



Determination of Some Element's Migrants in Aqueous Simulant from Plastic Food Contact Products by Inductively Coupled Plasma Mass Spectrometer

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Abstract

Various chemicals present at different stages in the food supply chain can lead to the leaching of heavy metals. These metals can accumulate in the human body through the consumption of contaminated food. Consequently, it is necessary to validate an analytical technique for the quantification chemical that could contaminate food. This study presents a rapid, straightforward, and efficient analytical method for the direct quantification of some potentially toxic elements in aqueous simulants from plastic food contact products using an inductively coupled mass spectrometer (ICP-MS). The method's validation encompassed the study of the estimated detection limits, practical quantification limits, linearity, accuracy, and measurement uncertainty of aluminium (Al), antimony (Sb), arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), nickel (Ni), and zinc (Zn) under optimized ICP-MS conditions. The estimated detection limits ranged from 7.5×10^{-4} to 0.074 mg/kg, while practical quantification limits spanned from 0.02 to 0.8 mg/kg. The average recoveries \pm standard deviations at different spiking levels were varied between 85.7 ± 1.51 and $115.6 \pm 0.88\%$ with coefficients of variation between 0.42 and 5.85%. The method trueness was verified by using references materials (test material in aqueous acetic acid) purchased from Food Chemistry Proficiency Testing and Analysis (FAPAS) yielding satisfactory results within acceptable recovery and Z-score values. The method precision, in terms of relative standard deviation (RSD), was being below 4.22%. The method uncertainty expressed as expanded uncertainty of all validated elements was found to be $\leq 21.9\%$. Validated method was employed to determine specific elements in aqueous simulants of thirty commercial plastic food packaging samples, representing three distinct types of plastic polymers. The results showed that the mean concentrations, in mg/kg, were as follows: 2.04 (Al), 0.02 (As), 0.02 (Cd), 0.02 (Co), 0.06 (Cr), 0.41 (Cu), 1.55 (Fe), 0.09 (Mn), 0.15 (Ni), 0.07 (Pb), 0.05 (Sb), and 0.81 (Zn). Furthermore, 30% of analyzed samples exceeding the maximum permissible limits of Al for plastic materials and articles intended to come into contact with food.

Keywords Method validation · ICP-MS · Plastic food packaging materials · Metal migration · Toxic and trace elements

Introduction

Heavy metals are generally defined as metals with a specific gravity of at least 5 g/cm³ and atomic weights between 63.5 and 200.6 g/mol (Srivastava and Majumder 2008; Gumpu et al. 2015). Common contaminants include As, Cr, Cd,

Cu, Pb, Hg, and Zn (Ghuniem et al. 2019a; Astolfi et al. 2020, 2021a, b; Oladoye et al. 2022; Conti et al. 2024). These potentially toxic elements can enter the environment through natural processes like erosion of metallic minerals and rocks, as well as through anthropogenic activities such as metal processing, energy production, farming, and waste management (Astolfi et al. 2020; Qin et al. 2021; Ghuniem et al. 2019b). Once in the environment, potentially toxic elements can be absorbed by plants, ingested by aquatic organisms, and accumulated by animals, eventually making their way into the food chain and posing a risk to human health (Ghuniem et al. 2019c; Román-Ochoa et al. 2021). The 5th China Total Diet Study reveals that vegetables and

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cereals are major dietary sources of Cd, As, Cr, and Al, while aquatic products primarily contribute to Hg intake. Pb exposure through diet comes from water, beverages, vegetables, cereals, and meats (Guo et al. 2021; Wei et al. 2019). Additionally, the presence of potentially toxic elements has been detected in the production, processing, storage, and transportation of food raw materials, as reported by Astolfi et al. (2020), Xiao et al. (2020), and El-Safty et al. (2020). The US Environmental Protection Agency and the Agency for Toxic Substances and Disease Registry classify most heavy metals as high-priority toxic chemicals, a classification supported by Rai et al. (2019).

The health hazards of potentially toxic elements are escalating due to their increasing presence and accumulation in the food chain, as well as their enduring nature in the environment (Verger and Boobis 2013). These contaminants are known to cause a range of acute and chronic diseases, such as renal dysfunction, lung cancer, heart failure, and osteoporosis (Ying et al. 2016; Ghuniem et al. 2020a). Overexposure to Cu has been linked to brain and kidney damage, gastrointestinal distress, and liver cirrhosis. Pb exposure impairs the neurological system, leading to loss of neurological functions. Cd exposure may result in lung cancer, emphysema, and osteoporosis. Hg exposure is associated with health issues like nephrotoxicity, neurotoxicity, carcinogenesis, and immunotoxicity (Chen et al. 2018; Huang et al. 2018; Joseph et al. 2019; Ghuniem et al. 2020b). Moreover, mercury exposure during early childhood can influence heart rate variability. C and As exposure can lead to severe skin conditions, including dermatitis and alopecia. Therefore, the detection of potentially toxic elements in foodstuffs is imperative and critical for ensuring food safety, quality, and public health (Genchi et al. 2017; Chen et al. 2020).

Plastics are widely utilized globally as food-contact packaging materials to preserve the freshness, aroma, and overall quality of food products during extended storage and transportation. The increasing use of plastic packaging materials has raised concerns about their environmental impact and public health implications, particularly in terms of food safety and non-biodegradability (Skrzydewska et al. 2003; Alam et al. 2018). Various thermoplastics, including polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), styrene acrylonitrile copolymer (SAN), polyvinyl chloride (PVC), and polycarbonate (PC), are commonly used in the production of these materials. Thermosets like melamine–formaldehyde (MF) resin and urea–formaldehyde (UF) resin are also used. These packaging materials come in different forms such as films, sheets, and containers, produced through various molding techniques like blow molding, injection molding, extrusion, and casting. During the manufacturing process, a range of additives, including antioxidants, plasticizers, UV and thermal stabilizers,

colors, lubricants, and fillers, are often incorporated with the virgin polymer. Catalysts like Cr and antimony trioxide (Sb_2O_3) are frequently used in the polymerization process to enhance the quality of plastics such as PVC, PE, PET, and PP (Bakircioglu et al. 2011; Whitt et al. 2012; Astolfi et al. 2020, 2021c). In the recycling of plastics and papers, potentially toxic elements like Co, Mn, Ni, Pb, Cd, Sb, and Cr compounds are used to improve their physicochemical properties (Linzner and Salhofer 2014). European Commission Commission Regulation (EU) (2011) sets quality standards for food contact packaging materials, emphasizing that the materials used must not pose a risk to human health (Commission Regulation 2011).

Analyzing migratory compounds in real food products can be a complex, expensive, and time-intensive task due to the varied composition of food matrices. As a result, food simulants are often used in migration studies as a substitute for actual food items (Astolfi et al. 2020, 2021c; Schmid and Welle 2020). A migration experiment involves two critical phases: the contact phase, where the food simulant is exposed to the material, followed by the analytical phase, where the concentration of the analyte within the simulant is measured. The migration process itself unfolds in three stages: the spread of the migrant, its dissolution and dispersion, and finally, its diffusion into the food. The diversity of migrants and the variability in their toxicity levels add complexity to these studies (Arvanitoyannis and Kotsanopoulos 2013).

