HNO_3-H_2O_2. P2: UAE with *aqua regia*. P3: UAE with 1 mol L^{-1} HCl. P4: UAE with 1 mol L^{-1} HNO_3. P5: UAE with 1 mol L^{-1} CH_3COOH. P6: UAE with 25% TMAH. [a] Slope of the calibration curve for Sn(IV). [b] The concentration range for Sn(IV). [c] The determination coefficient. [d] The limit of detection in measured sample solutions. [e] For a standard solution containing 20 ng g^{-1} of Sn(IV).

Finally, it was concluded that all tested sample preparation procedures were suitable for determining trace amounts of Sn by the HG-ICP OES method. Nevertheless, considering the examined figures of merit, the UAE with *aqua regia* (P2) appeared to be the most advantageous.

3.4. Determination of Sn in Canned Tomatoes by HG-ICP OES Combined with Different Sample Preparation Procedures

Afterward, the suitability of tested sample preparation procedures (P1–P6) along with the proposed sample pretreatment before the HG for the dependable Sn determination in the CT samples by HG-ICP OES was evaluated, considering the comparison of the results obtained for the CT1 material. The results obtained using the simplified UAE sample preparation procedures with different reagents (P2–P6) with the HG-ICP OES measurements were compared with those obtained using the reference method, which combined the MAD sample preparation (P1) with the HG-ICP OES measurements. At first, the trueness of the results of the Sn determination by the reference method was verified by the spike-and-recovery experiments (see details in Section 2.7). As a result, added amounts of Sn(IV) were quantitatively recovered, i.e., at the level of 98.0 ± 6.4% (for 20 ng g^{-1}) and 99.7 ± 6.3% (for 40 ng g^{-1}). This proved the lack of any Sn losses and confirmed that the selected reference method, comprising the MAD sample preparation (P1) with the HG-ICP OES detection, enabled accurate results.

The results obtained for CT1 when using HG-ICP OES in combination with the examined sample preparation procedures (P1–P6) are collected in Table 3.

Table 3. Total Sn (in mg kg^{-1} of wet weight) determined in CT1 through HG-ICP OES using different sample preparation procedures (P1–P6) [a].

Procedure	P1	P2	P3	P4	P5	P6
Content	1.48 ± 0.12	1.55 ± 0.09	0.283 ± 0.006	<1.9 [b]	<2.9 [b]	0.982 ± 0.040

P1: MAD in concentrated HNO_3-H_2O_2. P2: UAE with *aqua regia*. P3: UAE with 1 mol L^{-1} HCl. P4: UAE with 1 mol L^{-1} HNO_3. P5: UAE with 1 mol L^{-1} CH_3COOH. P6: UAE with 25% TMAH. [a] Mean values (n = 3) ± SDs. [b] Below the LOD (ng g^{-1}) value (in the analyzed sample solution).

The results achieved after applying the reference (P1) and simplified (P2–P6) sample preparation procedures differed and depended on the procedure used. The closeness of the average Sn concentration determined using the alternative methods to the average

Sn concentration determined with the reference method could be arranged as follows: P1~P2 > P6 > P3 >> P4~P5. These results did not agree with those regarding the previous reactivity of Sn for the HG carried out under selected experimental conditions, i.e., when simple matrix-matched standard solutions were used (see Figure 1 in Section 3.1). Referring to the analysis of the real sample matrix, the methods with the sample preparation by the UAE with 1 mol L^{-1} HNO_3 (P4) and 1 mol L^{-1} CH_3COOH (P5) failed. For these two procedures, the Sn content could not be measured in the prepared sample solutions (<LODs). Unfortunately, the results obtained by the UAE with 25% TMAH (P6) or 1 mol L^{-1} HCl (P3) were either useless; the determined Sn concentration was lower from 50% (P6) to over 5 times (P3) than the Sn concentration quantified using the reference method. Moreover, it should be commented that in the case of the Sn determination in the sample extracts prepared by using UAE with 25% TMAH (P6), the $NaBH_4$ solution had to contain Antifoam A to avoid extensive foam formation during the HG reaction. This effect was not observed in the case of other UAE procedures (P2–P5). As can be seen, only the UAE with *aqua regia* (P2) guaranteed the result, which was closely similar to this obtained for the MAD (P1). The procedure P2 also guaranteed better precision (5.8%) than this obtained when the procedure P1 was used (8.1%). To determine the statistical significance of the difference between the Sn concentrations obtained by the compared methods, i.e., HG-ICP OES with procedure P1 (the reference method) and with procedure P2 (the alternative method), the proper statistical tests were used.