Variations in the quality of packaging materials among different manufacturers can lead to differing levels of heavy metal leaching. These hazardous substances can migrate into the food and beverages consumed by humans (Cheng et al. 2010; Kang and Zhu 2014). Additionally, heavy metal leaching can occur at various points in the food supply chain when multiple compounds are present. The ingestion of food containing these migrating potentially toxic elements allows them to accumulate in the human body over time. Such accumulation can disrupt the proper functioning of biological systems and may result in health issues, even at low exposure levels (Fátima and Hogg 2007; Sood and Sharma 2019). The most common potentially toxic elements that pose a risk to human health include As, Pb, Hg, Sb, Cd, Cr, Co, Ni, and Zn. Exposure to potentially toxic elements beyond safe limits can lead to a range of carcinogenic and non-carcinogenic diseases, such as cancer, gastrointestinal disorders, tremors, diarrhea, hemoglobinuria, stomatitis, convulsions, depression, metabolic disruptions, and impaired fetal development (Mengistu 2021).

Therefore, the objective of this research is to optimize and validate an analytical method for the quantification of Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, and Zn in simulants derived from plastic food packaging materials utilizing (ICP-MS). This study presents a streamlined and effective

approach to sample preparation that covers a diverse range of plastic food packaging material samples.

Materials and Methods

Instruments and Apparatus

The analysis employs a Perkin Elmer NexION 2000 Inductively Coupled Plasma Mass Spectrometer (ICP-MS), complemented by an auto sampler SDX4, a copper coil RF, a SOGEVAC SV40 BI vacuum pump, hyper and standard skimmer cones, a sampler cone, a mist cyclonic spray chamber, a Meinhard concentric glass nebulizer C 0.5, a quartz torch, quadrupole ion deflector, and LabTech water cooler from the USA is in use. An Integral 5 (A10[®]) Millipore Water Purification System equipped with a Q-POD Element and associated with Merck Millipore – Q[®] / Model: ZRXQ005T0 from the USA is in use. For precise volume measurements, a Hirschman[®] Laborgerate variable micropipette ranging from 20 to 200 μ L from Germany is in use. A Mettler Toledo top bench balance has range from 0.1 mg to 210 g is in use.

Materials and Reagents

Glacial acetic acid with a purity of over 99.5% was sourced from Merck, Germany. A 3% v/v acetic acid solution was prepared by diluting 30 mL of glacial acetic acid to 1 L with deionized water. A certified NexION setup standard mixture solution containing 1 μ g/L of Be, Ce, Fe, In, Li, Mg, Pb, and U in 1% HNO₃ was obtained from PerkinElmer, USA. Certified reference metal stock standard solutions at 1000 mg/L for Mn, As, Sb, Pb, Cd, Al, Cu, Zn, Ni, Cr, Co, and Fe in 2–3% HNO₃ were procured from Merck, Germany. A certified NexION dual detector calibration solution with 200 μ g/L of Al, Ba, Ce, Co, Cu, In, Li in 2% HNO₃ was acquired from PerkinElmer, USA. Additionally, a certified internal standard mixed solution at 10 μ g/mL containing Bi, Ge, In, ⁶Li, Sc, Tb, and Y in 5% HNO₃ was sourced from PerkinElmer, USA. In the laboratory, water underwent deionization using a Water Purification System equipped with a Q-POD Element, in conjunction with the Merck Millipore – Q[®] Integral 5 (A10[®]) system.

Standards Preparation

Intermediate Standard Solutions

An intermediate standard solution with a concentration of 100 mg/L was prepared by diluting 10 mL of a metal stock standard solution, with a concentration of 1000 mg/L for elements Mn, As, Cd, Sb, Pb, Ni, Al, Cu, Zn, Cr, Co, and

Fe to a final volume of 100 mL using 3% v/v acetic acid. Similarly, an intermediate standard solution of 10 mg/L was obtained by diluting 10 mL of a 100 mg/L metal stock standard solution of the same elements to 100 mL with 3% v/v acetic acid. For the preparation of a 1 mg/L intermediate standard solution, 10 mL of a 10 mg/L metal stock standard solution was diluted to 100 mL with 2% v/v HNO₃. Lastly, a 0.1 mg/L intermediate standard solution was produced by diluting 10 mL of a 1 mg/L metal stock standard solution of the aforementioned potentially toxic elements to 100 mL with 3% v/v acetic acid.

Working Standard Solutions

A series of ten working standard solutions were prepared, covering concentrations from 0.05 to 1000 μ g/L for Cr, Co, Mn, and Ni. Additionally, nine working standard solutions were prepared for Al, Fe, Cu, and Zn, with concentrations ranging from 1 to 5000 μ g/L. For As, Cd, Sb, and Pb, eight working standard solutions were prepared, covering concentrations from 0.05 to 100 μ g/L.

To achieve the desired concentrations, successive dilutions were carried out until the desired concentration was reached using 0.1, 1, 10, and 100 mg/L solutions with 3% acetic acid as diluent.

Sample Collection

For recovery test, samples were spiked with suitable amount of standard solution to get 0.02, 0.04, 0.1, 0.2, 0.4, 2 and 5 mg/kg for Mn, As, Pb, Cd, Sb, Cr, Co, and Ni, to get 0.4, 0.8, 2, 4, 8, 20, and 50 mg/kg for Cu and Zn, and to get 0.8, 2, 4, 8, 20, and 50 mg/kg for Fe and Al.

For trueness, a reference material (RM) provided by FAPAS (test material 12114 in aqueous acetic acid). The reference material matrix is a metallic contaminates of Ba, Co, Cu, Fe, Li, Mn, Ni, and Zn in 3% aqueous acetic acid.

In this study, thirty plastic food packaging material samples corresponding to 3 different types were collected randomly from Giza, Egypt. The collected samples included 15 polypropylene (PP) plastic food packaging items, 8 polyethylene (PE) plastic food packaging items, and 7 polystyrene (PS) plastic food packaging items. The samples were coded and stored before analysis.

Sample Preparation

The small fractions of the plastic food packaging material samples was homogenized after cutting, then about 0.5 g of food packaging material samples was weighted into tubes. Forty milliliters of 3% acetic acid was added and gently shake. The samples was allowed to remain submerged for 72 h at controlled room temperature (23 ± 3 °C). After this

period, the simulant aqueous solutions was diluted (1:1) with 3% acetic acid and an appropriate amount of internal standard mixture solution (10 µg/mL) containing Bi, Ge, In, ⁶Li, Sc, Tb, Y was added. Analyze the samples using ICP-MS. Employ the same method for the reagent blank, which consists of 40 mL of 3% acetic acid and an appropriate volume of the internal standard mixture solution.

ICP-MS Analysis

The ICP-MS initialization process begins with the activation of the vacuum and water cooler prior to the ignition of the plasma. It is crucial to ignite the plasma at least 30 min before starting the optimization of the instrument. The measurement parameters are established as follows: plasma gas flow is set at 15 L/min, nebulizer gas flow (NEB) at 1.18 L/min, auxiliary gas flow at 1.2 L/min. The helium gas flow rate is adjustable, ranging from 0.5 to 4.6 mL/min. The ICP radiofrequency power is set at 1450 W, the analogue stage voltage at -1950 V, the pulse stage voltage at 1450 V, the deflector voltage at -16 V, and the cell entrance/exit voltage at -3 V.

Method Validation

The validation of the method incorporated an evaluation of several parameters: linear dynamic range, method linearity, recovery at seven levels, limit of detection (LOD), limit of quantification (LOQ), trueness ascertained by Certified Reference Materials (CRM), repeatability, within-laboratory reproducibility, and measurement uncertainty. The analytical technique validation for ICP-MS, targeting the analysis of elements such as ⁵⁵Mn, ⁷⁵As, ¹¹¹Cd, ¹²¹Sb, ²⁰⁸Pb, ⁶⁰Ni, ²⁷Al, ⁶³Cu, ⁶⁶Zn, ⁵²Cr, ⁵⁹Co, and ⁵⁶Fe was conducted in accordance with Eurachem and Eurachem/CITAC guidelines (Eurachem Guide 1998; Eurachem/CCITAC Guide 2012; Eurachem Guide 2014).

Results and Discussion

Optimization of ICP-MS Parameters

The NexION system was calibrated using a stock solution as part of the daily performance check before sample analysis. The results were automatically compared with the manufacturer's specifications, which are as follows: (^{9.01}Be > 4500 cps, ^{114.90}In > 80,000 cps, ^{238.05}U > 60,000 cps, BKgd 220 ≤ 3 cps, ^{155.90}CeO/^{139.91}Ce ≤ 0.025 cps and ^{69.95}Ce⁺⁺/^{139.90}Ce ≤ 0.03 cps). To meet these criteria, it is essential to fine-tune various instrumental parameters, including the torch position, nebulizer gas flow rates, calibration of the quadrupole ion deflector (QID), deflector voltage, mass calibration and resolution, cell entrance and exit

voltages, cell rod offset voltage (CRO), cell path voltage (QRO), detector voltage, and dual detector calibration.

Every one of these parameters has a substantial impact on the overall performance of the NexION system. Once adjusted, these components collaborate harmoniously to meet the manufacturer's specifications, guaranteeing that the instrument is operating at its highest level prior to commencing sample analysis. This meticulous optimization procedure not only ensures the accuracy of the analytical data but also enhances the durability and dependability of the instrument, making it an essential component of quality control in analytical chemistry.

Torch Position

The torch alignment was carried out utilizing the NexION setup stock solution under criteria achieving maximum intensity of (^{114.90}In). The torch underwent automatic adjustments ranging from -3 to 3 mm both vertically and horizontally until the optimal intensity of ^{114.904}In. The maximum intensity of ^{114.904}In was found to be (154,193.7 cps) located at (0.40 mm vertical and -0.05 mm horizontal).

Nebulizer Gas Flows

Nebulizer gas optimization was conducted utilizing the NexION setup stock solution. The goal of the instrumental optimization was to achieve maximum intensity of (^{114.90}In) and to ensure that the ratio of ^{155.90}CeO/^{139.91}Ce ≤ 0.025. The process began with an argon gas flow of 1.1 L/min, which was incrementally increased by 0.01 L/min until it reached 1.25 L/min. The optimal nebulizer flow was found to be 1.18 L/min. At this flow, maximum intensity of (^{114.90}In) was found to be equal to 149,285 cps and the ratio of ^{155.9}CeO/^{139.905}Ce was found to be equal to 0.0243 cps.

Quadrupole Ion Deflector Calibration (QID)

Calibration of the QID was successfully performed using the NexION setup stock solution, adhering to the instrumental criteria of a minimum correlation coefficient of 0.985 and a minimum intercept of -20. The ion deflector lens voltage was scanned from -20 to 0 V in increments of 0.5 V. The results of QID calibration showed that a perfect correlation coefficient of 1.00 and the intercept was found to be equal to -18.4. The DAC voltage values for ^{7.016}Li, ^{23.985}Mg, ^{114.904}In, ^{139.905}Ce, ^{207.977}Pb, and ^{238.05}U were -19, -19.5, -16.5, -17.5, -18, and -10 V, respectively.

Deflector Voltage

Optimization of the deflector voltage was performed using the NexION setup stock solution under criteria achieving

maximum intensity of ($^{114.90}\text{In}$). The voltage range for the deflector was methodically scanned from -16 to -8 V in increments of 0.25 V. The maximum intensity of $^{114.90}\text{In}$ was found to be ($90,077.1$ cps) when the deflector voltage was set to an optimal value of -16 V.

Mass Calibration and Resolution

Mass calibration and resolution was conducted utilizing the NexION setup stock solution. The instrument's criteria stipulate that the target mass accuracy should fall within ± 0.05 amu, reflecting the difference between the actual element masses (amu) and the measured masses (amu). Additionally, the target resolution accuracy should be within ± 0.03 amu, indicating the variance between the measured peak widths (amu) at 10% of the peak height and the target peak width resolution value of 0.7 amu. The results of the mass calibration showed that the measured masses of $^{7.016}\text{Li}$, $^{23.985}\text{Mg}$, $^{114.904}\text{In}$, $^{207.977}\text{Pb}$, and $^{238.05}\text{U}$ were found to be 7.025 , 23.975 , 114.875 , 207.975 , and 238.075 amu, respectively. This translates to mass accuracies of 0.009 , 0.01 , -0.029 , -0.002 , and 0.025 amu. Furthermore, measured peaks width of $^{7.016}\text{Li}$, $^{23.985}\text{Mg}$, $^{114.904}\text{In}$, $^{207.977}\text{Pb}$, and $^{238.05}\text{U}$ were found to be 0.703 , 0.683 , 0.697 , 0.716 , and 0.725 amu which represents resolution accuracy 0.03 , -0.017 , -0.003 , 0.016 , and 0.025 amu, respectively.

Cell Entrance/Exit Voltage

Optimization of the Cell Entrance/Exit voltage was achieved using the NexION setup stock solution under criteria achieving maximum intensity of ($^{9.01}\text{Be}$, $^{114.90}\text{In}$, and $^{238.05}\text{U}$), while maintaining a background (BKgd) at mass $220 \leq 5$ cps. The cell entrance/exit voltage was scanned -20 to 0 V in increments of 1 V. The maximum intensity of ($^{9.01}\text{Be}$, $^{114.90}\text{In}$, and $^{238.05}\text{U}$) was found to be 5865.2 , $100,387.5$, and $81,051.3$ cps, respectively, with a background at mass 220 of zero cps. This was achieved at an optimal cell entrance/exit voltage of -3 V.

Cell Rod Offset Voltage (CRO)

Optimization of the CRO was performed using the NexION setup stock solution under criteria achieving maximum intensity of ($^{9.01}\text{Be}$, $^{114.90}\text{In}$, and $^{238.05}\text{U}$), while maintaining a background (BKgd) at mass $220 \leq 5$ cps and the ratio of $^{69.95}\text{Ce} + ^{139.90}\text{Ce} \leq 0.03$ cps. The CRO was scanned from -20 to 0 V in increments of 1 V. The maximum intensity of ($^{9.01}\text{Be}$, $^{114.90}\text{In}$, and $^{238.05}\text{U}$) was found to be $13,988.9$, $116,642.3$, and $15,8201.1$ cps, with a background (BKgd) at mass 220 of 2 cps and $^{69.95}\text{Ce} + ^{139.90}\text{Ce}$ ratio of 0.008 cps at optimal value of cell rod offset voltage -18 V.