Firstly, the difference between the SDs of the average Sn concentrations was tested using the one-tailed Snedecor-Fisher *F*-test [47]. The calculated value of the *F*-test was 1.78 and was lower than its $F_{critical}$ (19.00, $\alpha = 0.05$). This showed that the precision of the Sn determination by HG-ICP OES with the procedure P2 (the UAE with *aqua regia*) was the same as this assessed for the reference method with the MAD (P1). For that reason, the two-sample Student *t*-test was used to compare the average Sn concentrations obtained with the compared methods [47]. The difference between the average concentrations of Sn determined with the reference method (with the MAD, P1) and the alternative method (with UAE with *aqua regia*, P2) were statistically insignificant as well, i.e., $t_{calculated}$ value (0.808) was lower than the $t_{critical}$ (2.776, $\alpha = 0.05$).

Finally, the validity of the alternative method with the sample preparation by the UAE with *aqua regia* (P2) was also checked using the recovery test. Accordingly, the samples of CT1 were enriched before extraction with known amounts of Sn(IV) standard to increase content by 20 (i) and 40 (ii) ng g^{-1} (in the prepared samples solutions) and then subjected to the whole analysis. The recoveries obtained were quantitative, i.e., 98.8 ± 7.4% and 104 ± 7% for the abovementioned (i) and (ii) analyte additions, respectively.

The developed methodology was also compared with novel methods proposed by others for the determination of Sn in foodstuffs (with special attention to canned food samples) combined with various sample preparation procedures before measurements. The results of the analytical performances of these methods, along with the sample preparation procedures, are detailed in Table 4.

As can be seen, the proposed methodologies by others mainly involve traditional sample preparation (based on wet digestion) followed by a preconcentration/separation step before detection (realized by different extraction techniques). Undoubtedly, this allows for a high enrichment of the analyte, which results in a significant decrease in the LOD value. It is worth noting that the method developed in this work allows for the direct extraction of the analyte from the sample matrix. Moreover, despite the lack of further preconcentration steps, it offers relatively good detectability, being applicable for determining (trace) amounts of Sn in food samples. In some cases, it was even lower than those obtained when the preconcentration step was included. In addition, comparing the RSD values, the developed method was characterized by lower or comparable precision than the published one. Finally, because it completely omits the traditional wet digestion of the sample, it significantly reduces analysis time.

Table 4. Comparison of the proposed method with other methodologies for determining Sn in foodstuffs.

Sample	Sample Preparation	Detection	Range [a] µg L^{-1}	R^2 [b], -	LOD [c] µg L^{-1}	PF/EF [d]	RSD, [e] %	Ref.
canned products								
pea and cheese	digestion + US-IL-ME	FAAS	0.14–6.0 mg L^{-1} 10–400 mg L^{-1} [f]	0.997 0.995 [f]	42 µg L^{-1} 2.7 mg L^{-1} [f]	60 (PF) 52.7 (EF)	1.6 0.5 [f]	[17]
tuna, peas, and olive	digestion + US-IL-DLLME	ETAAS		0.999	0.0034	200 (EF)	4.5	[18]
tomato paste, peas, and corn	digestion + CPE	FAAS	10–5.000	0.9895	2.86	25 (PF)	<3.0	[19]
tomatoes	digestion + UA-CPE	ICP OES	0.023–700	0.9976	0.007	144 (PF) 73.6 (EF)	1.3–3.8	[22]
tomato paste, tuna	digestion + UA-CPE	FAAS	0.1–225	0.987–0.995	0.03	111 (EF) 50 (PF)	2.6–5.4	[29]
peas, olives, corn, tuna fish	digestion + SPµE	ETAAS			0.0045	100 (EF) 100 (PF)	3.3	[26]
mushrooms and bamboo	2% HNO_3; pH adjustment; the 2-fold dilution with oxalic acid and CTAB	SWASV	10–250		0.26		<4.7	[21]
tomatoes	UAE with *aqua regia*	HG-ICP OES	2.4–100 µg kg^{-1}	0.992	0.74 µg kg^{-1}		2.1	this work
other products								
edible oils	EIEB (3% HNO_3 + 2% Triton X-114; 90 °C, 60 min)	ETAAS ICP-MS	10–100 0.1–10	0.9985	1.1 0.009		3.7	[42]
beverages	digestion + UA-IL-DLLME	ICP OES	0.0083–250	0.9991	0.0025	250 (PF)	2.1–3.9	[48]

CPE: cloud point extraction. CTAB: hexadecyltrimethylammonium bromide. EIEB: extraction induced by emulsion breaking. SPµE: solid-phase microextraction. SWASV: square wave anodic stripping voltammetry. UAE: ultrasound-assisted extraction. UA-CPE: ultrasound-assisted cloud point extraction. US-IL-DLLME: ultrasound-assisted ionic liquid dispersive liquid-liquid microextraction. [a] The concentration range for Sn. [b] The determination coefficient. [c] The limit of detection in measured solution. [d] PF: preconcentration factor, i.e., the ratio between the sample volume and the volume of the final solution after preconcentration. EF: the ratio between slopes of the calibration curves with and without preconcentration. [e] The relative standard deviation. [f] Without preconcentration procedure.