Cell Path Voltage (QRO)

QRO optimization was performed using the NexION setup stock solution under criteria achieving maximum intensity of ($^{9.01}\text{Be}$, $^{114.90}\text{In}$, and $^{238.05}\text{U}$), while maintaining a background (BKgd) at mass $220 \leq 5$ cps. The cell entrance/exit voltage was scanned from -10 to 0 V in increments of 1 V. The maximum intensity of ($^{9.01}\text{Be}$, $^{23.985}\text{Mg}$, $^{114.90}\text{In}$, and $^{238.05}\text{U}$) was found to be $11,539.7$, $147,617.8$, $132,760$, and $147,330.8$ cps and with a background (BKgd) at mass 220 of 0 cps. This was achieved at an optimal value of cell path voltage of 0 V.

Detector Voltage

Optimizing detector voltages is a critical step prior to dual detector calibration. This process involves adjusting the voltages for both pulse and analogue stages to improve detector efficiency. The use of solutions is unnecessary for this procedure, as the instrument utilizes $^{80}\text{Ar}_2$ and $^{76}\text{Ar}_2$ argon peaks for detector optimization. The pulse stage was optimized under acceptable criteria until the percentage of intensity change blew than 10% , the voltage started at 900 V, and was incrementally increased by 50 V increments up to 2500 V. Similarly, the analogue stage was optimized under acceptable criteria the gain value equal to $10,000$, the voltage began at -1500 V, and was decreased by 50 V increments until it reached -3000 V. The analogue stage detector voltage was decrease until the intensity of argon gas in the analogue stage equal $10,000$ times intensity of argon gas in the pulse stage (gain = $10,000$). The optimum detector voltages were found to be 1450 and -1950 V for pulse stage and analogue stage, respectively.

Dual Detector Calibration

The calibration of the dual detector was achieved using the NexION dual detector calibration solution. Dual detector calibration extends the dynamic range of the detector by normalizing the analogue stage to the pulse stage. This process enhances the dynamic range of the detector by equating the analogue stage with the pulse stage. The results of the dual detector calibration showed that all correlation coefficients exceeded 0.995 .

Under these optimization conditions the daily performance check was found to be $^{9.0122}\text{Be} = 12,005.4$ cps, $^{114.904}\text{In} = 166,164.7$ cps, $^{238.05}\text{U} = 188,673.7$ cps, BKgd $220 = 0.57$ cps, $^{155.9}\text{CeO}/^{139.905}\text{Ce} = 0.024$ cps, and $^{69.9527}\text{Ce}^{++}/^{139.905}\text{Ce} = 0.016$ cps.

Sample Preparation Method

In this study, two parameters that could influence the migration of potentially toxic elements (the contact time of migration process and the food simulant type) was optimized.

The optimization of the food simulant type was conducted using three different simulants: 3% acetic acid, deionized water, and 2% HNO₃ at controlled room temperature of 23 ± 3 °C. The findings revealed that the leaching of potentially toxic elements was notably higher from plastic materials when exposed to 3% acetic acid as compared to deionized water, and 2% HNO₃, as illustrated in Fig. 1.

The study assessed the optimization of contact time for the migration of potentially toxic elements, using 3% acetic acid as a food simulant over various durations: 24, 48, 72, and 96 h. The findings revealed that the migration levels of potentially toxic elements increased significantly with the

duration of contact up to 72 h, after which its almost stabilized as illustrated in Fig. 2.

The carbon effect is clearly demonstrated, particularly for elements like As, Cr, and Se, whereas the enhancement in sensitivity is less noticeable for other analytes. This increase in sensitivity is contingent upon the concentration of acetic acid, reaching a peak around 5% v/v acetic acid for As, Cr, and Se (Maranhão et al. 2011). In this study to eliminate the effect of this phenomena in the migration results the following steps are applied:

- The acetic acid concentration used in the leaching procedure is only 3% v/v.
- The acetic acid concentration in the standard solution was the same as in the extraction solution.
- A corresponding reagent blank was applied with every batch of sample.

Fig. 1 Food simulant type optimization

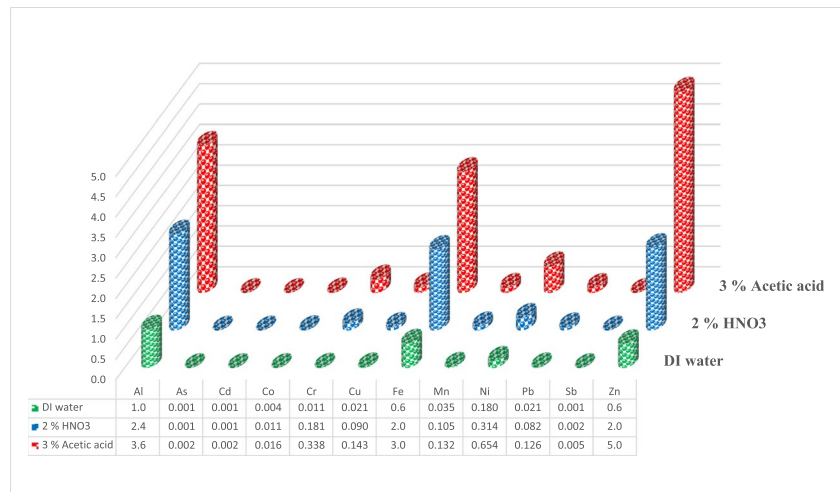
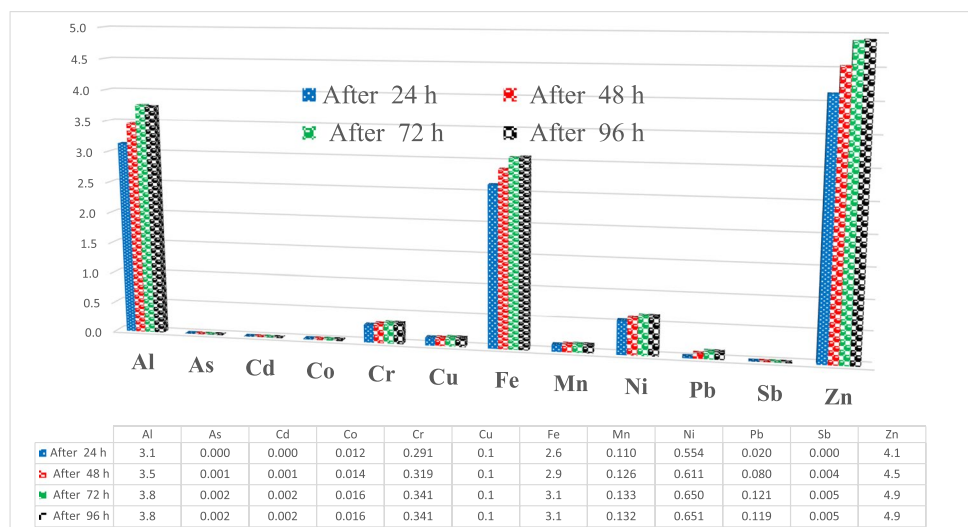


Fig. 2 Contact migration time optimization



- d) A corresponding control sample was applied with every batch of sample.
- e) The measurements of all elements was conducted under kinetic energy discrimination (KED) mode to eliminate any interferences like $^{40}\text{Ar}^{12}\text{C}^+$.
- f) The use of auxiliary gas flow at 1.2 L/min that was higher than the nebulizer gas flow (NEB) at 1.18 L/min, led to decrease in carbon deposits.

Method Validation

Validation was conducted to confirm the reliability of the method. Before being used for quantitative analysis of ^{55}Mn , ^{75}As , ^{111}Cd , ^{121}Sb , ^{208}Pb , ^{60}Ni , ^{27}Al , ^{63}Cu , ^{66}Zn , ^{52}Cr , ^{59}Co , and ^{56}Fe in aqueous simulant from plastic food contact products samples, the method was validated by determining various analytical parameters.

Estimated Limit of Detection (LOD)

The computation of the estimated LODs was performed by analyzing twelve independent plastic food contact products fortified at lowest acceptable concentration. The LODs were calculated as three times the standard deviation of the twelve replicates of these fortified samples at the lowest expected quantities (Eurachem Guide 1998; Eurachem Guide 2014; Ghuniem et al. 2019b; Ghuniem et al. 2019c). The estimated LODs were determined to be 7.5×10^{-4} for ^{55}Mn , 2.9×10^{-3} for ^{75}As , 1.0×10^{-3} for ^{111}Cd , 2.6×10^{-3} for ^{121}Sb , 1.1×10^{-3} for ^{208}Pb , 1.5×10^{-3} for ^{60}Ni , 0.04 for ^{27}Al , 0.01 for ^{63}Cu , 0.07 for ^{66}Zn , 3.2×10^{-3} for ^{52}Cr , 0×10^{-4} for ^{59}Co , and 0.04 mg/kg for ^{56}Fe .

Practical Limit of Quantification (LOQ)

The practical quantification limits are defined as the lowest validated spike level that meets the acceptable criteria for trueness and precision. The minimum practical concentrations of the elements tested in the materials analyzed, which can be quantified with acceptable accuracy, were established by analyzing independent plastic food contact products fortified at 0.02 mg/kg for ^{55}Mn , ^{75}As , ^{208}Pb , ^{111}Cd , ^{121}Sb , ^{52}Cr , ^{59}Co , and ^{60}Ni , at 0.4 mg/kg for ^{63}Cu and ^{66}Zn , and at 0.8 mg/kg for ^{56}Fe and ^{27}Al . These LOQ values were found to be significantly lower than the maximum permissible levels of metal contaminants in food simulants stated by European regulations for plastic materials and articles intended to come into contact with food (Commission Regulation (EU) 2016/1416). The study findings indicated that, at the levels of LOQs, the coefficients of variation, expressed as relative standard deviations (RSD%), for the validated elements in the migration method were all below the acceptable RSD% value stipulated by the Eurachem guidelines and the guidance document on analytical quality control and method validation procedures, which state that the RSD% should not exceed 20%. The results of the LOD, average concentrations at LOQ levels, coefficients of variation, and maximum permissible limits are detailed in Table 1.

Recovery Test

The recovery tests were performed using independent twelve replicates of spiking plastic food contact products samples fortified at seven different concentrations levels. The spiking levels used for recovery test were set at different

Table 1 Results of estimated LODs, practical LOQs, and maximum permissible limits, number of replicates = 12

Elements	Estimated values		Practical values			Maximum permissible limits (µg/kg) (EU) 2016/1416
	Standard deviation (S)	LOD (µg/kg)	LOQ (µg/kg)	Mean concentrations ± S	CV%	
^{55}Mn	0.25	0.75	20	18.6 ± 0.25	1.35	600
^{59}Co	0.30	0.90	20	17.7 ± 0.30	1.68	50
^{60}Ni	0.49	1.47	20	17.6 ± 0.49	2.79	
^{63}Cu	3.96	11.9	400	373.2 ± 3.96	1.06	5000
^{52}Cr	1.06	3.18	20	21.4 ± 1.06	4.97	
^{27}Al	14	41.9	800	774.0 ± 14	1.80	1000
^{56}Fe	13.9	41.6	800	802.6 ± 13.9	1.73	48,000
^{66}Zn	24.7	74.2	400	423.3 ± 24.7	5.85	5000
^{75}As	0.98	2.94	20	20.1 ± 0.98	4.85	
^{111}Cd	0.34	1.02	20	22.0 ± 0.34	1.55	
^{121}Sb	0.85	2.55	20	17.2 ± 0.85	4.94	
^{208}Pb	0.35	1.05	20	21.1 ± 0.35	1.65	

CV coefficient of variation

concentrations as mentioned previously in the materials section. The mean recoveries \pm standard deviations at various levels varied between 85.7 ± 1.51 and $115.6 \pm 0.88\%$ with coefficient of variation expressed as relative standard deviation ranged from 0.42 and 5.85%. The recovery test results indicate that the values for all recoveries of the validated element fall within the acceptable range (70–120%). Furthermore, all RSD % are below the acceptable RSD% value stipulated by the Eurachem guidelines and the guidance document on analytical quality control and method validation procedures, which state that the RSD% should not exceed 20%. The results of recovery test are shown in Table 2.

Linearity

The concept of linearity in an analytical procedure refers to its capacity to produce results that are directly proportional to the analyte concentration within the sample across a specified range. To demonstrate the linearity of the detector, measurements with clean standard preparations are necessary, while the linearity of the method itself should be assessed during the accuracy study (Eurachem Guide 2014; Deligannu et al. 2015; Ghuniem et al. 2019b, c). The established criteria for linearity acceptance include:

- A correlation coefficient (r^2) greater than 0.995 in linear regression analysis is essential for precise quantification, indicating a linear analytical response within certain concentration ranges.
- The y-intercept of the regression line should be insignificantly different from zero, adhering to the “linear to zero” principle.

Calibration Curves Linearity The linear dynamic range was determined to be from 0.05 to 1000 $\mu\text{g/L}$ for ^{59}Co , ^{52}Cr , ^{55}Mn , and ^{60}Ni , and from 1 to 5000 $\mu\text{g/L}$ for ^{27}Al , ^{63}Cu , ^{56}Fe , and ^{66}Zn . For ^{75}As , ^{111}Cd , ^{208}Pb , and ^{121}Sb the range was found to be from 0.05 to 100 $\mu\text{g/L}$. The correlation coefficients for all calibration curves were greater than 0.995 as illustrated in the Table 3.

Method Linearity Linearity of the method was assessed using seven spiking levels for plastic food contact product samples, fortified at 0.02, 0.04, 0.1, 0.2, 0.4, 2, and 5 mg/kg for ^{59}Co , ^{52}Cr , ^{55}Mn , ^{60}Ni , ^{75}As , ^{111}Cd , ^{208}Pb , and ^{121}Sb . For ^{27}Al and ^{56}Fe , six spiking levels were used: 0.8, 2, 4, 8, 20, and 50 mg/kg. Similarly, ^{63}Cu and ^{66}Zn were spiked at seven diverse levels: 0.4, 0.8, 2, 4, 8, 20, and 50 mg/kg. The method demonstrated linearity from the limit of quantitation (LOQ) up to 5 mg/L for ^{59}Co , ^{52}Cr , ^{55}Mn , ^{60}Ni , ^{75}As , ^{111}Cd , ^{208}Pb , and ^{121}Sb , and up to 50 mg/kg for ^{27}Al , ^{63}Cu , ^{56}Fe , and ^{66}Zn . The correlation coefficients for ^{55}Mn , ^{75}As ,

Table 2 Results of recovery test of elements in soft drink samples, Number of replicates = 12