Taking into account all the results, among five tested alternative sample preparation procedures, the UAE with *aqua regia* (P2) (i) appeared to be most advantageous before the Sn determination in canned tomatoes by HG-ICP OES and (ii) could replace the traditional MAD (P1) at the preparation step of such samples of canned tomatoes before the analysis. Consequently, the UAE with *aqua regia* was used next to prepare the remaining CTs and analyze them for the total Sn content by HG-ICP OES against the external calibration with the matrix-matched standards.

3.5. Analytical Application

The results (means (n = 3) along with SDs expressed in mg kg^{-1} of wet weight) of the total Sn content determined in the examined CTs by the proposed method are summarized in Table 5.

Table 5. The concentration of Sn (in mg kg^{-1} of wet weight) in canned tomato samples.

Sample Code	CT1	CT2	CT3	CT4	CT5	CT6	CT7
Can type	L [a]	L [a]	L [a]	L [a]	L [a]	UL [b]	UL [b]
Content	1.55 ± 0.09	0.773 ± 0.019	0.559 ± 0.015	1.74 ± 0.03	1.00 ± 0.02	12.7 [c] ± 0.7	14.7 [c] ± 0.5

[a] Lacquered can. [b] Unlacquered can. [c] Measurements after the additional 5-fold dilution of the sample extract before the pretreatment with LC.

The precision of the measurements was better than 6% (1.7–5.8%). The concentration of Sn in CTs ranged from 0.559 (CT3) to 14.7 (CT7) mg $kg^{-1,}$ and the results obtained in our work are consistent with those presented in the literature related to the Sn content in canned tomatoes (n.d.–122 mg kg^{-1}) [5,6,10,14,15,20,22,24,26,41]. As can be seen, the Sn content varied due to the presence of the internal coating of the can, being the highest in

tomatoes packed in unlacquered cans (CT6, CT7). Accordingly, it was ~11-fold higher than the average Sn content determined in the samples of tomatoes packed in lacquered cans (CT1–CT5). The same effect was observed by Divis and co-workers [29] in the case of fruits packaged in cans with and without a protective layer of lacquer. This confirmed that Sn can be leached from the material of the can and, consequently, can increase its concentration in the tomatoes even by about an order of magnitude [5,41]. Despite the higher content, it was below the maximum permissible level of Sn in food established by the Commission Regulation EC No. 1881/2006, i.e., 200 mg kg^{-1} [16].

4. Conclusions

Determining Sn in real samples using the HG technique combined with spectrometric detectors is not an easy task, due to the strong dependence of the Sn hydride formation on the reducing conditions (mainly the acid concentration). In this sense, the sample preparation procedure, referring to the reagents used and their final concentrations in the prepared sample solutions, may be critical for the analytical performance of such Sn determinations by HG-ICP OES.

Nevertheless, the effect of the high acidity of the prepared sample solutions was overcome in the present work by their dilution combined with the addition of LC, which enhanced the analyte signal in these conditions. As such, it was possible to replace the traditional MAD of samples before their analysis by HG-ICP OES with the easier (at room temperature) and faster (for 15 min) UAE of these samples with *aqua regia*, being adequate for the determination of Sn in CTs. Unfortunately, low-concentrated HNO_3, HCl, and CH_3COOH, as well as an alkaline TMAH solution, although suitable media for $NaBH_4$ decomposition, were unable to extract Sn from CT material.

The developed alternative method guaranteed the precise (RSD < 6%), true (98.8–104% as recoveries), and sensitive (LOD at 0.74 ng g^{-1}) determination of Sn in CTs. The determined Sn content in CTs was within 0.559–14.7 mg kg^{-1}. As expected, tomatoes stored in unlacquered cans were characterized by the highest concentration of Sn. Considering the highest permissible level of Sn in food (200 mg kg^{-1}), it was concluded that the analyzed canned tomatoes are safe and can be consumed without fear of causing health problems.

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