Elements	Spiking level ($\mu\text{g/kg}$)	Mean recovery (%) \pm S	CV%
^{55}Mn	20	93.00 \pm 1.26	1.35
	40	90.9 \pm 0.98	1.07
	100	105.2 \pm 1.24	1.18
	200	89.9 \pm 0.58	0.65
	400	89.7 \pm 0.86	0.96
	2000	104.3 \pm 0.64	0.62
	5000	94.7 \pm 2.74	2.90
^{59}Co	20	88.5 \pm 1.49	1.68
	40	91.6 \pm 0.95	1.04
	100	87.6 \pm 1.28	1.46
	200	90 \pm 0.51	0.56
	400	89.6 \pm 0.70	0.79
	2000	104.1 \pm 0.50	0.48
	5000	96.3 \pm 0.95	0.98
^{60}Ni	20	88.1 \pm 2.46	2.79
	40	92.3 \pm 1.50	1.62
	100	96.1 \pm 1.51	1.57
	200	97.6 \pm 0.69	0.70
	400	98.8 \pm 0.84	0.85
	2000	115.6 \pm 0.88	0.76
	5000	99.7 \pm 0.79	0.79
^{63}Cu	400	93.3 \pm 0.99	1.06
	800	93 \pm 0.71	0.76
	2000	88.8 \pm 0.82	0.93
	4000	91.6 \pm 0.56	0.61
	8000	90.5 \pm 0.69	0.76
	20,000	109.1 \pm 2.17	1.99
	50,000	103.7 \pm 2.81	2.71
^{52}Cr	20	106.7 \pm 5.30	4.97
	40	107.6 \pm 2.80	2.61
	100	94.9 \pm 1.50	1.58
	200	106.7 \pm 1.59	1.49
	400	107.7 \pm 0.54	0.50
	2000	111.3 \pm 0.58	0.52
	5000	110.1 \pm 0.71	0.65
^{27}Al	800	96.8 \pm 1.74	1.80
	2000	110.5 \pm 2.97	2.69
	4000	91.2 \pm 0.78	0.86
	8000	91.4 \pm 0.93	1.01
	20,000	86.3 \pm 0.67	0.78
	50,000	88.4 \pm 0.61	0.69
	^{56}Fe	800	100.3 \pm 1.73
2000		94.6 \pm 1.55	1.64
4000		100.8 \pm 0.71	0.70
8000		102.3 \pm 0.84	0.82
20,000		95.9 \pm 0.61	0.64
50,000		97.5 \pm 0.78	0.80

Table 2 (continued)

Elements	Spiking level (µg/kg)	Mean recovery (%) ± S	CV%
⁶⁶ Zn	400	105.8 ± 6.19	5.85
	800	101.3 ± 3.25	3.21
	2000	85.7 ± 1.51	1.76
	4000	96.1 ± 1.26	1.31
	8000	95.4 ± 0.82	0.86
	20,000	104.9 ± 0.93	0.89
⁷⁵ As	50,000	100.7 ± 0.80	0.80
	20	100.6 ± 4.88	4.85
	40	107.5 ± 3.24	3.01
	100	102.5 ± 3.39	3.31
	200	104.2 ± 1.28	1.23
	400	107 ± 0.65	0.61
¹¹¹ Cd -	2000	102.2 ± 0.62	0.61
	5000	102.5 ± 0.96	0.94
	20	110 ± 1.71	1.55
	40	109 ± 1.59	1.46
	100	107.0 ± 1.78	1.66
	200	113.2 ± 0.70	0.62
¹²¹ Sb	400	114.2 ± 0.77	0.68
	2000	98.5 ± 0.66	0.67
	5000	106 ± 0.56	0.53
	20	85.8 ± 4.24	4.94
	40	100.6 ± 4.42	4.40
	100	105.2 ± 1.41	1.34
²⁰⁸ Pb -	200	109.0 ± 3.25	2.98
	400	115.0 ± 1.84	1.60
	2000	104.7 ± 2.50	2.39
	5000	100.2 ± 1.13	1.13
	20	105.3 ± 1.74	1.65
	40	101.9 ± 0.94	0.92
²⁰⁸ Pb -	100	106.6 ± 1.24	1.17
	200	100.9 ± 0.52	0.52
	400	100.4 ± 0.58	0.58
	2000	110.4 ± 0.47	0.42
	5000	99.5 ± 0.50	0.50

CV coefficient of variation, S standard deviation

¹¹¹Cd, ¹²¹Sb, ²⁰⁸Pb, ⁶⁰Ni, ²⁷Al, ⁶³Cu, ⁶⁶Zn, ⁵²Cr, ⁵⁹Co, and ⁵⁶Fe were 0.99917, 0.99999, 0.99955, 0.99981, 0.99908, 0.99962, 0.99987, 0.99947, 0.99977, 0.99998, 0.99942, and 0.99992, respectively, all exceeding the threshold of 0.995, indicating excellent linearity as illustrated in the Table 3.

Method Accuracy

The study examined method accuracy by evaluating two distinct parameters: trueness and precision.

Trueness. The trueness of the validated method was substantiated through the utilization of a reference material (RM) provided by FAPAS (test material 12,114 in aqueous acetic acid). The Z-scores were computed employing the following equation:

$$Z - score = \frac{C_{found} - C_{assigned}}{S} \quad (1)$$

Z-score a statistical measure that quantifies the distance a data point is from the mean of a data set.

C_{Found} found concentrations in µg/L.

S standard deviation from FAPAS.

C_{assigned} assigned values in µg/L from FAPAS.

The analysis indicated that all the measured values fell within the satisfactory range, with Z-scores falling that were within acceptable limits, between -2 and 2, as detailed in Table 4.

Precision The study validated the method's precision by examining the repeatability and reproducibility components.

1. Repeatability

The repeatability test was carried out by analyzing 12 replicates of fortified plastic food contact products sample by the same operator and short intervals of time. The relative standard deviation results of the repeatability test were as follows: ⁵⁵Mn (0.96%), ⁷⁵As (0.61%), ¹¹¹Cd (0.68%), ¹²¹Sb (1.60%), ²⁰⁸Pb (0.58%), ⁶⁰Ni (0.85%), ²⁷Al (0.69%), ⁶³Cu (2.71%), ⁶⁶Zn (0.80%), ⁵²Cr (0.65%), ⁵⁹Co (0.98%), and ⁵⁶Fe (0.80%). The repeatability test results indicate that the values for all RSD % are below the acceptable RSD% value stipulated by the Eurachem guidelines and the guidance document on analytical quality control and method validation procedures, which state that the RSD% should not exceed 20%.

2. Reproducibility

In this study, an intra-laboratory reproducibility test was carried out by analyzing 20 replicates of fortified plastic food contact product samples. The samples were tested for ⁵⁹Co, ⁵²Cr, ⁵⁵Mn, ⁶⁰Ni, ⁷⁵As, ¹¹¹Cd, ²⁰⁸Pb, and ¹²¹Sb at a concentration of 5 mg/kg, and for ²⁷Al, ⁶³Cu, ⁵⁶Fe, and ⁶⁶Zn at 50 mg/kg. These analyses were carried out by various analysts over

Table 3 Results of correlation coefficients of calibration curves and method linearity

Elements	Calibration curves				Method linearity			
	Number of points	Range (mg/L)	Slope	Correlation coefficients (R^2)	Number of points	Range (mg/L)	Slope	Correlation coefficients (R^2)
^{27}Al	9	0.001–5	0.0004	0.99998	6	0.8–50	1.14	0.99987
^{75}As	8	0.00005–0.1	0.0231	0.99983	7	0.02–5	0.98	0.99999
^{111}Cd	8	0.00005–0.1	0.0083	0.99999	7	0.02–5	0.95	0.99955
^{59}Co	10	0.00005–1	0.0230	1.00000	7	0.02–5	1.03	0.99942
^{63}Cu	9	0.001–5	0.0264	0.99994	7	0.4–50	0.95	0.99947
^{52}Cr	10	0.00005–1	0.0334	0.99997	7	0.02–5	0.91	0.99998
^{56}Fe	9	0.001–5	0.0333	0.99997	6	0.4–50	1.03	0.99992
^{55}Mn	10	0.00005–1	0.0344	1.00000	7	0.02–5	1.04	0.99917
^{60}Ni	10	0.00005–1	0.0047	0.99997	7	0.02–5	1.00	0.99962
^{208}Pb	8	0.00005–0.1	0.0105	0.99998	7	0.02–5	0.99	0.99908
^{121}Sb	8	0.00005–0.1	0.0185	0.99998	7	0.02–5	1.00	0.99981
^{66}Zn	9	0.001–5	0.0607	0.99985	7	0.8–50	0.99	0.99977

Table 4 Results of different reference materials from FAPAS

CRM	Analyte	Found concentration (mg/kg)	Assigned value (mg/kg)	Satisfactory range (mg/kg)	Recovery %	Z-score
12114 test materials in aqueous acetic acid	Cobalt	0.0964	0.0994	0.0556–0.143	97.0%	–0.14
	Copper	4.82	5.09	3.81–6.36	94.7%	–0.42
	Iron	52.97	48.8	40.1–57.5	108.6%	0.96
	Manganese	0.57	0.606	0.397–0.815	94.1%	–0.34
	Nickel	0.0225	0.0205	0.0115–0.0295	110.0%	0.45
	Zinc	17.79	18.2	14.4–21.9	97.8%	–0.22

several days. The reproducibility of the test, expressed as the relative standard deviation, yielded results of 4.22% for ^{55}Mn , 2.75% for ^{75}As , 2.61% for ^{111}Cd , 2.94% for ^{121}Sb , 2.52% for ^{208}Pb , 2.66% for ^{60}Ni , 2.78% for ^{27}Al , 4.09% for ^{63}Cu , 2.63% for ^{66}Zn , 2.78% for ^{59}Co , 2.75% for ^{52}Cr , and 2.78% for ^{56}Fe . The reproducibility test results indicate that the values for all RSD % are below the acceptable RSD% value stipulated by the Eurachem guidelines and the guidance document on analytical quality control and method validation procedures, which state that the RSD% should not exceed 20%.

Measurement Uncertainty

Data accumulated from various quality control procedures were utilized to estimate measurement uncertainty. This parameter, associated with the measurement result, characterizes the dispersion of values that could reasonably be attributed to the measure. It may be represented by a standard deviation or the width of a confidence interval, for instance. To estimate overall uncertainty, it may be necessary to

individually assess each source of uncertainty to determine its contribution. These individual contributions are known as uncertainty components. When expressed as a relative standard deviation, an uncertainty component is termed relative standard uncertainty. The precision-related uncertainty component was examined through intra-laboratory precision.

Uncertainty was calculated by using the following values of relative standard uncertainty due to precision experiments ($U_{\text{Precision}}$) which expressed as relative standard deviation (RSD %). Standard Uncertainty can be calculated by using the following equation:

$$\text{Standard uncertainty} = \frac{S}{\sqrt{n}}$$

n number of samples

S standard deviation due to precision

The bias-related uncertainty component was investigated using recovery data from spiked samples, and a significance test (*t*-test) was applied to ascertain if the recovery significantly deviated from 100%.

$$t_{\text{calculated}} = \frac{|1 - \text{Recovery}|}{\text{Standard uncertainty}}$$

If the results of *t*-test found that $t_{\text{calculated}} > t_{\text{table}}$, in this case recovery was significantly different from 100%, the uncertainty due to bias was calculated from the following equation:

$$U_{\text{bias}} = \sqrt{(U_{\text{Standard}})^2 + \left(\frac{1 - \text{Recovery}}{K}\right)^2}$$

If the results of *t*-test found that $t_{\text{calculated}} > t_{\text{table}}$, in this case recovery was not significantly different from 100%, the uncertainty due to bias was calculated from the following equation:

$$U_{\text{bias}} = \frac{\text{Standard uncertainty}}{\text{Recovery}}$$

U_{bias} uncertainly due to bais

U_{standard} : standard unctainly

k degree of freedom (*n* = 1)

Recovery mean of recovery

The uncertainty component due to sample processing, representing the homogeneity of the analyte in the analytical sample as per Codex guidelines, was assumed to be a default value of 10% (Codex 2003; Eurachem Guide 2012; Ghuniem et al. 2019b, 2019c). Uncertainty arising from reference standard preparation was estimated by considering the purity of the reference standard, and the use of volumetric flasks and pipettes, employing normal and triangular distributions. The normal distribution was applied when calculating uncertainty due to the purity of reference stock standards, while the triangular distribution was used for calculating uncertainty due to volumetric flasks and pipettes. The uncertainty component resulting from reference standards preparation varied between 0.78 and 0.82%. The total uncertainty, termed combined standard uncertainty, is the positive square root of the sum of the squares of the individual uncertainties, as shown in the flowing equation:

$$U_{\text{Combined}} = \sqrt{(U_{\text{precision}})^2 + (U_{\text{Bias}})^2 + (U_{\text{Reference}})^2 + (U_{\text{Sample Processing}})^2}$$

In analytical chemistry, the use of expanded uncertainty is crucial for quantitative analysis. This expanded uncertainty is derived by multiplying the combined uncertainty with a coverage factor (*k*) of 2, corresponding to a 95% confidence level. The measurement uncertainties, when expressed as expanded uncertainties, were determined to be 21.85% for ^{55}Mn , 20.8% for ^{75}As , 20.8% for ^{111}Cd , 21% for ^{121}Sb , 20.7% for ^{208}Pb , 20.8% for ^{60}Ni , 20.9% for ^{27}Al , 20.8% for ^{63}Cu , 20.77% for ^{66}Zn , 20.86% for ^{59}Co , 20.86% for ^{52}Cr , and 20.86% for ^{56}Fe . Details of the uncertainty components can be found in Table 5.

Quality Control

Reagent Blank Each set of samples should include an analysis of the reagent blank sample. This blank sample should contain 40 mL of 3% acetic acid and a suitable volume of the internal standard mixture solution.

Control Samples The method's performance is consistently evaluated through recovery tests. Each analyzed batch of plastic food contact product samples must include a control sample. This sample is spiked with an appropriate quantity of standard solution to achieve concentrations of 5 mg/kg for ^{59}Co , ^{52}Cr , ^{55}Mn , ^{60}Ni , ^{75}As , ^{111}Cd , ^{208}Pb , and ^{121}Sb , and 50 mg/kg for ^{27}Al , ^{63}Cu , ^{56}Fe , and ^{66}Zn .

Control Charts The control chart serves as a tool to monitor the stability of analytical precision. It is used to record the

Table 5 Results of uncertainty components, bias, combined uncertainty and expanded uncertainty, at $U_{\text{Sample processing}} = 10\%$

Elements	Uncertainty components				
	Standard preparation	Bias	Precision	Combined uncertainty	Expanded uncertainty
^{55}Mn	0.78%	0.98%	4.22%	10.9%	21.9%
^{59}Co	0.78%	0.67%	2.78%	10.4%	20.9%
^{60}Ni	0.78%	0.61%	2.66%	10.4%	20.8%
^{63}Cu	0.78%	0.95%	4.09%	10.9%	20.8%
^{52}Cr	0.78%	0.79%	2.75%	10.4%	20.9%
^{27}Al	0.78%	0.90%	2.78%	10.5%	20.9%
^{56}Fe	0.78%	0.65%	2.78%	10.4%	20.9%
^{66}Zn	0.78%	0.60%	2.63%	10.4%	20.8%
^{75}As	0.78%	0.62%	2.75%	10.2%	20.8%
^{111}Cd	0.78%	0.66%	2.61%	10.4%	20.8%
^{121}Sb	0.82%	0.67%	2.94%	10.5%	21%
^{208}Pb	0.78%	0.58%	2.52%	10.4%	20.7%

Table 6 Elements migrates from plastic food materials samples, number of samples = 30

Detected elements	Element's concentrations (mg/kg)				Frequency		Free samples		Samples less than LOQ		Samples above LOQ		MPL (mg/kg)	The violated elements		The violated samples	
	Minimum	Maximum	Mean	Median	No	%	No	%	No	%	No	%		No	%	No	%
²⁷ Al	<0.8	9.63	2.04	0.81	22	73.3%	8	26.7%	11	36.7%	11	36.7%	1	9	30.0%	9	30.0%
⁷⁵ As	<0.02	<0.02	0.02	0.02	7	23.3%	23	76.7%	7	23.3%	0	0.0%	-	-	-	-	-
¹¹¹ Cd	<0.02	<0.02	0.02	0.02	14	46.7%	16	53.3%	14	46.7%	0	0.0%	-	-	-	-	-
⁵⁹ Co	<0.02	<0.02	0.02	0.02	13	43.3%	17	56.7%	13	43.3%	0	0.0%	0.05	0	0.00%	-	-
⁵² Cr	<0.02	0.20	0.06	0.04	12	40.0%	18	60.0%	6	20.0%	6	20.0%	-	-	-	-	-
⁶³ Cu	<0.4	0.51	0.41	0.40	23	76.7%	7	23.3%	22	73.3%	1	3.3%	5	0	0.00%	-	-
⁵⁶ Fe	<0.8	6.63	1.55	0.80	19	63.3%	11	36.7%	14	46.7%	5	16.7%	48	0	0.00%	-	-
⁵⁵ Mn	<0.02	0.46	0.09	0.02	16	53.3%	14	46.7%	9	30.0%	7	23.3%	0.6	0	0.00%	-	-
⁶⁰ Ni	<0.02	0.57	0.15	0.08	19	63.3%	11	36.7%	2	6.7%	17	56.7%	-	-	-	-	-
²⁰⁸ Pb	<0.02	0.57	0.07	0.02	12	40.0%	18	60.0%	9	30.0%	3	10.0%	-	-	-	-	-
¹²¹ Sb	<0.02	0.12	0.05	0.02	3	10.0%	27	90.0%	2	6.7%	1	3.3%	-	-	-	-	-
⁶⁶ Zn	<0.4	4.65	0.81	0.40	22	73.3%	8	26.7%	12	40.0%	10	33.3%	5	0	0.00%	-	-

LOQ limit of quantifications, *N.D* not detected, *MPL* maximum permissible limit

results of control samples. When an individual data point falls outside the established limits, such as the upper control limit (UCL), upper warning limit (UWL), mean central line, lower control limit (LCL), and lower warning limit (LWL), it is imperative to identify and correct the source or sources of error (Subramanian and Quevauviller 1995; Ghuniem et al. 2019b; Ghuniem et al. 2019c).

Analyses of Plastic Food Contact Products Samples

An analysis of thirty samples of plastic food packaging materials for metal migration was conducted using a validated method, and the results are presented in Table 6. The results indicated that the most frequently detected potentially toxic elements were ⁶³Cu which found in 23 times, followed by ²⁷Al and ⁶⁶Zn which detected in 22 times for each, ⁵⁶Fe and ⁶⁰Ni in 27 times for each, ⁵⁵Mn in 16 times, ¹¹¹Cd in 14 times, ⁵⁹Co in 13 times, ⁵²Cr and ²⁰⁸Pb in 12 times for each, ⁷⁵As in 7 times, and ¹²¹Sb in 3 times. The mean concentrations of ²⁷Al, ⁷⁵As, ¹¹¹Cd, ⁵⁹Co, ⁵²Cr, ⁶³Cu, ⁵⁶Fe, ⁵⁵Mn, ⁶⁰Ni, ²⁰⁸Pb, ¹²¹Sb, and ⁶⁶Zn were found to be 2.04, 0.02, 0.02, 0.02, 0.06, 0.41, 1.55, 0.09, 0.15, 0.07, 0.05, and 0.81 mg/kg, respectively. Furthermore, the measured levels of ⁶³Cu, ⁵⁶Fe, ⁵⁵Mn, and ⁶⁶Zn did not exceed the maximum permissible limits, while 30% of analyzed samples exceeding the maximum permissible limits of ²⁷Al set by European regulations for plastic materials and articles intended to come into contact with food (Commission Regulation (EU) 2016/1416). The findings also revealed that all PS and PE

samples that were analyzed did not surpass the regulatory limits, but only the PP type was represented in all samples that violated the plastic food contact regulatory limits of Al.

Conclusion

This research utilized the ICP-MS technique for validating an analytical method to determine the migration of ⁷⁵As, ²⁰⁸Pb, ¹¹¹Cd, ¹²¹Sb, ⁶³Cu, ⁶⁶Zn, ⁵⁶Fe, ²⁷Al, ⁵²Cr, ⁵⁹Co, ⁵⁵Mn, and ⁶⁰Ni from plastic food packaging materials. The methodology, which does not require acid or microwave digestion, proved to be fast, straightforward, and suitable for routine laboratory use. Optimized ICP-MS conditions enabled the accurate detection of these potentially toxic elements at extremely low ppb levels. The quantification limits of the method were significantly lower than the maximum permissible levels of metal contaminants in food simulants, as specified by European regulations for plastic materials and articles in contact with food. This method is applicable to a variety of plastic food packaging materials and is recommended as the Egyptian standard for determining metal migration from plastic food packaging. It also contributes to toxicological studies relevant to health. In a study involving 30 samples of plastic food packaging from Giza, Egypt, it was found that the levels of ⁶³Cu, ⁵⁶Fe, ⁵⁵Mn, and Zn were within permissible limits. However, 30% of the samples exceeded the permissible levels of ²⁷Al, highlighting the need for regulatory compliance. The findings are valuable for health authorities and researchers conducting epidemiological studies.

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Data Availability No datasets were generated or analysed during the current study.

Declarations

Competing Interests The authors declare no competing interests.

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